ON THE DYNAMICS OF IMPERFECT CRYSTALS

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By

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SCOPE AND CONTENTS:

An algebraic procedure for considering the general n-tuple problem for a random defect lattice is developed in this thesis. When specialized to pairs (n=2) the deviations from randomicity have also been considered. The low concentration defect theory (n=1) is used to calculate:

a) the frequencies and widths of phonons in disordered $Cu_{0.97}Au_{0.03}$

b) the frequency shift of singular points in the defect-induced (Na^+, Sm^{++}) far infrared spectrum of KBr as a function of defect concentration

c) the one phonon side bands of H_2, D_2, and N_2 in solid Ar.

In order to take into account the "long range" behaviour of random substitutional defects, an effective lattice theory is formulated. This theory proves essential to the discussion of the Cu/Au dispersion curves and the one phonon side band of the vibrational spectrum of a H_2, (D_2) molecule in solid Ar.

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The more philosophical aspects of this thesis have arisen from the many useful and provocative discussions I have had with Bruce Hayman, Jules Carbotte and Harold Chapman on the purpose and usefulness of contemporary science and scientific research.

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PREFACE

I have chosen the following ideas from various works of T.S. Kuhn because of our mutual agreement on the subject.

Scientists work from models acquired through education and through subsequent exposure to literature often without quite knowing or needing to know what characteristics have given these models the status of community paradigms. And because they do so, they need no full set of rules. The coherence displayed by the research tradition in which they participate may not imply even the existence of an underlying body of rules and assumptions that additional historical or philosophical investigation might uncover. That scientists do not usually ask or debate what makes a particular problem or solution legitimate tempts us to suppose that, at least intuitively, they know the answer. But it may only indicate that neither the question nor the answer is felt to be relevant to their research.

Philosophers of science have repeatedly demonstrated that more than one theoretical construction can always be placed upon a given collection of data. History of science indicates that, particularly in the early developmental stages of a new paradigm, it is not even very difficult to invent such alternates. But that invention of alternates is just what scientists seldom undertake. So long as the tools a paradigm supplies continue to prove capable of solving the problems it defines, science moves fastest and penetrates most deeply through confident employment of those tools. The reason is clear. As in manufacture so in science--retooling is an extravagance to be reserved for the occasion that demands it.

To scientists, at least, the results gained in normal research are significant because they add to the scope and precision with which the paradigm can be applied. That answer, however, cannot account for the enthusiasm and devotion that scientists display for the problems of normal research. No one devotes years to, say, the development of a better spectrometer or the production of an improved solution to the problem of vibrating strings simply because of the importance of the information that will be obtained. The data gained by computing ephemerides or by further measurements with an existing instrument are often just as significant, but those activities are regularly spurned by scientists because they are so largely repetitions of procedures that have been carried through before. That rejection provides a clue to the fascination of the normal research problem. Though its outcome can be anticipated, often in detail so great that what remains to be known is itself uninteresting, the way to achieve that outcome remains very much in doubt. Bringing a normal research problem to a conclusion is achieving the anticipated in a new way, and it requires the solution of all sorts of complex instrumental, conceptual, and mathematical puzzles. The man who succeeds proves himself an expert puzzle-solver, and the challenge of the puzzle is an important part of what usually drives him on.

It is no criterion of goodness in a puzzle that its outcome be intrinsically interesting or important. On the contrary, the really pressing problems, e.g., a cure for cancer or the design of a lasting peace, are often not puzzles at all, largely because they may not have any solution. Consider the jigsaw puzzle whose pieces are selected at random from each of two different puzzle boxes. Since that problem is likely to defy even the most ingenious of men, it cannot serve as a test of skill in solution. In any usual sense it is not a puzzle at all. Though intrinsic value is no criterion for a puzzle, the assured existence of a solution is.

In the development of any science, the first received paradigm is usually felt to account quite successfully for most of the observations and experiments easily accessible to that science's practitioners. Further development, therefore, ordinarily calls for the construction of elaborate equipment, the development of an esoteric vocabulary and skills, and a refinement of concepts that increasingly lessens their resemblance to their usual common-sense prototypes. That professionalization leads, on the one hand to an immense restriction of the scientist's vision and to a considerable resistance to paradigm change. The science has become increasingly rigid.

On the other hand, within those areas to which the paradigm directs the attention of the group, normal science leads to a detail of information and to a precision of the observation-theory match that could be achieved in no other way. Furthermore, that detail and precision-of-match have a value that transcends their not always very high intrinsic interest. Without the special apparatus that is constructed mainly for anticipated functions, the results that lead ultimately to novelty could not occur.

In the normal mode of discovery, even resistance to change has a use. By ensuring that the paradigm will not be too easily surrendered, resistance guarantees that scientists will not be highly distracted and that the anomalies that lead to paradigm change will penetrate existing knowledge to the core. The very fact that a significant scientific novelty so often emerges simultaneously from several laboratories is an index both to the strongly traditional nature of normal science and to the completeness with which that traditional pursuit prepares the way for its own change.

CHAPTER I

INTRODUCTION

"When philosophy is severed from its roots
in experience, whence it first sprouted and
grew, it becomes a dead thing."
--Francis Bacon

SECTION A

THESIS OUTLINE

The language of quantum mechanics, contrary to the Aristotelian physics of qualities and in contrast to the Newtonian physics of primary properties, is a language of interactions rather than attributes, of processes rather than properties. Formally, at least, it is in this vernacular that the particular problem in lattice dynamics of crystals with substitutional impurities is considered.

The excitations in crystals called phonons have been studied for more than half a century, beginning with the work of Born and Von Karman (1912). However, the study of the effects of substitutional defects on the vibrational properties of perfect crystals has been subjected to intensive investigation only in the last decade. Recently, the effects of impurities on the dynamical properties of crystals has been observed experimentally by such techniques as infrared absorption (A.A. Maradudin (1966_b)) and neutron scattering (Brockhouse (1966)). The main purpose of this thesis is to develop a theoretical structure by which the dynamical properties of crystals with substitutional impurities may be considered, and to apply this formal work to the discussion of experimental observation.

To achieve this goal, double-time thermal Green's functions served as the basic mathematical tool. The usage of these Green's functions follows closely that of Zubarev (1960) and has been adapted for particular application to lattice dynamics. Although the whole formalism is based on the Green's function approach, it is the configurational averaging procedure that, in the end, defines the defect lattice. This averaging method, which restores translational symmetry to the defect lattice, can be understood more precisely by using probability distribution functions similar to those of Lax (1951).

In this thesis, before approaching the actual problem of perfect lattice excitations scattering off of substitutional impurities, a discussion is presented on the approximations required to define the perfect crystal excitations. This approach is then extended to the defect lattice with substitutional impurities and forms the starting point for the lattice dynamical problem.

Section B of Chapter II considers the defect problem for a low enough concentration c of defects where the configuration averaged Green's function for the system is correct to c in concentration. The result obtained is the low concentration theory, previously derived by Taylor (1967). The point of interest in this section is not so much the exact form of the low concentration theory, as its extension to what is called the perturbative approximation.

In the exact form, the low concentration theory defines a scattering matrix which has the dimension of the defect space, the defect space being the spacial extent of an impurity mass and force constant disturbance from a previously perfect lattice. For a small disturbance that includes only the impurity site and the first nearest neighbour shell, the defect space, if not reduced, has a size so formidable as to make calculations on even the highest speed computers a lengthy process. Even with the reduction of the defect space by the use of group theory, as discussed in Section B of Chapter III, the problem is still one of sizable proportions --if not in dimension then certainly in the determination of all the appropriate Green's functions and the necessary group theory operations.

The remedy for these difficulties was found by making a perturbation on the change of the lattice potential (force constant matrix) while considering the mass defect scattering as exact. This approach to the low concentration theory considerably reduces the number of independent Green's functions necessary, and requires no group theory for reduction since it is already in compact form. Furthermore, this method can be extended to the consideration of larger defect spaces with no loss in simplicity of calculation. Section A of Chapter IV shows that, for reasonable mass changes, the perturbative approach to the low concentration theory gives agreement that differs negligibly from its exact form, for a wide range of force constant changes.

Since the low concentration theory is concerned in an exact fashion with only single site scattering, many higher order processes have been neglected. The general process for the scattering off of n sites is called the n-tuple process. Although the theory for pairs is a special case of the general n-tuple process with n=2 (as is the low concentration theory for n=1), it is presented separately in Section C of Chapter II because it is applied directly for comparison with experiment.

The algebraic method for the evaluation of the full n-tuple scattering, self energy, and configurational averaged Green's function is presented in Section D, Chapter II. The mechanism used in this derivation is similar to that of Section B and C. Here, only the case of a mass defect is considered, and the result obtained is correct to c^n. For algebraic simplicity, the discussion of this process has only been given for the truly random impurity, although it can be extended to a lattice with defect correlations.

The difficulty with the theory of n-tuple processes, as well as with low concentration theory, is that it does not allow for the changes that occur in the lattice due to the "long-range" effects of impurities. In Section E, Chapter II, a method for considering such effects of impurities is presented. Although the discussion proceeds along the lines of the low concentration theory it is easily generalized to incorporate any n-tuple process if the approximation,that the "short range" effects of the impurities are the mass change while the "long-range" effects are considered as the force constant change, is made. The visual pattern of this section is somewhat reminiscent of a self consistent approach, but the idea behind the pattern, and the development of it, differs from that of the self consistent method. The basic idea of this approach involves the redefining of the perfect lattice into which the impurities are placed, as an effective lattice into which "local" impurities are placed. In this lattice, the impurities do not possess any "long-range" effects, and there is little probability that any two defect spaces would overlap. If such a lattice can be found from a consideration of the atomic potentials between pairs of atoms, or from observed macroscopic changes--such as a change in the lattice constant--then the lattice Green's function used in the Dyson equation is taken to be that which describes the effective, rather than the perfect lattice. A knowledge of the atomic potentials and/or macroscopic changes of the lattice is required to make this approach useful.

In order to use the theoretical structures of Chapter II for comparison with experimental results, a development chapter, Chapter III, is used to bridge the gap between the formal theory and the computer oriented formalism necessary for applications. In this chapter, Section A gives the equations for finding the perfect or effective lattice Green's function, while Section B contains a brief discussion of the group theory necessary for reducing the labour involved in solving the impurity problem. In order to build up the idea of an atomic potential between atom pairs in a crystal, a brief discussion of interatomic potentials is presented in Section C. Since Section C, Chapter IV requires information on local modes, Section F of Chapter III gives a short discussion on local modes in a defect lattice. Finally, Section D (neutron scattering) and E (impurity induced infrared absorption) of the chapter are presented so that they can be used as the starting points for the discussion of experimental results of Sections A and B respectively, of Chapter IV.

The experimental application of theory is given in Chapter IV. Section A considers the work of Svensson, Brockhouse and Rowe (1967), Svensson and Brockhouse (1967), and Svensson and Kamitakahara (1971), by using low concentration theory along with the effective lattice theory. However, the theory for pairs is also used in comparison with the low concentration theory. This is done for the case of a mass impurity only, in order to evaluate the effect that pairs would have on the scattering. In the same section, the experimental neutron groups are compared with the appropriate Green's functions as they would be perceived in the experimental situation.

For far infrared absorption, it is impossible, within the framework of the low concentration theory, to observe directly the changes in position of Van Hove singularities as a function of defect concentration. Thus, in Section B, Chapter IV, the experimental results for far infrared absorption given by Timusk and Ward (1969) are considered by looking directly at the phonons involved in the absorption process and following their movement with concentration. Also in this section, a convolution model is developed and proved to be a useful tool for considering the absorption induced by Sm^{++} impurities in KBr. For Na^{+} impurities in KBr, both the low concentration theory and the effective lattice are used to explain the results observed experimentally for the movement of singular points in the Na^{+} defect induced spectra of KBr.

The most direct method to obtain information about the immediate environment around an impurity is through the local mode. Section C of Chapter IV relates the local mode work of Chapter III to the induced near infrared absorption of molecular impurities in Ar. The theoretical work of the thesis is compared to the experiments of Kriegler and Welsh (1968) for H_2, De Remigis and Welsh (1970) for D_2 and De Remigis (1971) for N_2 dissolved in Ar, by using the information obtained from Batchelder, Collins, Haywood and Sidney (1970) on the Ar phonons, and from Batchelder, Haywood and Sanderson (1970) on the temperature dependence of phonons in solid Ar. Because of this information on Ar, the position of the local mode can be theoretically determined for any temperature. This is applied to the experimental observations of N_2 in Ar as a function of temperature. Here, the effective lattice theory proves most useful in the treatment of H_2 and D_2 in Ar.

This work on the lattice dynamics of crystals with substitutional impurities has the advantage of an algebraic formalism which is not the case for other authors. An outline of previous work in the field follows in the next section.

"Truth emerges more readily from error than
from confusion."
--Francis Bacon

SECTION B

HISTORICAL SURVEY

The introduction of impurity atoms by substitution into a lattice changes the vibrational properties of that lattice. For such a lattice, the phonons of a given wave vector are shifted in frequency, and in general, phonons no longer have infinite lifetimes since they can now scatter off of impurities. This means that the lattice excitation is now not described by a delta function but rather by a pseudo-Lorentzian. In such a defect lattice, the defect atom and those atoms which define the defect space may prefer to vibrate at particular frequencies. If these frequencies of vibration are within the perfect lattice band modes (as for a heavy impurity and/or a weakening of the lattice force constants in the defect space) then they are called "resonance modes", while if they occur above the perfect lattice band modes (as in the case of a light impurity and/or a strengthening of the lattice force constants in the defect space) then they are called "localized modes".

The quantitative aspects of a perturbed lattice have been studied and discussed extensively in recent years.

Lifshitz (1965) was one of the first to describe a general theory of defect modes based on the method of normal Green's functions. Theories of perturbed lattices having a low concentration of impurities have also been developed by Langer (1961), Takeno (1962_a, 1963) and Davies and Langer (1963). These authors considered lattices with a random array of defects and were correct in their approach to order c. An excellent summary and review of much of this work was given by Maradudin, Montroll and Weiss (1963) and also by Maradudin (1965, 1966_a).

The use of double-time thermal Green's functions was first introduced by Zubarev (1960) and was applied by Elliott and Taylor (1967) to the defect problem in lattice dynamics for a three dimensional lattice containing a small concentration of substitutional impurities. Taylor (1967) used this Green's function form to derive algebraically the low concentration theory and Hartmann (1968) extended the theory to include correlations between defects through a short range density function (in the author's words, "an order parameter") about any defect site. In considering short ranged order in this paper, Hartmann does not indicate what his extension of the low concentration theory has excluded or included. It seems that the author treats only single site scattering, weighted by an appropriate conditional probability function, and has excluded pair scattering.

Although Hartmann (1968) tends to give slightly better agreement for the experimental results of Svensson, Brockhouse and Rowe (1965) than does Behara and Deo (1967), both retain the same qualitative features for the description of the frequency shift of the dispersion curve for the 9.3% Au/90.7% Cu system. These approaches then, do not form a complete explanation for the experimentally observed results.

Behara and Deo's (1967) analysis uses an approximate method to treat force constant changes in the defect space. The complete low concentration theory treatment of force constant changes, in the defect space of the first nearest neighbour shell for the f.c.c. lattice and in the defect space of the first and second nearest neighbour shell for the b.c.c. lattice was performed by Lakatos and Krumhansl (1968, 1969). The factors which limit the usefulness of the Lakatos and Krumhansl (1968) scheme are: (a) only the self energy was determined (this is not related directly to the neutron groups observed experimentally), (b) the method for finding the k-space representation of the self energy was unnecessarily difficult. Furthermore, the similarity transformation given by Lakatos (1967) for the reduction of the defect space does not reduce the space properly.

The dynamics of a defect crystal with large distortion have been discussed by Lifshitz and Kosevich (1967). The drawback of their method is related to their formalism and the fact that the approach is similar to that of the one impurity problem. Litzman and Rozsa (1965) present a rather cumbersome matrix method which is not readily applicable to a calculation.

The pair problem has been considered from a theoretical viewpoint by Takeno (1962_b) for an isolated pair of defects and by Langer (1961) for a large number of pairs where no correction was made for multiple occupancy of sites by defects. Leath and Goodman (1968) dealt with pairs by using a cluster expansion, but this led to an over-correction and certain spurious features. Recently, Aiyer, Elliott, Krumhansl and Leath (1969) considered pairs from a diagrammatic point of view and have included the proper corrections for multiple occupancy in their treatment which is correct to c^2.

Up to the present, no algebraic scheme has been proposed to consider the general n-tuple or cluster processes, nor has any algebraic means been formulated to obtain the pairs result of Aiyer, Elliott, Krumhansl and Leath (1969). The advantage of such a scheme (as presented in Chapter II) over the diagrammatic approach adopted by the above authors is that it readily lends itself to the consideration of not only the purely random defect lattice but also of a crystal where the defects are correlated, and have some degree of spacial order.

It has been shown, Takeno (1962_b), that the presence of a finite number of impurities in a crystal, even at low concentrations, has an effect on the lattice vibrations in the local mode frequency region. Lifshitz (1963) demonstrated that the amplitude of a local mode dies away in an approximately exponential manner; thus, the local mode is not localized, since the vibrations due to one defect can affect those of nearby defects. The machine calculations of Dean (1961, 1965) found a density of states in a frequency of range about the local mode frequency. Since the carrier of these vibrations is the host lattice, it is expected that the density of vibrations in the local mode frequency range mirrors, in some way, the vibrations of the host lattice. In fact, it is the higher order correlations (such as pairs, triplets, etc.) that give rise to the fine structure about the local mode (Dean (1961)). This problem has been considered by many authors, such as Agacy (1964), using machine calculations, and Taylor (1967) using a self consistent Green's function treatment. The self consistent approach given by Taylor (1967) defines an effective lattice such that no scattering occurs. In this approach, Taylor used an approximation that eliminated the scattering from single sites. Aiyer, Elliott, Krumhansl and Leath have extended Taylor's work to include pairs. Unlike the effective lattice theory (Chapter II, Section E) which uses phonons of infinite lifetime for the effective lattice, the self consistent Green's function theory uses the perturbed phonons of the defect lattice as the starting point in an iterative process for the averaged Dyson equation.

The usual approach to defect induced far infrared absorption in ionic crystals uses the one defect theory. Even though this theoretical method is rather crude, it has produced some interesting comparisons with experiment (Woll, Gethins and Timusk (1968)). In Part B of the proceedings of the Irvine Conference (Wallis (1967)) there is a good review of the subject of defect modes in ionic crystals. Timusk and Ward (1969) found that certain points of the absorption which are associated with Van Hove singularities shift in frequency as the concentration of impurities is changed. Although any perturbative approach in terms of the perfect lattice Green's functions will always reflect the perfect lattice Van Hove singularities--or at most, produce a metamorphosis of these singularities (Okazaki et al. (1967)) in the absorption constant--Taylor (1971) has shown by using a model density of states for a monatomic crystal, that singular points do shift if a self consistent calculation is made. So far. a self consistent treatment of a three-dimensional diatomic lattice has not been attempted.

Recently, some interesting experimental work has been done on rare gas crystals with molecular impurities. Kriegler and Welsh (1968) have considered the interaction of the lattice vibrations of Ar on the rotational and vibrational excitations of H_2. De Remigis and Welsh (1970) have repeated the same experiment for D_2 in Ar, and also, De Remigis (1971) has considered the change of this interaction for N_2 in Ar as a function of temperature. The theory for infrared absorption in rare gas crystals has been developed in an article by Davies and Healey (1968) for one phonon absorption, however, they do not consider the interaction between the lattice vibrations and the rotational/vibrational excitations of the impurity. A comprehensive study of this interaction of H_2 has been given by Noolandi and Van Kranendonk ($1970_{a,b}$). Although Noolandi and Van Kranendonk have only considered this problem in solid hydrogen, it can easily be extended to near infrared absorption of molecular impurities in solid argon.

A large body of work on atomic potentials for molecules in either the gaseous or liquid state is contained in Hirshfelder, Curtiss and Bird (1954), and Hirshfelder (1967). Girifalco and Wiezer (1959) have considered the Morse potential for metallic crystals by fitting the parameters to the heat of sublimation, Born stability condition, and the bulk modulus. Cotterill and Doyama (1967) note that Girifalco and Wiezer's use of the heat of sublimation in determining the Morse potential parameters for metallic crystals is incorrect. They argue that the heat of vacancy formation should be used, since it takes into account the electron redistribution. The use of an interatomic potential to discuss the lattice dynamics of a perfect crystal lattice was demonstrated by de Wette, Cotterill and Doyama (1966). Here, a Morse potential, found by using the technique of Cotterill and

Doyama (1967), was employed to obtain the dispersion curves of copper. Although the parameters of de Wette, Cotterill and Doyama (1966), and Cotterill and Doyama (1967) for Cu differ, the derived dispersion curves are correct to within 5% and 10% respectively, of the experimental results. Since the work undertaken in this thesis is applied to metals for which pseudopotentials have not been used to calculate phonons, the idea of using an interatomic potential to discuss the lattice dynamics of a crystal is of great interest. Though a knowledge of the interatomic forces is very limited, rough approximations have been used for crystals in the study of dislocations and stacking faults. Christian and Vitek (1970) present an excellent review of the interatomic potentials necessary to the study of dislocations and stacking faults. Discussion of potentials in ionic crystals are standard (Seitz, 1940). For rare gas crystals, the gas pair potentials remain valid even in the crystal state (Kriegler and Welsh, 1968).

A theoretical account of the change of force constants about an impurity atom was presented by Parlinski (1970) using a pseudo-harmonic approach. In the article, this method is restricted to one dimension and assumes that the bare potential of the impurity atoms is the same as that of the host lattice. Page (1970) uses the "lattice statics" method to compute the lattice relaxation about point defects. The displacement of the atoms about the impurity site is found relative to unit relaxation of the nearest neighbour atoms. The usual methods used in calculating the distortion of the lattice about an impurity involves either the minimum energy principle or the balancing of interatomic forces in the defect space. In this thesis, relaxations will be considered via the latter method.

CHAPTER II

THEORY

> "So far as the work of the intellect is concerned, I may perhaps successfully accomplish it by my own powers, but the materials for the intellect to work upon are so widely scattered that, to borrow a metaphore from the world of commerce, factors and merchants must seek them out from all sides and import them."
> --Francis Bacon

SECTION A

GENERAL FORMALISM

1. Double-Time Thermal Green's Functions

In statistical mechanics, Green's functions are generally connected with the concept of correlation functions and intimately linked with the evaluation of observables.

In general, the quantities of interest in systems with large numbers of interacting particles are the correlation functions of the following form:

$$F_{AB}(t-t') = \langle A(t)B(t')\rangle$$

and

$$F_{BA}(t-t') = \langle B(t')A(t)\rangle$$

where $\langle\cdots\rangle$ denotes the usual thermodynamic average,

$$\langle\cdots\rangle = \mathrm{Tr}(e^{-H/k_BT}\ldots)/\mathrm{Tr}(e^{-H/k_BT})$$

and $A(t)$, $B(t')$ are Heisenberg operators.

By expressing these correlation functions explicitly in terms of the exact eigenvalues E_n and eigenvectors $|n\rangle$ of the Hamiltonian, it is found that they can be written in terms of the spectral intensity $J(\omega)$.

$$F_{AB}(t-t') = \int_{-\infty}^{\infty} J(\omega)\exp(\beta\omega)e^{-i\omega(t-t')}\,d\omega \qquad \text{(II-1)}$$

$$F_{BA}(t-t') = \int_{-\infty}^{\infty} J(\omega)\exp(-i\omega(t-t'))\,d\omega \qquad \text{(II-2)}$$

where $\beta=\hbar/k\ T$ and equation (II-1) and (II-2) are ralated by

$$F_{BA}(t+i\beta) = F_{AB}(t) \qquad \text{(II-3)}$$

The spectral intensity is given by

$$J(\omega) = \frac{1}{\mathrm{Tr}(e^{-H/k_BT})}\sum_{mn} \langle m|A(0)|n\rangle\langle n|B(0)|m\rangle \exp -\left(\frac{E_n}{k_BT}\right)\delta\left(\frac{E_n-E_m}{\hbar}-\omega\right)$$

$$= \frac{1}{2\pi i\mathrm{Tr}(e^{-H/k_BT})}\sum_{mn} \langle m|A(0)|n\rangle\langle n|B(0)|m\rangle \exp\left(-\frac{E_n}{k_BT}\right)$$

$$\left\{\frac{1}{\frac{E_n-E_m}{\hbar}-\omega-i\varepsilon} - \frac{1}{\frac{E_n-E_m}{\hbar}-\omega+i\varepsilon}\right\}_{\varepsilon\to 0^+}$$

where the term in the sum of $J(\omega)$ has poles in ω at every excited state of the system.

By using advanced and retarded double-time thermal Green's functions:

$$G_a(t,t') = \langle\langle A(t);B(t')\rangle\rangle_a = i\theta(t'-t)\langle[A(t),B(t')]\rangle \qquad \text{(II-4)}$$

$$G_r(t,t') = \langle\langle A(t);B(t')\rangle\rangle_r = -i\theta(t-t')\langle[A(t),B(t')]\rangle \qquad \text{(II-5)}$$

where $\theta(t) = \begin{matrix} 1 & t>0 \\ 0 & t<0 \end{matrix}$ and $[A,B] = AB-\eta BA$, $\eta=\pm1$, this spectral intensity can be evaluated without any knowledge of the eigenfunction of the Hamiltonian. The sign of η indicates the

the commutator or anticommutator. If A and B are Bose operators, the commutator or positive sign of η is taken, whereas if they are Fermi operators, the negative sign is taken. This thesis considers only Bose operators.

Stating explicitly the time dependence of these Green's functions, clearly demonstrates that they depend only on differences in time, i.e.,

$$G_{(a,r)}(t,t') = G_{(a,r)}(t-t') \qquad \text{(II-6)}$$

To establish the relation between the Green's functions and the spectral intensity, it is necessary to define the Fourier transforms:

$$G(t) = \int_{-\infty}^{\infty} G(\omega)e^{-i\omega t}d$$

$$G(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} G(t)e^{i\omega t}dt \qquad \text{(II-7)}$$

Using the definition (II-5) of, say, $G_r(t)$, the frequency representation $G_r(\omega)$ becomes

$$G_r(\omega) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} d\omega' J(\omega')(e^{\beta\omega'}-1)\int_{-\infty}^{\infty} dt\theta(t)e^{i(\omega-\omega')t} \qquad \text{(II-8)}$$

Since the step function can be written in the form

$$\theta(t) = \frac{i}{2\pi}\int_{-\infty}^{\infty} \frac{e^{ixt}}{x+i\varepsilon}\,dx \qquad \varepsilon\to o^{+} \qquad \text{(II-9)}$$

equation (II-8) can be expressed as

$$G_r(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{(e^{\beta\omega'}-1)J(\omega')}{\omega-\omega'-i\varepsilon} \qquad \text{(II-10)}$$

and similarly

$$G_a(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{(e^{\beta\omega'}-1)J(\omega')}{\omega-\omega'+i\varepsilon} \qquad \text{(II-11)}$$

The functions $G_r(\omega)$ and $G_a(\omega)$, as expressed in (II-10) and (II-11) respectively, can be continued analytically in the complex ω plane. Indeed, by taking $\omega=z$ as complex, equations (II-10) and (II-11) become

$$G(z) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{(e^{\beta\omega'}-1)J(\omega')}{z-\omega'} = \begin{matrix} G_r(z) & \text{Im } z>0 \\ G_a(z) & \text{Im } z<0 \end{matrix} \qquad \text{(II-12)}$$

If a cut is made along the real axis, G can be considered as one analytical function in the complex plane. In this case, G is made up of two branches, one defined in the upper (G_r) and the other in the lower (G_a) half of the complex z-plane.

If G(z) is known, the spectral intensity $J(\omega)$ can be found from the relation

$$G(\omega+i\varepsilon)-G(\omega-i\varepsilon) = -i(e^{\beta\omega}-1)J(\omega) \qquad \text{(II-13)}$$

for real ω, ε and $\varepsilon\to 0^+$. Equation (II-13) is a direct result of the properties of G(z) as expressed by (II-12).

Now the Green's function must be found in order to solve the problem. Although this depends upon the physical problem under consideration, in general the equation of motion for the Green's function is used. To obtain this equation, the Green's function is differentiated with respect to one of the times. The form of this equation is the same for both the retarded and advanced Green's functions.

$$i\hbar\frac{dG(t-t')}{dt} = \hbar\delta(t-t')<[A(t),B(t')]>+<<[A(t),H(t)];B(t')>> \qquad \text{(II-14)}$$

The evaluation of the commutator in the last term of equation (II-14) generates new Green's functions, and thus, a chain of coupled equations. It is these equations that form the starting point for the discussion of lattice dynamics.

2. The Hamiltonian For Lattice Dynamics

This part of Section A presents the approximations made in developing the lattice dynamics of crystals and demonstrates the quantization of lattice vibrations. The discussion in this part is similar to that of Born and Oppenheimer (1927).

a. The Adiabatic Approximation

Following the approach of Seitz (1940) the full Hamiltonian operator, H', for a crystal is given by

$$H' = -\sum_{i}\frac{\hbar^2}{2m}\nabla_i^2-\sum_{\alpha\tilde{\ell}}\frac{\hbar^2}{2M_\alpha(\tilde{\ell})}\nabla_{\alpha\tilde{\ell}}^2+\sum_{i<j}\frac{e^2}{|\tilde{r}_i-\tilde{r}_j|}+V_{ei}(\bar{\bar{u}},\bar{\bar{r}})+V_{ii}(\bar{\bar{u}})$$

where $\bar{\bar{u}} = (\tilde{u}_{\alpha_1}(\tilde{\ell}_1),\ldots,\tilde{u}_{\alpha_{N_s}}(\tilde{\ell}_{N_s}))$, $\bar{\bar{r}} = (\tilde{r}_1,\ldots,\tilde{r}_n)$;

the indices i, j, extend over electrons while the indices α and $\tilde{\ell}$ extend over the ions; $M_\alpha(\tilde{\ell})$ is the mass of the α^{th} ion in the $\tilde{\ell}^{th}$ unit cell; $V_{ei}(\bar{\bar{u}},\bar{\bar{r}})$ is the electron-ion interaction potential with the ions displaced $\bar{\bar{u}}$ from their equilibrium positions while the electrons are at position $\bar{\bar{r}}$; and $V_{ii}(\bar{\bar{u}})$ is the interaction potential of the rigid ions displaced by $\bar{\bar{u}}$ from their equilibrium positions.

Although the exact eigenfunction Ψ of H' is an involved function of $\bar{\bar{u}}$ and $\bar{\bar{r}}$, the decomposition of Ψ into the form

$$\Psi(\bar{\bar{u}},\bar{\bar{r}}) = \chi(\bar{\bar{u}},\bar{\bar{r}})\phi(\bar{\bar{u}}) \tag{II-15}$$

is attempted. If χ in (II-15) is regarded as electronic wave function satisfying the Schrödinger equation

$$\left\{-\sum_i \frac{\hbar^2}{2m}\nabla_i^2+\sum_{i<j}\frac{e^2}{|\tilde{r}_i-\tilde{r}_j|}+V_{ei}(\bar{\bar{u}},\bar{\bar{r}})\right\}\chi(\bar{\bar{u}},\bar{\bar{r}}) = E_e(\bar{\bar{u}})\chi(\bar{\bar{u}},\bar{\bar{r}}) \tag{II-16}$$

for electrons in a static lattice, with the ℓ^{th} ion fixed at $\tilde{u}\ (\ell)$, then the result is what is commonly called the adiabatic approximation. Here the u's are regarded as parameters for the description of the electronic system, It is assumed that χ, the many-electron wave function, has eigenvalues $E_e(\bar{\bar{u}})$ which can be considered as a set of quasi-particle levels. Since these eigenvalues are functions of $\bar{\bar{u}}_\alpha(\ell)$, the energy of the electron gas will depend on the position of the ions.

This adiabatic approximation is only true if the electrons move much more rapidly than the ions. It will be shown that the accuracy of this approach depends on the ionic masses being much larger than the electron mass.

Applying the operator H' to the wave function Ψ,

$$H'\Psi = \chi(\bar{\bar{u}},\bar{\bar{r}})\left\{-\sum_{\alpha,\ell}\frac{\hbar^2}{2M_\alpha(\ell)}\nabla^2_{\alpha,\ell}+E_e(\bar{\bar{u}})+V_{ii}(\bar{\bar{u}})\right\}\phi(\bar{\bar{u}}) \qquad (\text{II-17}_a)$$

$$+\left\{-\sum_{\alpha,\ell}\frac{\hbar^2}{2M_\alpha(\ell)}\nabla_{\alpha,\ell}\phi(\bar{\bar{u}})\cdot\nabla_{\alpha,\ell}\chi(\bar{\bar{u}},\bar{\bar{r}})-\sum_{\alpha,\ell}\frac{\hbar^2}{2M_\alpha(\ell)}\phi(\bar{\bar{u}})\nabla^2_{\alpha,\ell}\phi(\bar{\bar{u}},\bar{\bar{r}})\right\} \qquad (\text{II-17}_b)$$

If (II-17_b) can be ignored, then the complete eigenvalue problem

$$H'\Psi = \Xi\Psi$$

can be solved by having $\phi(\bar{\bar{u}})$ satisfy the Schrodinger equation

$$\left\{-\sum_{\alpha,\ell}\frac{\hbar^2}{2M_\alpha(\ell)}\nabla^2_{\alpha,\ell}+E_e(\bar{\bar{u}})+V_{ii}(\bar{\bar{u}})\right\}\phi(\bar{\bar{u}})=\Xi\phi(\bar{\bar{u}}) \qquad (\text{II-18})$$

It is this equation for a wave function of only the ions that leads to a quantum mechanical solution of the lattice dynamical problem.

In order to show that the second term of (II-17_b) may ordinarily be neglected for stationary state problems, two extreme cases are considered. In the first case, the electrons are considered as free, and in the second, they are considered to be completely bound. Multiplying (II-17_b) by $\chi^*(\bar{\bar{u}},\bar{\bar{r}})$ and integrating over the electron coordinates produces

$$\left\{-\sum_{\alpha,\ell}\frac{\hbar^2}{2M_\alpha(\ell)}\left[\left(\int\chi^*(\bar{\bar{u}},\bar{\bar{r}})\nabla_{\alpha\ell}\chi(\bar{\bar{u}},\bar{\bar{r}})d\bar{\bar{r}}\right)\cdot\nabla_{\alpha\ell}\phi(\bar{\bar{u}}) + \phi(\bar{\bar{u}})\int\chi^*(\bar{\bar{u}},\bar{\bar{r}})\nabla^2_{\alpha,\ell}\chi(\bar{\bar{u}},\bar{\bar{r}})d\bar{\bar{r}}\right]\right\} \qquad (\text{II-19})$$

In the free electron case, the wave functions are of the form $e^{i\bar{K}.\tilde{r}}$ and hence are practically independent of the ion coordinates. Thus (II-19) is vanishingly small. For the opposite case, the electrons are tightly bound to "their" ions

$$\chi(\bar{\bar{u}},\bar{\bar{r}}) = \chi(\bar{\bar{r}}-\bar{\bar{u}})$$

Therefore, the second term of (II-19) gives a contribution like

$$\int\chi^*(\bar{\bar{r}}-\bar{\bar{u}})\ \frac{\hbar^2}{2M_\alpha(\ell)}\ \nabla^2_{\alpha,\ell}\chi(\bar{\bar{r}}-\bar{\bar{u}})d\bar{\bar{r}} = \int\chi^*(\bar{\bar{r}}-\bar{\bar{u}})\ \frac{\hbar^2}{2M_\alpha(\ell)}\ \nabla^2_i\chi(\bar{\bar{r}}-\bar{\bar{u}})d\bar{\bar{r}}$$

$$= \frac{m}{M_\alpha(\ell)}\left(\int\chi^*\frac{\hbar^2}{2m}\ \nabla^2_i\chi d\bar{\bar{r}}\right)$$

which is just $\frac{m}{M_\alpha(\ell)}$ times the kinetic energy of the electrons. Since $\frac{m}{M_\alpha(\ell)} \sim 10^{-4}$ or 10^{-5} this term is negligible in comparison with ordinary thermal energies.

The first term of (II-19) for tightly bound electrons may also be dropped in stationary state problems since χ can then be chosen as a real function and

$$\int\chi^*(\bar{\bar{u}},\bar{\bar{r}})\nabla_{\alpha,\ell}\chi(\bar{\bar{u}},\bar{\bar{r}})d\bar{\bar{r}}=\tfrac{1}{2}\nabla_{\alpha,\ell}\int|\chi(\bar{\bar{u}},\bar{\bar{r}})|^2d\bar{\bar{r}}$$

$$= \tfrac{1}{2}\nabla_{\alpha,\ell}1 = 0$$

Thus, in the adiabatic approximation, the effective potential function for the ion motion

$$\Phi(\bar{\bar{u}}) = E_e(\bar{\bar{u}})+V_{ii}(\bar{\bar{u}}) \tag{II-20}$$

which contains information about the total energy of the electron system as a function of ion positions, is used to describe the lattice dynamical problem.

b. The Harmonic Approximation and Quantized Lattice Vibrations

If the adiabatic approximation is assumed, the Hamiltonian for the ions becomes

$$H = \sum_{\alpha\ \ell} \frac{p_\alpha^2(\ell,t)}{2M_\alpha(\ell)} + \Phi(\bar{\bar{u}})$$

At finite temperature, the atoms of the crystalline solid execute small oscillations about their equilibrium positions as a result of thermal fluctuation. If $\tilde{u}(\ell)$ defines the displacement of the atom ℓ from its equilibrium position, then for small oscillations the potential energy may be expanded in powers of displacement. This series expansion may be expected to converge rapidly if the displacements are small compared to the interatomic spacing.

$$\Phi(\bar{\bar{u}}) = \Phi(0)+\sum_{\beta,\ell} u_\beta(\ell,t)\left[\frac{\partial\Phi}{\partial u_\beta(\ell)}\right]_0 +\frac{1}{2}\sum_{\substack{\beta_1\ell_1\\ \beta_2\ell_2}} u_{\beta_1}(\ell_1,t)u_{\beta_2}(\ell_2,t)$$

$$\times \left[\frac{\partial^2\Phi}{\partial u_{\beta_1}(\ell_1)\partial u_{\beta_2}(\ell_2)}\right]_0 + \cdots \tag{II-21}$$

where $\beta = (\underline{\beta},\ b)$

In this expansion of Φ, $u_\beta(\tilde{\ell},t)$ is the displacement of the bth atom of the $\tilde{\ell}^{th}$ unit cell in the $\underline{\underline{\beta}}^{th}$ direction at time t. Here, $\Phi(0)$ is just the static (equilibrium) potential energy of the crystal and may be neglected for this discussion. The coefficient of the linear term in (II-21) must vanish since the crystal is near equilibrium; thus the first term of importance must be the quadratic term.

By dropping terms of higher order than two, the harmonic approximation is obtained. Such a curtailment of the series guarantees the dynamical independence of different modes of vibration in a perfect lattice.

Accepting this approximation, the Hamiltonian is now defined by

$$H = \frac{1}{2}\sum_{\alpha,\tilde{\ell}} \frac{p_\alpha^2(\tilde{\ell},t)}{M_\alpha(\tilde{\ell})} + \frac{1}{2}\sum_{\substack{\alpha\ \beta \\ \tilde{\ell}\ \tilde{\ell}'}} u_\alpha(\tilde{\ell},t)\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')u_\beta(\tilde{\ell}',t) \qquad \text{(II-22)}$$

where

$$\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}') = \left(\frac{\partial^2\Phi(\overline{\overline{u}})}{\partial u_\alpha(\tilde{\ell})\,\partial u_\beta(\tilde{\ell}')}\right)_0$$

is the force felt by the ath atom of the $\tilde{\ell}^{th}$ unit cell in the $\underline{\underline{\alpha}}^{th}$ direction due to a unit displacement of the bth atom of the $\tilde{\ell}'^{th}$ unit cell in the $\underline{\underline{\beta}}^{th}$ direction ($\alpha = (\underline{\underline{\alpha}},a)$, $\beta = (\underline{\underline{\beta}},b)$). $\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')$, which is called the force constant matrix, satisfies the symmetry relation

$$\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}') = \Phi_{\beta\alpha}(\tilde{\ell}',\tilde{\ell})$$

and also

$$\sum_{\tilde{\ell},a} \Phi_{(\underline{\alpha},a),(\underline{\beta},b)}(\tilde{\ell},\tilde{\ell}') = 0$$

The latter relation is a result of invariance of the lattice under rigid body translations.

Attention is now focused on the perfect lattice. In the case of the perfect crystal, $M_\alpha(\tilde{\ell})$ is obviously independent of $\tilde{\ell}$. The Heisenberg operators, $u_\alpha(\tilde{\ell},t)$ and $p_\alpha(\tilde{\ell},t)$ satisfy the commutation relations

$$[u_\alpha(\tilde{\ell},t),\ p_\beta(\tilde{\ell}',t)] = i\hbar\delta_{\alpha\beta}\delta(\tilde{\ell},\tilde{\ell}')$$

$$[u_\alpha(\tilde{\ell},t),\ u_\beta(\tilde{\ell}',t)] = [p_\alpha(\tilde{\ell},t),\ p_\beta(\tilde{\ell}',t)] = 0$$

Using the ordinary Lagrangian procedure, the equation of motion for $u_\alpha(\tilde{\ell},t)$ is found to be

$$\sum_{\beta,\tilde{\ell}'} \left[M_\alpha \frac{d^2}{dt^2} \delta_{\alpha\beta}\delta(\tilde{\ell},\tilde{\ell}') + \Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}') \right] u_\beta(\tilde{\ell}',t) = 0 \qquad \text{(II-23)}$$

The solution is found by expanding $u_\alpha(\tilde{\ell},t)$ and $p_\alpha(\tilde{\ell},t)$ in normal coordinates $Q^j(\tilde{k},t)$ and $P^j(\tilde{k},t)$, taking into account the translational symmetry of the lattice.

$$u_\alpha(\tilde{\ell},t) = \frac{1}{\sqrt{NM_\alpha}} \sum_{j,\tilde{k}} \sigma_\alpha^{*j}(k) Q^j(\tilde{k},t) e^{-i\tilde{k}\cdot\tilde{\ell}}$$

$$p_\alpha(\tilde{\ell},t) = \sqrt{\frac{M_\alpha}{N}} \sum_{j,\tilde{k}} \sigma_\alpha^j(\tilde{k}) P^j(\tilde{k},t) e^{-i\tilde{k}\cdot\tilde{\ell}} \qquad \text{(II-24)}$$

where N is the number of unit cells in the crystal and S is the number of atoms per unit cell. There are N quasi-continuous values of wave vector $\tilde{k}$ filling the first Brillouin zone and for each vector $\tilde{k}$ there are 3S normal modes or branches labelled by j.

The normal coordinates $Q^j(\tilde{k},t)$ satisfy the equation of motion

$$\frac{d^2}{dt^2} Q^j(\tilde{k},t) = -\omega_j^2(\tilde{k}) Q^j(\tilde{k},t)$$

where $\omega^2(\tilde{k})$ are the eigenvalues and $\sigma_\alpha(\tilde{k})$ the eigenvectors of

$$\sum_\beta d_{\alpha\beta}(\tilde{k}) \sigma_\beta^{*j}(\tilde{k}) = \omega_j^2(\tilde{k}) \sigma_\alpha^{*j}(\tilde{k}) \qquad \text{(II-25)}$$

with the dynamical matrix

$$d_{\alpha\beta}(\tilde{k}) = \sum_{\tilde{\ell}'} \frac{\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')}{\sqrt{M_\alpha M_\beta}} e^{i\tilde{k}\cdot(\tilde{\ell}-\tilde{\ell})}$$

$\sigma_\alpha^j(\tilde{k})$ is chosen in such a way that it satisfies the orthoganility and closure conditions

$$\sum_\alpha \sigma_\alpha^{*j}(\tilde{k}) \sigma_\alpha^{j'}(\tilde{k}) = \delta_{j'j} \qquad \text{and} \qquad \sum_j \sigma_\alpha^{*j}(\tilde{k}) \sigma_\beta^j(\tilde{k}) = \delta_{\alpha\beta}$$

These eigenvectors, although complex in general, are real for Bravais lattices.

Of the branches j, three are called acoustical with $\omega_j(\tilde{k}) \to 0$ as $\tilde{k} \to 0$ while the remainder are called optical, and in a diatomic lattice

$$\frac{\sigma^j_{(\underline{\alpha},1)}(0)}{\sqrt{M_1}} = \frac{\sigma^j_{(\underline{\alpha},2)}(0)}{\sqrt{M_2}} \qquad \text{for j= acoustical}$$

whereas $\sqrt{M_1}\sigma^j_{(\underline{\underline{\alpha}},1)}(0) = - \sqrt{M_2}\sigma^j_{(\underline{\underline{\alpha}},2)}(0)$ for j=optical.

The normal coordinates can be conveniently written in terms of new variables

$$Q^j(\tilde{k},t) = \sqrt{\frac{\hbar}{2\omega_j(\tilde{k})}}\,(a_j^\dagger(\tilde{k},t)+a_j(\tilde{k},t))$$

$$P^j(\tilde{k},t) = i\sqrt{\frac{\hbar\omega_j(\tilde{k})}{2}}\,(a_j^\dagger(\tilde{k},t)-a_j(\tilde{k},t)) \qquad \text{(II-26)}$$

which satisfy the commutation relations:

$$[a_j(\tilde{k},t),a_{j'}^\dagger(\tilde{k}',t)] = \delta_{jj'}\delta(\tilde{k},\tilde{k}')$$

$$[a_j(\tilde{k},t),a_{j'}(\tilde{k}',t)] = [a_j^\dagger(\tilde{k},t),a_j^\dagger\ (\tilde{k}',t)] = 0 \qquad \text{(II-27)}$$

These are the usual boson relations and in the number representation these new operators have only the following non-zero matrix elements:

$$\langle n|a^\dagger|n-1\rangle = n^{\frac{1}{2}}$$

and

$$\langle n|a|\ n+1\rangle = (n+1)^{\frac{1}{2}}$$

where n is the occupation number of a given mode.

Thus, $a^\dagger$ and a can be considered to create and annihilate respectively normal mode excitations or phonons of the perfect crystal. In terms of these operators, the Hamiltonian (II-22) reduces to the simple form

$$H = \sum_{j,\tilde{k}} \frac{\hbar\omega_j(\tilde{k})}{2}\,[a_j^\dagger(\tilde{k},t)a_j(\tilde{k},t)+a_j(\tilde{k},t)a_j^\dagger(\tilde{k},t)]$$

3. The Probability Distribution Function

This discussion of probability and density distribution functions which follows that given by Lax (1951) is necessary only for the consideration of the $n>1$ tuple processes since the procedure for the $n=1$ process is rather intuitive.

The determination of the statistical distribution for any sub-set of a set of scatterers is a fundamental problem of statistical physics. It should be noted that the probabilistic nature of the results of the statistical process adopted is not an inherent property of the objects considered, but simply arises from the fact that these results are derived from much less information than would be necessary for a complete mechanical description.

The probability that the set of d_{N_σ} of N_σ scatterers will be located at any set $\{s\}_{d_{N_\sigma}}$ contained in U_s of N_σ sites $\{s\}_{d_{N_\sigma}} = \{s\}_{N_\sigma} = (s_1, s_2, \ldots s_{N_\sigma})$ is given by

$$p(\{s\}_{N_\sigma}) = p(s_1, \ldots, s_{N_\sigma})$$

where U_s is the set of all possible sites. The sum of these N_σ scatterers in p over all sites possible, is normalized to unity.

The probability distribution for a single scatterer is obtained by summing the remaining $(N_\sigma - 1)$ scatterers over all sites

$$p(s_1) = \sum_{s_2, \ldots, s_{N_\sigma}} p(s_1, s_2, \ldots, s_{N_\sigma})$$

Similarly, the correlation probability for the simultaneous location of a pair of scatterers is obtained by summing the remaining (n -2) scatterers over all sites

$$p(s_1,s_2) = p(\{s\}_2) = \sum_{s_3,\ldots,s_{N_\sigma}} p(\{s\}_{N_\sigma})$$

In general, the correlation probability for the simultaneous location of $n \leq N_\sigma$ scatterers can be written as

$$p(\{s\}_n) = \sum_j p(\{s\}_n, S^j_{N_\sigma - n}) \qquad \text{(II-28)}$$

where the j^{th} configuration of the remaining $(N_\sigma - n)$ scatterers is

$$S^j_{N_\sigma - n} = (s^j_{n+1},\ldots,s^j_{N_\sigma})$$

If the scatterers are equivalent, then a relabelling of the configuration produces

$$S^i = (s^j_{n+1},\ldots,s^j_{N_\sigma}) = (s^i_1,\ldots,s^i_{N_\sigma - n})$$

where the $N_\sigma - n$ is understood.

If the set of d_{N_σ} of N_σ scatterers is considered as the universal set, U_σ, of scatterers, then (II-28) becomes

$$p(\{s\}_n) = \sum_j p(\{s\}_n, \{s^j\}_{n^c}) \qquad \text{(II-29)}$$

where
$$\{s\}_{n^c} = \{s\}_{(d_n{}^c)}$$

is the set of $N_\sigma - n$ scatterers, $(d_n{}^c)$, located at the sites $s_{m_1}, s_{m_2}, \ldots, s_{m_{N_\sigma - n}}$ respectively. The superscript c for the set d_n in brackets indicates the complement.

For a truly random distribution, the probabilities associated with a single scatterer are not influenced by the information concerning other scatterers, and so the complete distribution breaks down as follows:

$$p(\{s\}_{N_\sigma}) = p(s_1)p(s_2)\ldots p(s_{N_\sigma}) \qquad \text{(II-30)}$$

It should be noted that for a random crystal lattice equation (II-30) holds only if $s_i \neq s_j \ \forall\ i \neq j$, otherwise this probability is zero. Clearly the quantity

$$p(s_1,s_2) - p(s_1)p(s_2) \qquad \text{(II-31)}$$

can give a measure of correlation or non-randomness between pairs.

Even if the distribution is non-random, it is possible to introduce a pseudo-factorization by using conditional probabilities:

$$p(\{s\}_{N_\sigma}) = p(s_1)p(s_1|\{s\}_{1c}) \qquad \text{(II-32)}$$

where the second term of (II-32) represents the conditional probability distribution for scatterers 2, 3,...,N if it is known that scatterer 1 is at s_1. Generally,

$$p(\{s\}_{N_\sigma}) = p(\{s\}_n,\{s\}_{nc}) = p(\{s\}_n)p(\{s\}_n|\{s\}_{nc}) \qquad \text{(II-33)}$$

In this notation, the average of an operator O, which depends on all the N_σ scatterers over the ensemble of scatterers, is given by

$$\langle O\rangle = \sum_j O(\{s^j\}_{N_\sigma})p(\{s^j\}_{N_\sigma}) \tag{II-34}$$

(the configurational average). If the scatterers 1,...,n are held fixed at $s_1,\ldots,s_n$, and all other scatterers are averaged over, then the average of O will be denoted by

$$\langle O\rangle_{s_1,\ldots s_n} = \langle O\rangle_{\{s\}_n} = \sum_j O(\{s\}_n,\{s^j\}_{nc})p(\{s\}_n|\{s^j\}_{nc})\cdot p(\{s\}_n) \tag{II-35}$$

and is referred to as the conditional configuration average. Here, j refers to configurations of N_σ-n scatterers.

Using the normalization condition, the probability distribution for a single scatterer in a lattice having N equivalent sites is

$$p(s_1) = \frac{1}{N_s} \tag{II-36}$$

It can be shown from (II-33) that

$$p(\{s\}_n|\{s\}_{nc}) = \frac{p(\{s\}_m)}{p(\{s\}_n)}\,p(\{s\}_m|\{s\}_{mc}) \tag{II-37}$$

Before discussing the crystal system one more point should be added to this rather general discussion of probability distribution functions--that is, that probability distributions may be converted to density distributions by multiplying by some power of the number of scatterers

$$\rho(\{s\}_n) = (N_\sigma)^n p(\{s\}_n) \tag{II-38}$$

The relative fluctuations of physical quantities describing a crystal should occur with a vanishing probability, if the crystal system contains a sufficiently large number of sites N_s. In such a system, the number of sites contained, even in a small part N_σ of N_s sites, may still be very large, i.e., $N_s \to \infty$ but $\frac{N_\sigma}{N_s}$ remains finite.

The configurational average is now considered in such a system. If T is an operator that depends only on a single scatterer M and O is an operator that depends on all the scatterers of the system, then the configurational average of

$$\sum_{M \varepsilon U_\sigma} T(S_M) O(S_M, \{S\}_{M^c}) = \sum_{M \varepsilon U_\sigma} T(M) O(M, M^c) \qquad \text{(II-39)}$$

is given by

$$<\cdots\cdot> = \sum_j p(\{S^j\}_{N_\sigma}) \sum_{R \varepsilon \{S^j\}_{N_\sigma}} T(R) O(R, \{S^{j'}\}_{N_\sigma - 1}) \qquad \text{(II-40)}$$

where in equation (II-39) each scatterer M is associated with a different possible crystal scattering site S_M, and in equation (II-40) the M^{th} scatterer is associated with the possible crystal scattering site R. The configuration j' in (II-40) is a configuration of N_σ-1 scatterers. It should be noted that for a crystal system the probability distribution function has absorbed the information that no two scatterers can occupy the same possible crystal scattering site. With the aid of equation (II-32), equation (II-40) becomes

$$<\cdots\cdot> = \sum_j p(S^j_M) p(S^j_M | \{S^j\}_{M^c}) \sum_{R \varepsilon \{S^j\}_{N_\sigma}} T(R) O(R, \{S^{j'}\}_{N_\sigma - 1}) \qquad \text{(II-41)}$$

expanding the second summation and rearranging the first (II-41) may be rewritten as

$$\begin{aligned} \langle \cdot\cdot\cdot\cdot \rangle = & \sum_{S_{M_1}} p(S_{M_1}) T(S_{M_1}) \sum_{j'} p(S_{M_1} | \{S^{j'}\}_{M_1^c}) \; O(S_{M_1}, \{S^{j'}\}_{M_1^c}) \\ & + \cdots\cdot \\ & + \sum_{S_{M_{N_\sigma}}} p(S_{M_{N_\sigma}}) T(S_{M_{N_\sigma}}) \sum_{j'} p(S_{M_{N_\sigma}} | \{S^{j'}\}_{M_{N_\sigma}}) O(S_{M^c_{N_\sigma}}, \{S^{j'}\}_{M^c_{N_\sigma}}) \end{aligned} \tag{II-42}$$

and by using (II-35) this is the same as

$$\langle \cdot\cdot\cdot\cdot \rangle = \sum_{i=1}^{N_\sigma} \sum_{S_i} p(S_i) T(S_i) \langle O \rangle_{S_i} \tag{II-43}$$

Now, assuming that all the crystal lattice sites of U_s are equivalent and also that all the scatterers of U_σ are equivalent, then by using equation (II-38), equation (II-43) becomes

$$\langle \cdot\cdot\cdot\cdot \rangle = \sum_{R} \rho(R) T(R) \langle O \rangle_R \tag{II-44}$$

where the sum in equation (II-44) extends over all possible different crystal scattering sites which can be made up of the crystal sites and $\rho(R)$, the density distribution, is the probability that any scatterer of U_σ can be found at any possible crystal scattering site R.

> "We are under obligation to the ancients for having exhausted all the false theories that could be formed."
>
> --Fontenelle

SECTION B

THE LOW CONCENTRATION THEORY

1. Exact Single Scattering

In lattice dynamics, the Hamiltonian H for any crystal can be expressed as

$$H = \frac{1}{2}\sum_{\alpha,\tilde{\ell}} \frac{p^2(\tilde{\ell},t)}{M_\alpha(\tilde{\ell})} + \frac{1}{2}\sum_{\substack{\alpha,\beta\\ \tilde{\ell},\tilde{\ell}'}} u_\alpha(\tilde{\ell},t)\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')u_\beta(\tilde{\ell}',t) \qquad \text{(II-45)}$$

in the harmonic approximation.

The crystal lattice under consideration, formed from the perfect lattice by the introduction of substitutional impurities, has a mass change expressed by

$$M_\alpha - M_\alpha(\tilde{s}_n) = M_\alpha \varepsilon_\alpha^n \qquad \text{(II-46)}$$

and a force constant change of

$$\Delta\Phi^n_{\alpha\beta}(\tilde{\ell}_n,\tilde{\ell}'_n) = \Phi_{\alpha\beta}(\tilde{\ell}_n,\tilde{\ell}'_n) - \Phi^o_{\alpha\beta}(\tilde{\ell}_n,\tilde{\ell}'_n) \qquad \text{(II-47)}$$

where n refers to the defect space $(\tilde{\ell}_n,\tilde{\ell}'_n)$ of the n^{th} impurity located at $\tilde{s}_n$. In (II-46) and (II-47) M_α is the mass of the a^{th} atom, and

$$\Phi^o_{\alpha\beta}(\tilde{\ell}_n,\tilde{\ell}'_n) \qquad \text{(II-48)}$$

is the force constant between $(\alpha,\tilde{\ell}_n)$ and $(\beta,\tilde{\ell}'_n)$ in the perfect lattice.

The Green's function relevant to optical absorption and neutron scattering is the displacement-displacement double-time thermal Green's function

$$G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';t,t')_{(r,a)} = \frac{2\pi}{\hbar} \langle\langle u_\alpha(\tilde{\ell},t);u_\beta(\tilde{\ell}',t')\rangle\rangle_{(r,a)} \quad \text{(II-49)}$$

$$= G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';t-t')_{(r,a)}$$

Using equation (II-14), the equation of motion for this Green's function may be written as

$$\frac{d}{dt} G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';t) = \frac{2\pi i}{\hbar}(\delta(t)\langle[u_\alpha(\tilde{\ell},0),u_\beta(\tilde{\ell}',0)]\rangle$$

$$+ \frac{1}{i\hbar}\frac{2\pi i}{\hbar}\,\theta(t)\langle[[u_\alpha(\tilde{\ell},t)H],u_\beta(\tilde{\ell}',0)]\rangle$$

$$= \frac{2\pi i}{\hbar}\,\frac{\theta(t)}{M_\alpha(\tilde{\ell})}\langle[p_\alpha(\tilde{\ell},t),u_\beta(\tilde{\ell}',0)]\rangle \qquad \text{(II-50)}$$

Differentiating (II-50) with respect to time produces

$$\frac{d^2}{dt^2} G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';t) = \frac{2\pi i}{\hbar M_\alpha(\tilde{\ell})}(-\delta(t))\langle[p_\alpha(\tilde{\ell},0),u_\beta(\tilde{\ell}',0)]\rangle$$

$$+ \frac{2\pi i}{\hbar M_\alpha(\tilde{\ell})}\,\frac{\theta(t)}{i\hbar}\langle[[p_\alpha(\tilde{\ell},t),H],u_\beta(\tilde{\ell}',0)]\rangle \quad \text{(II-51)}$$

which simplifies to

$$M_\alpha(\ell)\frac{d^2}{dt^2}G_{\alpha\beta}(\ell,\ell';t) = -2\pi\delta_{\alpha\beta}\delta(\ell,\ell')\delta(t) - \sum_{\gamma\tilde{\ell}''}\Phi_{\alpha\gamma}(\tilde{\ell},\tilde{\ell}'')G_{\gamma\beta}(\tilde{\ell}'',\tilde{\ell}';t) \tag{II-52}$$

an expression involving only G.

Using equation (II-7), the Fourier transform of (II-52) is

$$M_\alpha\omega^2G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) = \delta_{\alpha\beta}\delta(\tilde{\ell},\tilde{\ell}')+\sum_{\tilde{\ell}''\gamma}\Phi^0_{\alpha\gamma}(\tilde{\ell},\tilde{\ell}'')G_{\gamma\beta}(\tilde{\ell}'',\tilde{\ell}';\omega) + \sum_n\sum_{\tilde{\ell}''\gamma}V^n_{\alpha\gamma}(\tilde{\ell},\tilde{\ell}'';\omega)G_{\gamma\beta}(\tilde{\ell}'',\tilde{\ell}';\omega) \tag{II-53}$$

where

$$V^n_{\alpha\beta}(\tilde{\ell}_n,\tilde{\ell}'_n;\omega) = \Delta\Phi^n_{\alpha\beta}(\tilde{\ell}_n,\tilde{\ell}'_n)+M_\alpha\varepsilon_\alpha\omega^2\delta(\tilde{\ell}_n,\tilde{\ell}'_n)\delta_{\alpha\beta} \tag{II-54}$$

The total defect matrix is written as $V = \sum_n V^n$

where

$$V^n = \begin{array}{cc} & \begin{array}{ccc} & s_n & \end{array} \\ s_n & \left(\begin{array}{c|c|c} 0 & 0 & 0 \\ \hline 0 & v^n & 0 \\ \hline 0 & 0 & 0 \end{array}\right) \end{array}$$

and v^n = the perturbation matrix spanning the defect space of defect n. In order to facilitate the handling of these equations, the full matrix notation is adopted. In the notation, (II-53) becomes

$$MG = I+\Phi^0G+\sum_n V^nG \tag{II-55}$$

where

$$(M)_{\alpha\beta}(\ell,\ell') = M_\alpha\omega^2\delta_{\alpha\beta}\delta(\ell,\ell')$$

and the other terms are self evident.

If P is the perfect lattice Green's function, (II-55) can be simplified into the following equation

$$MP = I+\Phi^{o}P$$

or

$$P = (M-\Phi^{o})^{-1} \tag{II-56}$$

by noting that in the perfect lattice

$$V^{n}= 0 \quad \forall n\varepsilon U_{\sigma}$$

It is observed that (II-56) is intimately related to (II-23). Thus, a knowledge of the dynamics of the perfect lattice implies a knowledge of P and vice-versa.

Using equation (II-56), equation (II-55) becomes

$$P^{-1}G = I+ \sum_{m} V^{m}G$$

or

$$G = P+ \sum_{m} PV^{m}G \tag{II-57}$$

The Dyson equation (II-57) defines the starting point for the discussion of the impurity problem.

If the concentration of impurities is "low enough" and the change of environment about an impurity "local enough", so that the probability of any two defect spaces overlapping is small, then it seems reasonable to assume that G is dominated by whether or not any individual defect matrix affects the space of its definition. This suggests separating out the Green's function associated with a given defect as follows:

$$G-PV^nG = (I-PV^n)G = G^n \qquad \text{(II-58)}$$

where

$$G^n = P+\sum_{m\neq n} PV^mG \qquad \text{(II-59)}$$

Using equation (II-58), equations (II-57) and (II-59) become

$$G = P+\sum_{m} PV^m(I-P_1V^m)^{-1}G^m \qquad \text{(II-60)}$$

and

$$G^n = P+\sum_{m\neq n} PV^m(I-P_1V^m)^{-1}G^m \qquad \text{(II-61)}$$

where the matrix P_1 only has a contribution in the defect space of the defect m and this contribution is equal to P in that space.

From (II-60) and (II-61), it is observed that

$$T_1^m = V^m(I-P_1V^m)^{-1} = \begin{array}{cc} & \begin{array}{ccc} & s_m & \end{array} \\ s_m & \left(\begin{array}{c|c|c} 0 & 0 & 0 \\ \hline 0 & t_1^m & 0 \\ \hline 0 & 0 & 0 \end{array}\right) \end{array} \qquad \text{(II-62)}$$

is the usual t-matrix describing the scattering of lattice excitations due to the perturbation introduced by one defect atom in an otherwise perfect crystal (Klein (1963)).

After substituting (II-62) into (II-60) and (II-61) the resulting equations are averaged over all configurations of defects in the set of U_σ and n^c, respectively, where U_σ is now considered as the universal set of defects.

$$\langle G\rangle = P+P\langle \sum_{m\varepsilon U_\sigma} T_1^m G^m\rangle \qquad \text{(II-63)}$$

$$\langle G^n\rangle_n = P+P\langle \sum_{m\varepsilon n^c} T_1^m G^m\rangle_n \qquad \text{(II-64)}$$

Assuming that only one type of impurity is being substituted for only one type of host atom, then all the lattice sites into which a defect atom can be placed substitutionally are equivalent, and by using (II-35) and (II-44), equations (II-63) and (II-64) become:

$$\langle G\rangle = P+P\sum_{s_m\varepsilon U_s} cT_1^{s_m}\langle G^{s_m}\rangle_{s_m} \qquad \text{(II-65)}$$

$$\langle G^{s_n}\rangle_{s_n} = P+P\sum_{s_m\neq s_n\varepsilon U_s} cT_1^{s_m}\langle G^{s_m}\rangle_{s_m,s_n} \qquad \text{(II-66)}$$

or

$$\langle G\rangle = P+P\sum_{s_m} cT^{s_m}\langle G^{s_m}\rangle_{s_m} \qquad \text{(II-67)}$$

$$\langle G^{s_n}\rangle_{s_n} = P+P\sum_{s_m\neq s_n} cT_1^{s_m}\langle G^{s_m}\rangle_{s_m,s_n} \qquad \text{(II-68)}$$

where c is the defect concentration and the universal set of all possible different crystal defect sites , U_s, is understood in the summation. These are only two of a whole hierarchy of conditionally averaged equations that can be defined in an attempt to obtain $\langle G^{s_m}\rangle_{s_m}$. This infinite set of equations can only be terminated by making an approximation. This approximation can be found by using the information given to define G^n, i.e., that only single site scattering information is retained at "sufficiently low" c. Therefore, in the configurational average of the effective field G^{s_n}, seen by the atoms, the wave has been allowed to scatter off all other defects before it scatters off the perturbation due to the defect n at s_n. The T_1 matrix describes this final scattering explicitly. The logical approximation is to neglect the effect of variations in local environment due to other defects and "remember" those defects of which the field has an immediate knowledge. This leads to

$$<G^{s_m}>_{s_m,s_n} \simeq <G^{s_m}>_{s_m} \qquad \text{(II-69)}$$

and breaks the infinite set of equations into

$$<G> = P+\sum_{s_1} PcT_1^{s_1}<G^{s_1}>_{s_1} \qquad \text{(II-70)}$$

$$<G^{s_2}>_{s_2} = P+\sum_{s_1\neq s_2} PcT_1^{s_1}<G^{s_1}>_{s_1} \qquad \text{(II-71)}$$

Subtracting (II-71) from (II-70) gives

$$<G^{s_2}>_{s_2} = (I+PcT_1^{s_2})^{-1}<G> \qquad \text{(II-72)}$$

and so the configurational averaged Green's function is given by

$$<G> = P+\sum_{s\varepsilon U_s} PcT_1^{s}(I+P_1cT_1^{s})^{-1}<G> \qquad \text{(II-73)}$$

which by (II-62) can be written in terms of the defect matrices

$$<G> = P+\sum_{s\varepsilon U_s} PcV^{s}(I-(1-c)P_1V^{s})^{-1}<G> \qquad \text{(II-74)}$$

Equation (II-74) is the low concentration theory result for a concentration c of defects.

2. Perturbative Approximation

Clearly, from (II-57), the configurationally averaged G has the general form

$$\langle G\rangle = P+P\Sigma\langle G\rangle \qquad \text{(II-75)}$$

where Σ is the self energy.

In the low concentration theory

$$\Sigma_1^s = cV^s(I-(1-c)P_1V^s)^{-1} \qquad \text{(II-76)}$$

where $$\Sigma = \Sigma_1 = \sum_{s\varepsilon U_s} \Sigma_1^s$$

Even if the defect space defined by the extent of V^s is small, Σ_1^s is a formidable "creature" to calculate.

In order to simplify the calculation for Σ_1^s, an approximation to Σ_1^s is found. The first step is to decompose the defect matrix

$$V^s = V_o^s+V_p^s \qquad \text{(II-77)}$$

where V_o^s is the major local change in environment and will be treated exactly in the low concentration theory, while V_p^s is a perturbation to V_o^s and the perfect lattice. The simplest and most obvious V_o^s is the mass change, but in general, this need not be the case.

The self energy for the process whose scattering is treated exactly is

$$\Sigma_o^s = cX_o^s \tag{II-78}$$

where $$X_o^s = V_o^s(I-(1-c)P_1V_o^s)^{-1} \tag{II-79}$$

while the self-energy Σ_1^s, in the low concentration theory (II-76) is given by

$$\Sigma_1^s = cX^s \tag{II-80}$$

where $$X^s = V^s(I-(1-c)P_1V^s)^{-1} \tag{II-81}$$

Using equation (II-79), V_o^s may be written as

$$V_o^s = (I+(1-c)X_o^sP_1)^{-1}X_o^s \tag{II-82}$$

With the aid of equations (II-77) and (II-82), equation (II-81) becomes

$$X^s(I-(1-c)P_1[(I+(1-c)X_o^sP_1)^{-1}X_o^s+V_p^s])=(I+(1-c)X_o^sP_1)^{-1}X_o^s+V_p^s \tag{II-83}$$

After some rearrangement of the terms, equation (II-83) becomes

$$X^s(I-(1-c)P_1V_p^s[I+(1-c)P_1X_o^s]) = X_o^s+V_p^s(I+(1-c)P_1X_o^s) \tag{II-84}$$

Since V_p^s is taken as a perturbation to the defect system described exactly by the defects V_o^s, equation (II-84) (to first order in V_p^s) becomes

$$\begin{aligned} X^s &\approx (X_o^s+V_p(I+(1-c)P_1X_o^s))(I+(1-c)P_1V_p^s(I+(1-c)P_1X_o^s)) \\ &\approx X_o^s+V_p^s+(1-c)V_p^sP_1X_o^s+(1-c)X_o^sP_1V_p^s+(1-c)^2X_o^sP_1V_p^sP_1X_o^s \end{aligned} \tag{II-85}$$

and so the self energy to first order in V_p^s is

$$\Sigma_1^s = \Sigma_o^s + cV_p^s + (1-c)V_p^s P_1 \Sigma_o^s + (1-c)\Sigma_o^s P_1 V_p^s + \frac{(1-c)^2}{c} \Sigma_o^s P_1 V_p^s \Sigma_o^s \qquad \text{(II-86)}$$

If Σ_o^s describes only the mass impurity, then the advantage of this form for Σ_1^s is obvious. In the first place, P_1 does not span the whole defect space in (II-86) (i.e., does not link all sites of the defect space), but rather, is limited to the space where the impurity site is connected to any site of the defect space. Secondly, except for the trivial terms

$$\Sigma_o^s \quad , \qquad \frac{(1-c)^2}{c} \Sigma_o^s P_1 V_d^s P_1 \Sigma_o^s$$

and cV_p^s (this term is said to be trivial since it is known and does not have to be computed), the terms in the expansion (II-86) of Σ_1^s only connect the impurity site to a site in the defect space.

It should be stressed that this approximation of the low concentration theory result is only valid for force constant changes that are small relative to the mass change. These force constant changes may, nevertheless, if c is "low enough", have a large extent. Even if the mass change is large, it is obvious that for low enough ω the perturbative approximation will not be valid (for the Cu/Au system this frequency corresponds to a wavevector of about 1/40).

"The last product of an antecedent stage is always the basis of that which is subsequent."

--L.Oken

SECTION C

PAIRS WITH CORRELATION

In order to obtain any analytic theory of normal modes in a lattice having substitutional impurities, some account must be taken of the formations of clusters and the cluster contribution to scattering. This section, which was motivated by the work of Aiyer, Elliott, Krumhansl and Leath (1969), contains the formal treatment of defect pairs with the possibility of pair type correlations. The analytic expressions will be derived for mass defects and will be found simple enough to use for calculations. It is assumed throughout that only one type of impurity is being substituted for only one type of host atom.

Again, the starting point is the Dyson equation (II-57). It is assumed here, that only pair scattering information is retained, while any higher order process is not "remembered". With this assumption, it seems reasonable to state that G is governed principly by whether or not the space of its definition is affected by any pair of defects. This suggests separating out the Green's functions associated with a given pair of defects as follows:

$$G-PV^{n_1}G-PV^{n_2}G = (I-PV^{n_1}-PV^{n_2})G = G^{(n_1,n_2)} \qquad \text{(II-87)}$$

where $n_1 \neq n_2$ and

$$G^{(n_1,n_2)} = P + \sum_{m \neq n_1, n_2 \varepsilon U_\sigma} PV^m G \qquad \text{(II-88)}$$

Since the space of V^{n_1} does not overlap that of V^{n_2} for $s_{n_1} \neq s_{n_2}$, equation (II-87) may be rewritten as

$$G^{(n_1,n_2)} = (I-PV^{(n_1,n_2)})G \qquad \text{(II-89)}$$

where

$$V^{(n_1,n_2)} = \begin{array}{c|c|cc|c}
 & & s_{n_1} & s_{n_2} & \\
 & 0 & 0 & & 0 \\ \hline
s_{n_1} & & V^{n_1} & 0 & \\
 & 0 & & & 0 \\
s_{n_2} & & 0 & V^{n_2} & \\ \hline
 & 0 & 0 & & 0
\end{array}$$

In this notation

$$\sum_m PV^m G = \sum_{m_1} PV^{m_1}G + \sum_{m_2} PV^{m_2}G$$

$$= \sum_{(m_1,m_2)\varepsilon U_\sigma} PV^{(m_1,m_2)}G \qquad \text{(II-90)}$$

The error in stating that U_σ can be arbitrarily broken up into

$$U_\sigma = ((1,2),(3,4),\ldots,(N_\sigma-1),N_\sigma)) \qquad \text{(II-91)}$$

is, at most, $\frac{1}{2N_\sigma} \sim 10^{-23}$, and therefore negligible.

Using the notation of Part 3, Section A, Chapter II, equations

(II-89) and (II-90) may be written as

$$G^N = (I-PV^N)G \tag{II-92}$$

$$\sum_{m\varepsilon U_\sigma} PV^m G = \sum_{M\varepsilon U_\sigma} PV^M G \tag{II-93}$$

where $N = (n_1,n_2)\varepsilon U_\sigma$ of (II-91), and $M = (m_1,m_2)\varepsilon U_\sigma$ of (II-91).

With the aid of equations (II-92) and (II-93), equations (II-57) and (II-88) may be written as

$$G = P+\sum_{M\varepsilon U_\sigma} PV^M(I-P_2V^M)^{-1}G^M \tag{II-94}$$

and

$$G^N = P+\sum_{M\varepsilon N^c} PV^M(I-P_2V^M)^{-1}G^M \tag{II-95}$$

where

$$P_2 = \begin{array}{c|c|cc|c|}
 & & s_{m_1} & s_{m_2} & \\
 & 0 & 0 & & 0 \\ \hline
s_{m_1} & 0 & P(0) & P(s_{m_1},s_{m_2}) & 0 \\
s_{m_2} & & P(s_{m_2},s_{m_1}) & P(0) & \\ \hline
 & 0 & 0 & & 0
\end{array}$$

Furthermore, if

$$T_1^M = \begin{array}{c|c|cc|c|}
 & & s_{m_1} & s_{m_2} & \\
 & 0 & 0 & & 0 \\ \hline
s_{m_1} & 0 & t_1^{m_1} & 0 & 0 \\
s_{m_2} & & 0 & t_1^{m_2} & \\ \hline
 & 0 & 0 & & 0
\end{array}$$

and

$$P_1 = \begin{array}{c|c|cc|c} & & s_{m_1} & s_{m_2} & \\ \hline & 0 & 0 & & 0 \\ \hline s_{m_1} & 0 & P(0) & 0 & 0 \\ s_{m_2} & & 0 & P(0) & \\ \hline & 0 & 0 & & 0 \end{array}$$

then, by using (II-62), equations (II-94) and (II-95) become

$$G = P+\sum_{M\varepsilon U_\sigma} PT_1^M(I+(P_1-P_2)T_1^M)^{-1}G^M \qquad \text{(II-99)}$$

$$G^N = P+\sum_{M\varepsilon N^c} PT_1^M(I+(P_1-P_2)T_1^M)^{-1}G^M \qquad \text{(II-100)}$$

It is observed from (II-99) and (II-100) that

$$\underline{\underline{T}}_2^M = T_1^M(I+(P_1-P_2T_1^M)^{-1} \qquad \text{(II-101)}$$

is just the t-matrix describing the scattering of lattice excitations, due to the perturbation introduced by two defect atoms of an otherwise perfect lattice. In its present form, $\underline{\underline{T}}_2^M$ contains all the information about the scattering due to two defect atoms m_1 and m_2. Thus, $\underline{\underline{T}}_2^M$ is made up of two parts--one non-decomposable (where the scatterer is a pair of defects), and the other decomposable (where the scatterers are two separate defect atoms) into smaller spaces. The first of these,

$$T_2^M = \underline{\underline{T}}_2^M-T_1^{m1}-T_1^{m2} = \underline{\underline{T}}_2^M-T_1^M \qquad \text{(II-102)}$$

contains all the information about pure pair scatterings, and therefore is not decomposable into the smaller spaces m_1 and m_2. On the other hand,

$$T_1^M = T_1^{m_1}+T_1^{m_2} \tag{II-103}$$

which contains all the information about pure single scattering of two different defects M, is decomposable into the smaller spaces m_1 and m_2. With the information contained in (II-101), (II-102) and (II-103), equations (II-99) and (II-100) may be rewritten as

$$G = P+\sum_{M\varepsilon U_\sigma} PT_2^M G^M+\sum_{M\varepsilon U_\sigma} PT_1^M G^M \tag{II-104}$$

$$G^N = P+\sum_{M\varepsilon N^c} PT_2^M G^M+\sum_{M\varepsilon N^c} PT_1^M G^M \tag{II-105}$$

These equations are now averaged over all configurations of defects of the set U_σ and N^c, respectively:

$$<G> = P+P<\sum_{M\varepsilon U_\sigma} T_2^M G^M>+P<\sum_{M\varepsilon U_\sigma} T_1^M G^M> \tag{II-106}$$

and $$<G^N>_N = P+P<\sum_{M\varepsilon N^c} T_2^M G^M>_{(s_{n_1},s_{n_2})} +P<\sum_{M\varepsilon N^c} T_1^M G^M>_{(s_{n_1},s_{n_2})} \tag{II-107}$$

There are now four averages which must be resolved; they are:

$$<\sum_{M\varepsilon U_\sigma} T_2^M G^M> \tag{II-108$_a$}$$

$$<\sum_{M\varepsilon N^c} T_2^M G^M>_{(s_{n_1},s_{n_2})} \tag{II-108$_b$}$$

$$<\sum_{M\varepsilon U_\sigma} T_1^M G^M> \tag{II-108$_c$}$$

and $$<\sum_{M\varepsilon N^c} T_1^M G^M>_{(s_{n_1},s_{n_2})} \tag{II-108$_d$}$$

In $(II\text{-}108_a)$ it is observed that the scatterer is a defect pair and so by using (II-44) it is found that

$$<\sum_{M\epsilon U_\sigma} T_2^M G^M> = \sum_{\tilde{R}_{s_{m_1},s_{m_s}}} \rho(s_{m_1},s_{m_s})\, T_2^{(s_{m_1},s_{m_2})} <G^{(s_{m_1},s_{m_2})}>_{(s_{m_1},s_{m_2})} \qquad (II\text{-}109_a)$$

where the sum is over all different pair separations $\tilde{R}_{s_{m_1},s_{m_2}}$ between a pair of possible crystal defect sites (s_{m_1},s_{m_2}) associated with the defect pair (m_1,m_2). Furthermore, using (II-35) and realizing that, as for $(II\text{-}108_a)$, equation $(II\text{-}108_b)$ also has the scatterer as a defect pair. Thus, by (II-44),

$$<\sum_{M\epsilon U_\sigma} T_2^M G^M>_{(s_{n_1},s_{n_2})}$$

$$= \sum_{\tilde{R}_{s_{m_1}s_{m_2}} \neq \tilde{R}_{s_{n_1}s_{n_2}}} \rho(s_{m_1},s_{m_2})\, T_2^{(s_{m_1},s_{m_2})} <G^{(s_{m_1},s_{m_2})}>_{(s_{m_1},s_{m_2})(s_{n_1},s_{n_2})} \qquad (II\text{-}109_b)$$

The expressions $(II\text{-}108_c)$ and $(II\text{-}108_d)$ obviously depend on the scatterer being a single defect. Expanding $(II\text{-}108_c)$ as follows:

$$<\sum_{M\epsilon U_\sigma} T_1^M G^M> = <\sum_{(m_1,m_2)\epsilon U_\sigma} (T_1^{m_1}+T_1^{m_2})\, G^{(m_1,m_2)}>$$

the configuration average of this term is now determined.

$$<\sum_{M\epsilon U_\sigma} T_1^M G^M> = \sum_{s_1\ldots s_{N_\sigma}} p(s_1\ldots s_{N_\sigma}) \sum_{(s_{m_1},s_{m_2})\epsilon(s_1\ldots s_{N_\sigma})} (T_1^{s_{m_1}}+T_1^{s_{m_2}}) \times G^{(s_{m_1},s_{m_2})}$$

$$= \sum_{s_1's_2'} \sum_{s_3'\ldots s_{N_\sigma}'} p(s_1's_2'\ldots s_{N_\sigma}')\, (T_1^{s_1'}+T_1^{s_2'})\, G^{(s_1',s_2')}$$

$$+ \cdots\cdot$$

$$+\sum_{s'_{N_\sigma-1},s'_{N_\sigma}} \sum_{s'_1\ldots s'_{N_\sigma-2}} p(s'_{N_\sigma-1},s'_{N_\sigma},s'_1,\ldots s'_{N_\sigma-2})(T_1^{s'_{N_\sigma-1}}+T_1^{s'_{N_\sigma}}) \times G^{(s'_{N_\sigma-1},s'_{N_\sigma})}$$

$$= \frac{N_\sigma}{2}\sum_{s_{m_1},s_{m_2}} p(s_{m_2})p(s_{m_2}|s_{m_1})T_1^{s_{m1}}\sum_{s_{m_3}\ldots s_{m_{N_\sigma}}} p(s_{m_1},s_{m_2}|s_{m_3}\ldots s_{m_{N_\sigma}}) \times G^{(s_{m1},s_{m2})}$$

$$+ \frac{N_\sigma}{2}\sum_{s_{m_1},s_{m_2}} p(s_{m_1})p(s_{m_1}|s_{m_2})T_1^{s_{m_2}}\sum_{s_{m_3}\ldots s_{m_{N_\sigma}}} p(s_{m_1},s_{m_2}|s_{m_3}\ldots s_{m_{N_\sigma}}) \times G^{(s_{m1},s_{m2})}$$

(II -110)

Since the indices are only dummy indices (II-110) becomes

$$<\sum_{M\varepsilon U_\sigma} T_1^M G^M> = N_\sigma N_s \sum_{s_{m_1}} \frac{1}{N_s}\, p(s_{m_1}|s_{m_2})T_1^{s_{m1}}<G^{(s_{m_1},s_{m_2})}>_{(s_{m_1},s_{m_2})}$$

$$= \sum_{\tilde{R}_{s_{m_1},s_{m_2}}} \rho(s_{m_1}|s_{m_2})T_1^{S_M}<G^{S_M}>_{S_M} \qquad \text{(II-111}_a\text{)}$$

It should be realized that, after averaging, the above expressions depend only on the distance between s_{m_1} and s_{m_2}, hence s_{m_2} can be any arbitrary site. Similarly, by using (II-35), it is seen that

$$<\sum_{M\varepsilon Nc} T_1^M G^M>_{S_N} = \sum_{\tilde{R}_{S_M}\neq\tilde{R}_{S_N}} \rho(s_{m_1}|s_{m_2})T_1^{S_M} <G^{S_M}>_{S_M,S_N} \qquad \text{(II-111}_b\text{)}$$

Therefore, by using the results of (II-109$_a$), (II-109$_b$), (II-111$_a$) and (II-111$_b$), equations (II-106) and (II-107) simplify to

$$\langle G\rangle = P + P\sum_{\tilde{R}_{S_M}} \rho(s_{m_1},s_{m_2})T_2^{S_M}\langle G^{S_M}\rangle_{S_M} + P\sum_{\tilde{R}_{S_M}} \rho(s_{m_1}|s_{m_2})T_1^{S_M}\langle G^{S_M}\rangle_{S_M} \tag{II-112}$$

$$\begin{aligned}\langle G^{S_N}\rangle_{S_N} &= P + P\sum_{\tilde{R}_{S_M}\neq\tilde{R}_{S_N}} \rho(s_{m_1},s_{m_2})T_2^{S_M}\langle G^{S_M}\rangle_{S_M,S_N}\\ &\quad + P\sum_{\tilde{R}_{S_M}\neq\tilde{R}_{S_N}} \rho(s_{m_1}|s_{m_2})T_1^{S_M}\langle G^{S_M}\rangle_{S_M,S_N}\end{aligned} \tag{II-113}$$

where $S_M = (s_{m_1},s_{m_2})$ and $S_N = (s_{n_1},s_{n_2})$. More simply, (II-112) and (II-113) can be written as

$$\langle G\rangle = P + P\sum_{\tilde{R}_{S_M}} (\rho(s_{m_1},s_{m_2})T_2^{S_M} + \rho(s_{m_1}|s_{m_2})T_1^{S_M})\langle G^{S_M}\rangle_{S_M} \tag{II-114}$$

and

$$\langle G^{S_N}\rangle_{S_N} = P + P\sum_{\tilde{R}_{S_M}\neq\tilde{R}_{S_N}} (\rho(s_{m_1},s_{m_2})T_2^{S_M} + \rho(s_{m_1}|s_{m_2})T_1^{S_M})\langle G^{S_M}\rangle_{S_M,S_N} \tag{II-115}$$

It is obvious that these are only two of a whole hierarchy of conditionally averaged equations that can be defined in an attempt to solve <G>. This infinite set of equations can only be terminated by making an approximation.

G^{S_N} can be thought of as the effective field seen by the atoms, where the wave has been allowed to scatter off all other defects before it scatters off the perturbation due to the defects N at S_N. It is noted that $\underline{\underline{T}}_2^{S_N}$ describes this final scattering explicitly. Using the information given in defining G^N (i.e., that only pair type scattering information is retained for a set of non-overlapping defects), an approximation can now be found. The logical approximation is to neglect the effect of variations in the environment due to any other defects, and "remember" those defects of which the field has an immediate knowledge. This leads to

$$\langle G^{s_M}\rangle_{s_M,s_N} \simeq \langle G^{s_M}\rangle_{s_M} \qquad \text{(II-116)}$$

and breaks the infinite set of equations into equation (II-114) and

$$\langle G^{s_N}\rangle_{s_N} = P+P\sum_{\tilde{R}_{s_M}\neq\tilde{R}_{s_N}} (\rho(s_{m_1},s_{m_2})T_2^{s_M}+\rho(s_{m_1}|s_{m_2})T_1^{s_M})\langle G^{s_M}\rangle_{s_M} \qquad \text{(II-117)}$$

Subtracting (II-117) from (II-114), and using (II-29) and (II-32), $\langle G^{s_N}\rangle_{s_N}$ can be expressed as

$$\langle G^{s_N}\rangle_{s_N} = (I+P\rho(s_{n_1}|s_{n_2})[cT_2^{s_N}+T_1^{s_N}])^{-1}\langle G\rangle \qquad \text{(II-118)}$$

and so, the configurational averaged Dyson equation becomes

$$\langle G\rangle = P+P\Sigma_2\langle G\rangle \qquad \text{(II-119)}$$

where

$$\Sigma_2 = \sum_{\tilde{R}_{s_N}} (\rho(s_{n_1}|s_{n_2})[cT_2^{s_N}+T_1^{s_N}])(I+P_2\rho(s_{n_1}|s_{n_2})[cT_2^{s_N}+T_1^{s_N}])^{-1} \qquad \text{(II-120)}$$

For random defects

$$\rho(s_{n_1}|s_{n_2}) = \frac{\rho(s_{n_1},s_{n_2})}{\rho(s_{n_1})} = \frac{c^2}{c} = c \qquad \text{(II-121)}$$

and the self energy becomes

$$\Sigma_2 = \sum_{\tilde{R}_{s_N}} (c^2T_2^{s_N}+cT_1^{s_N})(I+P_2(c^2T_2^{s_N}+cT_1^{s_N}))^{-1} \qquad \text{(II-122)}$$

which is the result that Aiyer, Elliott, Krumhansl and Leath (1969) find for a random alloy with their diagrammatic method.

> "The ovary of an ancestress will contain not
> only her daughter, but also her grand-daughter,
> her great-granddaughter, and her great-great-
> grand-daughter, and if it is once proved that
> an ovary can contain many generations, there
> is no absurdity in saying that it contains them
> all." --Albrecht von Haller

SECTION D

THE N-TUPLE PROCESS

The method used in Section C of Chapter II is certainly not limited to pairs but can also be extended to treat the corresponding "n-cluster" or n-tuple self energy. Although the configuration averaged result can be expressed in terms of any type of site correlations, the procedure to obtain this general result tends to be quite involved. Thus, only the random defect is considered while the general defect correlation result is not attempted. It is assumed in this section that the pure single, pair, triplet,...(n-1)-tuple scatterings have already been solved for, and that $n<<<N_\sigma$.

The notation of this section will be modeled on that of the previous two sections, and also on that of Part 3, Section A of this chapter.

As has been the case before, the discussion begins with the Dyson equation (II-57). It is assumed that the defects are mass defects of one type and that they are being substituted for only one type of host atom. Also, it is assumed that at most n-tuple scattering information is retained while any higher order process is not "remembered". With this last assumption, it seems reasonable to say that G is governed principally by whether or not the space of its definition is affected by any set of n defects. This suggests separating out the Green's functions associated with a set of n defects as follows:

$$G-PV^{1\delta}G-PV^{2\delta}G-\dots-PV^{n\delta}G = (I-PV^{1\delta}-\dots-PV^{n\delta})G = G^{(1_\delta,2_\delta,\dots n_\delta)} \qquad \text{(II-123)}$$

where $1_\delta \neq 2_\delta \neq \dots \neq n_\delta$

$$G^{(1_\delta,2_\delta,\dots,n_\delta)} = P+\sum_{m\neq 1_\delta,2_\delta,\dots n_\delta} PV^{m}G \qquad \text{(II-124)}$$

and δ indicates an arbitrary selection of n defects. Since the space of $V^{i\delta}$ does not overlap that of $V^{k\delta}$ for $s_{i_\delta} \neq s_{k_\delta}$, equation (II-123) may be written as

$$G^{(1_\delta,\dots,n_\delta)} = (I-PV^{(1_\delta,\dots,n_\delta)})G \qquad \text{(II-125)}$$

where

$$V^{N_n} = V^{(1_\delta,\dots,n_\delta)} = \left(\begin{array}{c|c|c|c} & & s_{1_\delta}\cdots s_{n_\delta} & \\ & 0 & 0 & 0 \\ \hline \begin{matrix} s_{1_\delta} \\ \vdots \\ s_{n_\delta} \end{matrix} & 0 & \begin{matrix} V^{1\delta} & & 0 \\ & \ddots & \\ 0 & & V^{n\delta} \end{matrix} & 0 \\ \hline & 0 & 0 & 0 \end{array}\right)$$

In this notation

$$\sum_{m} PV^{m}G = \sum_{m_1} PV^{m_1}G + \dots + \sum_{m_n} PV^{m_n}G$$

$$= \sum_{(m_1,\dots,m_n)\varepsilon U_\sigma} PV^{(m_1,\dots m_n)}G \qquad \text{(II-126)}$$

The error in stating that U_σ can be broken up into

$$U_\sigma = ((1_\delta,\dots n_\delta),((n+1)_\delta,\dots,(2n)_\delta),\dots,((N_\sigma-n)_\delta,\dots(N_\sigma)_\delta) \qquad \text{(II-127)}$$

is at most $\frac{n}{2N_\sigma} <<< 1$ and is therefore negligible.

Thus, equations (II-57) and (II-124) may be written in the form

$$G = P + \sum_{M_n \varepsilon U_\sigma} PV^{M_n}(I - P_n V^{M_n})^{-1} G^{M_n} \qquad \text{(II-128)}$$

and

$$G^{N_n} = P + \sum_{M_n \varepsilon N_n^c} PV^{M_n}(I + P_n V^{M_n})^{-1} G^{M_n} \qquad \text{(II-129)}$$

where

$$M_n = (m_1,\dots,m_n)$$

and

$$P_n = \begin{array}{c} \\ \\ s_{m_1} \\ \vdots \\ s_{m_n} \\ \\ \end{array} \left(\begin{array}{c|c|c} & s_{m_1}\cdots\cdots\cdots s_{m_n} & \\ 0 & 0 & 0 \\ \hline 0 & \begin{matrix} P(0) & \cdots & P(s_{m_1},s_{m_n}) \\ \vdots & \ddots & \vdots \\ P(s_{m_n},s_{m_1}) & \cdots & P(0) \end{matrix} & 0 \\ \hline 0 & 0 & 0 \end{array} \right)$$

It is observed from equations (II-128) and (II-129) that

$$\underline{\underline{T}}_n = V^{M_n}(I-P_n V^{M_n})^{-1} \qquad \text{(II-131)}$$

is just the t-matrix describing the scattering of lattice excitations due to the perturbation introduced by n defect atoms M_n of an otherwise perfect lattice. In its present form $\underline{\underline{T}}_n^{M_n}$ contains all the information about the scattering due to any set of n defects. Thus, $\underline{\underline{T}}_n^{M_n}$ is made up of n parts, one of which is non-decomposable and has the scatterer as the n defects, while the others are decomposable into smaller spaces and have as the scatterers i defects where i=1,...,n-1.

The pure i-tuple scattering matrix $T_i^{M_{i\alpha}}$, i.e., where the scatterer is i defects, for any set of i defects

$$M_{i_\alpha} = (1_\alpha, 2_\alpha, \ldots, i_\alpha) \qquad \forall \quad i = 1,\ldots,n-1$$

and α is assumed known. Using this notation, $T_i^{M_n}$ is defined as

$$T_i^{M_n} = \sum_\alpha T_i^{M_{i\alpha}} \qquad \text{(II-132)}$$

where α is the α^{th} set of i different defects chosen from the set M_n of n different arbitrary defects of U_σ. Therefore $T_i^{M_{i\alpha}}$, for all i=1,...n-1 and all possible α's associated with a given i, form all the possible "pure" scatterings that can occur, except $T_n^{M_n}$ --the "pure" n-tuple scattering. Thus, the "pure" n-tuple scattering is obtained by subtracting from $\underline{\underline{T}}_n^{M_n}$ (the total n-tuple scattering in the space of n defects) all the possible "pure" scatterings in any sub-space of the space defined by these n defects

$$T_n^{M_n} = \underline{\underline{T}}_n^{M_n} - \sum_{i=1}^{n-1} \sum_{\alpha} T_i^{M_{i\alpha}} \qquad \text{(II-133)}$$

Using (II-133), equations (II-128) and (II-129) become

$$G = P + \sum_{M_n \varepsilon U_\sigma} P T_n^{M_n} G^{M_n} + \sum_{M_n \varepsilon U_\sigma} P \sum_{i} \sum_{\alpha} T_i^{M_{i\alpha}} G^{M_n} \qquad \text{(II-134)}$$

and $$G^{N_n} = P + \sum_{M_n \varepsilon N_n^c} P T_n^{M_n} G^{M_n} + \sum_{M_n \varepsilon N_n^c} P \sum_{i} \sum_{\alpha} T_i^{M_{i\alpha}} G^{M_n} \qquad \text{(II-135)}$$

in terms of the non-decomposable scattering matrices.

These equations can now be averaged over all configurations of defects of the set U_σ and N_n^c, respectively.

$$\langle G \rangle = P + P \langle \sum_{M_n \varepsilon U_\sigma} T_n^{M_n} G^{M_n} \rangle \qquad \text{(II-136}_a\text{)}$$

$$+ P \langle \sum_{M_n \varepsilon U_\sigma} \sum_{i} \sum_{\alpha} T_i^{M_{i\alpha}} G^{M_n} \rangle \qquad \text{(II-136}_b\text{)}$$

$$\langle G^{N_n} \rangle_{S_{N_n}} = P + P \langle \sum_{M_n \varepsilon N_\sigma^c} T_n^{M_n} G^{M_n} \rangle_{S_{N_n}} \qquad \text{(II-137}_a\text{)}$$

$$+ P \langle \sum_{M_n \varepsilon N_n^c} \sum_{i} \sum_{\alpha} T_i^{M_{i\alpha}} G^{M_n} \rangle_{S_{N_n}} \qquad \text{(II-137}_b\text{)}$$

Using equations (II-44) and (II-35), the average in equations (II-136_a) and (II-137_a) becomes

$$<\sum_{M_n \varepsilon U_\sigma} T_n^{M_n} G^{M_n}> = \sum_{R_{S_{M_n}}} c^n T_n^{S_{M_n}} <G^{S_{M_n}}>_{S_{M_n}} \qquad \text{(II-138)}$$

$$<\sum_{M_n \varepsilon N_n^c} T_n^{M_n} G^{M_n}>_{S_{N_n}} = \sum_{R_{S_{M_n}} \neq R_{S_{N_n}}} c^n T_n^{S_{M_n}} <G^{S_{M_n}}>_{S_{M_n}, S_{N_n}} \qquad \text{(II-139)}$$

respectively, where the sum over $R_{S_{M_n}}$ extends over all possible different crystal scattering n-sites associated with an arbitrary set of n defects S_{M_n}.

It is now necessary to consider the averages in (II-136$_b$) and (II-137$_b$). The configurational average of these expressions is determined for an arbitrary i=1,...,n-1.

$$\sum_{M_n \varepsilon U_\sigma} \sum_\alpha T_i^{M_{i\alpha}} G^{M_n} = \sum_j p(\{s\}_{N_\sigma}^j) \sum_{S_{M_n} \varepsilon \{s\}_{N_\sigma}^j} \sum_\alpha T_i^{S_{M_{i\alpha}}} G^{S_{M_n}}$$

$$= N_i \sum_{R_{S_i}} p(S_i) T_i^{S_i} \sum_{j'} p(S_i | S_{ic}^{j'}) G^{S_{M_n}}$$

$$= \sum_{R_{S_i}} \rho(S_i) T_i^{S_i} \sum_{\{s\}_{n-i}} \frac{p(S_{M_n})}{p(S_i)} \sum_{j''} p(S_{M_n} | S_{M_n c}^{j''}) G^{S_{M_n}}$$

(II-140$_a$)

where N_i is the number of i-defect scatterers and the sum over R_{S_i} extends over all possible different i-defect crystal scattering sites. For the random crystal lattice,

$$\rho(S_i) = c^i \quad , \quad \frac{p(S_{M_n})}{p(S_i)} = \frac{1}{(N_s)^{n-i}}$$

therefore, by using (II-35), equation (II-140$_a$) may be written as

$$<\sum_{M_n \varepsilon U_\sigma} \sum_{\alpha} T_i^{M_i \alpha} G^{M_n}> = \sum_{\{s\}_{n-i}} \frac{1}{(N_s)^{n-i}} \sum_{R_{S_i}} c^i T_i^{S_i} <G^{S_{M_n}}>_{S_{M_n}} \qquad \text{(II-140}_b\text{)}$$

Reshuffling the sums in (II-140$_b$) brings this equation into the form

$$<\sum_{M_n \varepsilon U_\sigma} \sum_{\alpha} T_i^{M_i \alpha} G^{M_n}> = \frac{1}{(N_s)^{n-i}} \sum_{\{s'\}_{n-i}} \sum_{R_{S_{M_n}}} c^i T_i^{S_{M_n}} <G^{S_{M_n}}>_{S_{M_n}}$$

$$= \sum_{R_{S_{M_n}}} c^i T_i^{S_{M_n}} <G^{S_{M_n}}>_{S_{M_n}} \qquad \text{(II-141)}$$

where $T_i^{S_{M_n}}$ is the scattering matrix in the space of S_{M_n} sites containing all the information about pure i-tuple scatterings resulting from n defects. Similarly, by using (II-35) the expression (II-137$_b$) becomes, for an arbitrary i=1,...n-1

$$<\sum_{M_n \varepsilon N_n^c} \sum_{\alpha} T_i^{M_i \alpha} G^{M_n}>_{S_{N_n}} = \sum_{R_{S_{M_n}} \neq R_{S_{N_n}}} c^i T_1^{S_{M_n}} <G^{S_{M_n}}>_{S_{M_n}, S_{N_n}} \qquad \text{(II-142)}$$

Substituting (II-138), (II-139), (II-141) and (II-142) into (II-136) and (II-137), these equations can be rewritten as

$$<G> = P + P \sum_{R_{S_{M_n}}} \sum_{i=1}^{n} c^i T_i^{S_{M_n}} <G^{S_{M_n}}>_{S_{M_n}} \qquad \text{(II-143)}$$

$$\langle G^{S_{N_n}}\rangle_{S_{N_n}} = P+P\sum_{R_{S_{M_n}}\neq R_{S_{N_n}}} \sum_{i=1}^{n} c^i T_i^{S_{M_n}} \langle G^{S_{M_n}}\rangle_{S_{M_n},S_{N_n}} \tag{II-144}$$

As has been the case before, these are only two equations of a whole hierarchy of conditionally averaged equations that will be terminated by an approximation. Following the same argument as is given for n=2 in the previous section, the approximation that is made is

$$\langle G^{S_{M_n}}\rangle_{S_{M_n},S_{N_n}} \simeq \langle G^{S_{M_n}}\rangle_{S_{M_n}} \tag{II-146}$$

which breaks the infinite set of equations into (II-143) and

$$\langle G^{S_{N_n}}\rangle_{S_{N_n}} = P+P\sum_{R_{S_{M_n}}\neq R_{S_{N_n}}} \sum_{i=1}^{n} c^i T_i^{S_{M_n}} \langle G^{S_{M_n}}\rangle_{S_{M_n}} \tag{II-147}$$

Subtracting (II-147) from (II-143) gives

$$\langle G^{S_{N_n}}\rangle_{S_{N_n}} = (I+P\sum_{i=1}^{n} c^i T_i^{S_{N_n}})^{-1}\langle G\rangle \tag{II-148}$$

and therefore, the configuration averaged Dyson equation becomes

$$\langle G\rangle = P+P\Sigma_n\langle G\rangle \tag{II-149}$$

where

$$\Sigma_n = \sum_{R_{S_{N_n}}} (\sum_{i=1}^{n} c^i T_i^{S_{N_n}})(I+P_n\sum_{i=1}^{n} c^i T_i^{S_{N_n}})^{-1} \tag{II-150}$$

> "They have, and can have, no properties, and
> their concepts can include no attributes,
> save these relations, or rather, our mental
> representation of them."
>
> --J.B. Stallo

SECTION E

THE EFFECTIVE LATTICE THEORY

The purpose of the present section is to present a different, but intuitively simple, method for determining the lattice dynamics of a lattice with substitutional impurities, where the manifestation of the "long range" effects of these impurities tends to affect the whole crystal. The "long range" effects that are being considered are those that produce "considerable" distortion in the neighbourhood of an impurity, and so define a reasonably large defect space for a given concentration. These distortions in the one defect picture usually manifest themselves on a macroscopic scale when extended to many defects placed randomly in a lattice. This macroscopic manifestation can be seen as a change in lattice constant of the crystal or as a change of the average environment about a host atom.

From (II-23) and the derivation of (II-57), it has been seen that the lattice dynamics problem can be approached from

$$Lu = 0 \tag{II-151}$$

where

$$L_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) = M_\alpha(\tilde{\ell})\omega^2\delta_{\alpha\beta}\delta(\tilde{\ell},\tilde{\ell}') - \Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')$$

In the perfect crystal

$$L^\circ u = 0 \qquad \text{(II-152)}$$

and

$$P = L^{\circ\,-1} \qquad \text{(II-153)}$$

Then, in the crystal made by placing impurities substitutionally into the perfect lattice,

$$(L^\circ - V)u = 0 \qquad \text{(II-154)}$$

where $L = L^\circ - V$

and the Green's function for this system is

$$G = (L^\circ - V)^{-1} \qquad \text{(II-155)}$$

By using (II-153), the usual Dyson equation is found:

$$G = P + PVG \qquad \text{(II-156)}$$

If the element of V referring to a defect site n (i.e., V^n) contains both "long range" contributions V^n_{LR} (where V^{n1}_{LR}, and V^{n2}_{LR}, $n_1 \neq n_2$ have a large extent and a reasonable probability of overlapping) and also "short range" contributions V^n_L (where V^{n1}_L and V^{n2}_L, $n_1 \neq n_2$ have a very small probability of overlapping for a suitably small concentration c of defects), then to proceed further than equation (II-156) almost becomes an academic exercise in futility. To get around this difficulty, it is necessary to start from (II-151) again.

The matrix $\overline{V}$ is now defined to be an arbitrary force constant matrix that has the symmetry properties of L° and depends, as L°, only on the difference in position of two sites in the crystal. In Section C of Chapter III, a discussion of the nature of $\overline{V}$, using interatomic potentials, is given. Then,

$$(L^{\circ}-\overline{V}) \qquad \text{(II-157)}$$

defines an effective crystal lattice made up of the atoms of the perfect lattice and kept stable by the application of pressure. The defect lattice can obviously be described by

$$((L^{\circ}-\overline{V})-(V-\overline{V}))u = 0 \qquad \text{(II-158)}$$

and if the effective lattice Green's function is

$$G^{\circ} = (L^{\circ}-\overline{V})^{-1} \qquad \text{(II-159)}$$

then, from equation (II-158), the Green's function (II-155) of the defect lattice can be found from

$$G = G^{\circ}+G^{\circ}(V-\overline{V})G \qquad \text{(II-160)}$$

Qualitatively, this means that the defects that are placed randomly into this lattice "relieve the pressure" required to maintain the effective lattice. The question that remains to be answered is how this is done exactly.

From the above discussion, it is obvious that any V can be broken up into

$$V = V_L + V_{LR} \tag{II-161}$$

and that

$$V_L = \sum_{m\varepsilon U_\sigma} V_L^m \tag{II-162$_a$}$$

while

$$V_{LR} = \sum_{m\varepsilon U_\sigma} V_{LR}^m \tag{II-162$_b$}$$

where two properties, the "local" aspects and the "long range" aspects, have been associated with a defect, and these two properties give to each element m of the universal set of defects, U_σ , a two valued nature. Since V_{LR}^m has a reasonable probability of overlap with some V_{LR}^n, $m \neq n$, for a configuration (arbitrary) of defects, it should be noted that the information concerning force changes due to any defect-defect interaction is also contained in the "long range" defect space of any defect.

Obviously, $\overline{V}$ can be expressed as a sum over all sites as follows:

$$\overline{V} = \sum_{s\varepsilon U_s} \overline{V}^s \tag{II-163}$$

Equation (II-160) may now be rewritten as

$$G = G^\circ + \sum_{m\varepsilon U_\sigma} G^\circ V_L^m G + \sum_{m\varepsilon U_\sigma} G^\circ V_{LR}^m G - \sum_{s\varepsilon U_s} G^\circ \overline{V}^s G \tag{II-164}$$

If, upon configuration averaging equation (II-164), $\overline{V}^s$ removes all the information related to the "long range" effects of random defects at a concentration c, then the scattering in the effective lattice would occur only off the defects as defined by V_L^m . Assuming this to be the case (for if it is not, it will show up as a contradiction below), then it is further assumed that only single scattering information is retained in this effective lattice with defects V_L^m, and that any higher order process is not "remembered". As well, it seems reasonable to state that G is governed principally by whether or not the space of its definition is affected by any single defect V_L^m. This suggests separating out the Green's function associated with a given defect V_L^m as follows:

$$G-G^\circ V_L^n G = (I-G^\circ V_L^n)G = G^n \qquad \text{(II-165)}$$

and
$$G^n = G^\circ + \sum_{m \neq n \varepsilon U_\sigma} G^\circ V_L^m G + \sum_{m \varepsilon U_\sigma} G^\circ V_{LR}^m G - \sum_{s \varepsilon U_s} G^\circ \overline{V}^s G \qquad \text{(II-166)}$$

So, by using (II-165), equations (II-164) and (II-166) may be written as

$$G = G^\circ + \sum_{m \varepsilon U_\sigma} G^\circ V_L^m (I-G_1^\circ V_L^m)^{-1} G^m + \sum_{m \varepsilon U_\sigma} G^\circ V_{LR}^m G - \sum_{s \varepsilon U_s} G^\circ \overline{V}^s G \qquad \text{(II-167)}$$

and
$$G^n = G^\circ + \sum_{m \neq n \varepsilon U_\sigma} G^\circ V_L^m (I-G_1^\circ V_L^m)^{-1} G^m + \sum_{m \varepsilon U_\sigma} G^\circ V_{LR}^m G - \sum_{s \varepsilon U_s} G^\circ \overline{V}^s G \qquad \text{(II-168)}$$

where
$$T_1^m = V_L^m (I-G_1^\circ V_L^m)^{-1} \qquad \text{(II-169)}$$

is just the usual t-matrix describing the scattering of lattice excitations due to the perturbation introduced by a single defect V_L^m of an otherwise perfect effective lattice.

Since the term

$$\sum_{m\varepsilon U_\sigma} G^\circ V_{LR}^m G - \sum_{s\varepsilon U_s} G^\circ \overline{V}^s G \qquad \text{(II-170)}$$

is repeated in both (II-167) and (II-168), this suggests that by taking

$$<\sum_{m\varepsilon U_\sigma} G^\circ V_{LR}^m G - \sum_{s\varepsilon U_s} G^\circ \overline{V}^s G>_{s_{d_i^j}} = 0 \qquad \text{(II-171)}$$

for all subsets j of i defects of U_σ and "necessary" integers i, the "long range" effects have been removed from any equation for <G> or $<G^{n_1}>_{n_1,\ldots n_i}$, i'=1,...,i, in terms of G°. Thus, by configuration averaging equations (II-167) and (II-168) over all configurations of defects of the set U_σ and n^c respectively, it is found that

$$<G> = G^\circ + G^\circ <\sum_{m\varepsilon U_\sigma} T_1^m G^m> \qquad \text{(II-172)}$$

and

$$<G_{s_n}^n>_{s_n} = G^\circ + G <\sum_{m\neq n\varepsilon U_\sigma} T_1^m G^m>_{s_n} \qquad \text{(II-173)}$$

It is obvious that these are only two of a whole hierarchy of conditionally averaged equations that can be defined in an attempt to solve for <G>.

Before going any farther, it should be stated that for an operator O, which depends on all U_σ, if

$$\langle 0\rangle_{s_{d_m^j}} = 0 \qquad \text{(II-174)}$$

for all subsets j of m defects of U_σ, then by using (II-35) and (II-37) it can easily be shown that

$$\langle 0\rangle_{s_{d_n^{j'}}} = 0 \qquad \forall \quad n\le m \text{ and } j' \qquad \text{(II-175)}$$

Therefore, in equation (II-171), only the maximum value of i need be considered.

Since all information related to the "long range" effects of these random defects has been removed from the discussion of the configuration averaged system with truly random defects, as is obvious from (II-172) and (II-173), the problem has now been reduced to a low concentration theory problem with impurities V_L^m and perfect lattice Green's functions G°. Thus, by the same arguments as Section B of this chapter, the approximation

$$\langle G^{s_m}\rangle_{s_m,s_n} \simeq \langle G^{s_m}\rangle_{s_m} \qquad \text{(II-176)}$$

is made. By (II-174) and (II-175) it is implied that i=2, for for equation (II-171) is the condition "necessary" to give the usual low concentration theory result for $\langle G\rangle$ with G° replacing P.

$$\langle G\rangle = G^\circ + G^\circ \sum_{s_m \varepsilon U_s} cT_l^m (I+G_l^\circ cT_l^m)^{-1}\langle G\rangle \qquad \text{(II-177)}$$

where G_l° has a contribution only in the "local" defect space and that contribution is the same as G° in this space. This condition, that for a given concentration c of defects

$$<\sum_{m\varepsilon U_\sigma} G^\circ V_{LR}^m G - \sum_{s\varepsilon U_s} G^\circ \overline{V}^s G>_{s_{n_1},s_{n_2}} = (<\sum_{m\varepsilon U_\sigma} V_{LR}^m G>_{s_{n_1},s_{n_2}} - \sum_{s\varepsilon U_s} \overline{V}^s <G>_{s_{n_1},s_{n_2}}) = 0 \tag{II-178$_a$}$$

or

$$\overline{V} = <\sum_{m\varepsilon U_\sigma} V_{LR}^m G>_{s_{n_1},s_{n_2}} (<G>_{s_{n_1},s_{n_2}})^{-1} \tag{II-178$_b$}$$

where from (II-172) and (II-35)

$$\begin{aligned} <G>_{s_{n_1},s_{n_2}} &= G^\circ + G^\circ \sum_{s_m \neq s_{n_1}, s_{n_2} \varepsilon U_s} cT_1^m (I + G_1^\circ cT_1^m)^{-1} <G> \\ &+ \frac{G^\circ}{N_s} (T_1^{n1} (I + G_1^\circ cT^{n1})^{-1} + T_1^{n2} (I + G_1^\circ cT_1^{n2})^{-1}) <G> \end{aligned} \tag{II-179}$$

is a statement of what $\overline{V}$ is, in terms of V_{LR}. Clearly, there is no unique choice of $\overline{V}$, V_{LR} and V_L since there are only two linear equations (II-161) and (II-178) for three unknowns. This seems to imply that all this work of the preceeding pages was done for nothing. No. This is not the case, for the distortion itself, that brings the lattice into an average form (II-157) and defines the effective lattice, has not been treated here. This, in itself, is a major undertaking which will not be considered here. Then, how can this effective lattice be determined? This has already been done to a large extent by the defect crystal; for instance, by looking at the defect crystal, one can find out experimentally the change of the lattice constant due to V_{LR}, and the change of the average energy per host atom due to V_{LR}. These changes define $\overline{V}$, i.e., the effective lattice. Once $\overline{V}$ is known, V_L can easily be found by using the interatomic potentials $\phi_{host,host}$, $\phi_{host,defect}$, in the effective lattice, thus resolving the apparent problem.

This method is not restricted only to the low concentration theory approach used here, for if V_L can be approximated by a mass defect, then this work can be carried through for any n-tuple process, on the condition that i of (II-171) be

$$i = n+1$$

"To tell us that every species of things is endowed with an 'occult' specific quality by which it acts and produces manifest effects, is to tell us nothing, but to derive two or three general principles from phenomena and afterwards to tell us how the properties and actions follow from these manifest principles would be a very great step." --I. Newton

CHAPTER III

DEVELOPMENT

Any formal theory, conceived by a scientist, is nothing more than a peculiar artistic sketch, until it is made usable. To physicists today, usability means computer programs. This chapter, which is sandwiched between Theory and Application, is given in order to develop the tools and ideas necessary for any application.

SECTION A

PERFECT AND EFFECTIVE LATTICE GREEN"S FUNCTIONS

Since the procedure for finding both the perfect and the effective lattice Green's functions is the same, the discussion will first be restricted to the perfect crystal Green's functions.

The fundamental information about the perfect lattice is contained in the eigenvectors and eigenvalues described in Part 2b of Section A, Chapter II. Since the arguments of P are the displacements, it follows that an expansion should be made in the style of the normal coordinates, and that the Green's function for the normal coordinates (or the annihilation and creation operators) be determined.

The perfect crystal Green's function, (II-56), is given by

$$P_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) = \frac{1}{\hbar}\int_{-\infty}^{\infty} \sum_{j\tilde{k}} \sum_{j'\tilde{k}'} \sigma_{\alpha}^{*j}(\tilde{k})\sigma_{\beta}^{j'}(\tilde{k}')e^{-i(\tilde{k}.\tilde{\ell}-\tilde{k}'.\tilde{\ell}')}$$

$$\times\langle\langle Q^{j}(\tilde{k},t);Q^{j'}(\tilde{k}',t')\rangle\rangle e^{i\omega(t-t')}d(t-t') \qquad \text{(III-1)}$$

in the "massless" formulation which involves the following reduction of variables:

$$u_{\alpha}(\tilde{\ell},t) = \sqrt{M_{\alpha}}\, u_{\alpha}(\tilde{\ell},t)$$

$$p_{\alpha}(\tilde{\ell},t) = \frac{1}{\sqrt{M_{\alpha}}}\, p_{\alpha}(\tilde{\ell},t)$$

while

$$\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}') = \frac{\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')}{\sqrt{M_\alpha M_\beta}}$$

and the perfect crystal Hamiltonian becomes

$$H = \frac{1}{2}\sum_{\substack{\alpha \\ \tilde{\ell}}} p_\alpha^2(\tilde{\ell},t) + \frac{1}{2}\sum_{\substack{\alpha\ \beta \\ \tilde{\ell}\ \tilde{\ell}'}} u_\alpha(\tilde{\ell},t)\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')u_\beta(\tilde{\ell}',t)$$

The Green's function described in (III-1) is $\frac{1}{\sqrt{M_\alpha M_\beta}}$ times the mass formulated Green's function.

In equation (III-1), $\sigma_\alpha^j(\tilde{k})$ is the eigenvector, and $Q^j(\tilde{k},t)$ the normal coordinate of the appropriate branch j, of eigenvalue $\omega_j(\tilde{k})$ and wave vector $\tilde{k}$, in a crystal described by force constants $\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')$ (mass formulation) connecting atoms of mass M_α and M_β.

Writing the normal coordinate operator in terms of the phonon annihilation and creation operators, (II-26) and using

$$a_j(\tilde{k},t) = e^{iHt/\hbar}a_j(\tilde{k})e^{-iHt/\hbar}$$

$$a_j^\dagger(\tilde{k},t) = e^{iHt/\hbar}a_j^\dagger(\tilde{k})e^{-iHt/\hbar}$$

and the commutation relations (II-27), the normal coordinate Green's function of equation (III-1) becomes

$$<<Q^j(\tilde{k},t);Q^{j'}(\tilde{k}',t')>>_r = \frac{-i\hbar\theta(t-t')}{2\sqrt{\omega_j(\tilde{k})\omega_{j'}(\tilde{k}')}} <e^{i(\omega_j(k)t-\omega_{j'}(k')t)}$$

$$\times\ [a_j^\dagger(\tilde{k},t),a_{j'}(\tilde{k}',t')]+e^{-i(\omega_j(\tilde{k})t-\omega_{j'}(\tilde{k}')t')}[a_j^\dagger(\tilde{k},t),a_{j'}(\tilde{k}',t)]>$$

(III-2)

Substituting (III-2) into (III-1), and using (II-9), $P_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')$ is found to be

$$P_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega)=\frac{1}{N}\sum_{j}\sum_{\tilde{k}}\frac{\sigma_{\alpha}^{*j}(\tilde{k})\sigma_{\beta}^{j}(\tilde{k})e^{-i\tilde{k}.(\ell-\ell')}}{\omega^{2}-\omega_{j}^{2}(\tilde{k})} \qquad \text{(III-3)}$$

where $\omega = \omega+i\varepsilon$ and $\varepsilon\to 0^{+}$ (III-4)

If the advanced Green's function had been evaluated, instead of the retarded, then equation (III-3) would remain the same, but (III-4) would have $\omega=\omega-i\varepsilon$.

Transforming the sum over k in equation (III-3) to an integral by

$$\sum_{\tilde{k}} \equiv \frac{V}{(2\pi)^{3}}\int d^{3}k$$

and taking ω=real, equation (III-3) becomes

$$P_{\alpha\beta}(\ell,\ell';\omega) = \frac{1}{(2\pi)^{3}}\frac{V}{N}\sum_{j}\int d^{3}k\,\frac{\sigma_{\alpha}^{*j}(\tilde{k})\sigma_{\beta}^{j}(\tilde{k})e^{-i\tilde{k}.(\ell-\ell')}}{\omega^{2}-\omega^{2}(\tilde{k})+i\delta} \qquad \text{(III-5)}$$

where V=crystal volume and $\delta\to 0^{+}$.

Next, by applying the theorem

$$\lim_{\delta\to 0^{+}}\int_{a}^{b}\frac{f(x)}{x-y\pm i\delta}\,dx = \underline{\underline{P}}\int_{a}^{b}\frac{f(x)}{x-y}\,dx \mp i\pi f(y) \qquad a<y<b$$

where $\underline{\underline{P}}$ indicates the principal value integral and f(x) is a continuous function of x, equation (III-5) may be rewritten as

$$P_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) = \underline{\underline{P}}\int_{0}^{\omega_{max}}\frac{\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega')}{\omega^{2}-\omega'^{2}}\,d\omega' - \frac{i\pi}{2\omega}\,\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega) \qquad \text{(III-6)}$$

$$0<\omega<\omega_{max}$$

where

$$\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega) = \frac{1}{(2\pi)^3}\frac{1}{n_A}\sum_j \int d^3k\sigma_\alpha^{*j}(\tilde{k})\sigma_\beta^j(\tilde{k})e^{-i\tilde{k}\cdot(\tilde{\ell}-\tilde{\ell}')}\delta(\omega_j(\tilde{k})-\omega) \tag{III-7}$$

and n_A= the number of atoms per unit cell. It is observed that for $\tilde{\ell}=\tilde{\ell}'$, $\nu_{\alpha\beta}(0;\omega)$ is just the usual density of states.

Once $\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega)$ is found, it is a trivial exercise to find

$$\mathrm{Im}\ P_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega)=-\frac{\pi}{2\omega}\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega) \tag{III-8}$$

and numerically obtain

$$\mathrm{Re}\ P_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) = \underline{\underline{P}}\int_0^{\omega_{\max}} \frac{\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega')}{\omega^2-\omega^{\ 2}}\,d\omega'$$

$$= \left\{\int_0^{\omega-\Delta} d\omega'\,\frac{\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega')}{\omega^2-\omega'^2} + \int_{\omega+\Delta}^{\omega_{\max}} d\omega'\,\frac{\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega')}{\omega^2-\omega'^2}\right\}$$

$$+\left\{\underline{\underline{P}}\int_{\omega-\Delta}^{\omega+\Delta} d\omega'\,\frac{\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega')}{\omega^2-\omega'^2}\right\} \tag{III-9}$$

where the second term in (III-9) becomes vanishingly small as $\Delta\to0^+$, and the greater contribution, coming from the first term of (III-9) in brackets, can be found by using Simpson's rule.

The method used to find $\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega)$, of equation (III-7), was similar to that introduced by Raubenheimer and Gilat (1966) for the evaluation of the density of states. The particulars of this very accurate method can be found in their report, and only an outline of certain ideas is presented here.

The important points to consider are: that the integral of equation (III-7) is transformed into an integral over the irreducible zone, by taking advantage of the transformation properties of the eigenvectors $\sigma_{\alpha}^{*j}(k)$ and $\sigma_{\beta}^{j}(k)$, and also the factor $e^{-i\tilde{k}\cdot(\tilde{\ell}-\tilde{\ell}')}$; and, that the sum and integral for this Brillouin zone is found by subdividing this irreducible zone into cubes of desired mesh size. It is obvious that not all of this zone can be cut into cubes, and thus an appropriate weight is given to each subvolume of the unit volume, i.e., the chosen mesh cube size. That is to say, when a cube falls in the irreducible zone, it is given a weight 1, while if $(1/n)^{th}$ of a cube falls in this zone it is given a weight (1/n). Also, this mesh can be made smaller, near $\tilde{k}=0$, where accuracy is more difficult to obtain. No cube is centered at $\tilde{k}=0$ or on any symmetry axis, so that degeneracies, other than accidental ones, are avoided. The only input parameters necessary for this calculation are those which are required for defining the eigenvectors, $\sigma_{\alpha}^{j}(\tilde{k})$, and the eigenfrequencies $\omega_j(\tilde{k})$, for the system. These parameters (i.e., $\Phi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')$ and M_{α}) are taken to be either experimentally determined, as in the case of the perfect lattice, or experimentally and/or theoretically determined for the effective lattice.

Apart from the mass defect, it now seems that even for the simplest defect space, the number of "weighted" densities of states, $\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega)$, is enormous. This is not really the case, for by using the symmetry properties of the system, the number of independent $\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega)$ needed is very much less than the number that seems to be needed to define the defect space. The equivalence of many of these functions can be found by the reduction procedure, and by noting that these functions, within a rotation, depend on $|\tilde{\ell}-\tilde{\ell}'|$. The results, and some discussion of such a procedure, are presented in Appendix I for an f.c.c. lattice.

Since Φ° and $\overline{V}$ are defined to have the same symmetry properties, the only difference in the above discussion between the derivation of P and G° is that $\Phi=\Phi^{\circ}$ is used for defining P, while $\Phi=(\Phi^{\circ}-\overline{V})$ is used to define G°.

SECTION B

GROUP THEORY AND THE SUBSTITUTIONAL IMPURITY

In this section, a brief synthesis of certain sections of Maradudin (1965), Tinkham (1964), Koster (1957), Agrawal (1969), and Ludwig (1964) is presented. The purpose of doing this is to briefly describe the mechanism by which the defect space can be reduced. Since the low concentration theory requires only the single defect scattering t-matrix, the techniques for matrix manipulation are those for the single defect problem, and so it is this which is considered below.

If n_n is the number of neighbours in the defect space, and m_σ is the number of times the σ^{th} irreducible representation appears in the representation of the group, then, with this method of reduction, the $3(n_n+1) \times 3(n_n+1)$ matrix, which defines the defect space, is reduced into a set of $m_\sigma \times m_\sigma$ matrices. These matrices usually have $m_\sigma << 3(n_n+1)$ and

$$\sum_{\sigma=1}^{nr} m_\sigma < 3(n_n+1)$$

where n_r is the number of distinct irreducible representations. Such a scheme is obviously useful, since it greatly decreases the amount of work necessary to solve any defect problem.

The reduction of any matrix $Q_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')$, which spans the defect space and has the symmetry of the group, is made by a similarity transformation

$$Q_{(\sigma^j_i),(\sigma^{j'}_{i'})} = \sum_{\substack{\alpha \; \beta \\ \tilde{\ell} \; \tilde{\ell}'}} M_{(\sigma^j_i),(\tilde{\ell},\alpha)} Q_{\alpha\beta}(\tilde{\ell},\tilde{\ell}') M^{\dagger}_{(\sigma^{j'}_{i'}),(\tilde{\ell}',\beta)} \qquad \text{(III-10)}$$

where the matrix $M_{(\sigma^j_i),(\tilde{\ell},\alpha)}$, connects the i^{th} row of the $\sigma^{j\,th}$ irreducible representation to the Cartesian coordinate $\underline{\underline{\alpha}}$, of the a^{th} atom in the $\tilde{\ell}^{th}$ unit cell, and j runs over $1,\ldots m_\sigma$.

Using (II-153) and (II-154), the single defect problem may be rewritten as

$$PVu = u \qquad \text{(III-11)}$$

which can be broken up into a pair of equations (Maradudin (1965)), one of which is in the space of the defect. Generally, the form of (III-11) in the defect space, can be expressed as

$$P_1 v^1 \Psi^{(s)} = \lambda_s \Psi^{(s)} \qquad \text{(III-12)}$$

where s labels the possible solutions to this equation of eigenvalue λ_s and eigenvector $\Psi^{(s)}$.

The Green's function matrix $P_{1\alpha\beta}(\tilde{\ell},\tilde{\ell}')$, under an operation of the point group, transforms as

$$P_{1\alpha'\beta'}(\tilde{L},\tilde{L}') = \sum_{\alpha\;\beta} S_{\alpha'\beta}\, P_{1\alpha\beta}(\tilde{\ell},\tilde{\ell}') S^{\dagger}_{\beta'\beta} \qquad \text{(III-13)}$$

where the 3×3 matrix, S, is a real orthogonal transformation of the coordinate axes applied at the defect site. This transformation takes the crystal into itself, and thus, the lattice site $(\tilde{\ell},\alpha)$ into $(\tilde{L},\alpha')$. A similar transformation law holds for v^1, when the symmetry operations are applied to the defect site. These transformations (i.e., the group elements) are the same if v^1 has the same symmetry at a defect site as L° of equation (II-152) has at any atom, for the same extent. This is assumed to be the case in the discussion that follows.

Returning to the eigenvalue problem (III-12), it can be said that there is a possibility of some eigenvalues λ_s being the same, but belonging to different, linearly independent $\Psi^{(s)}$'s. Explicitly, this can be expressed by

$$\sum_{\tilde{\ell}',\beta} A_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')\Psi_{\beta}^{(\sigma_i)}(\tilde{\ell}') = \lambda_\sigma \Psi_{\sigma}^{(\sigma_i)}(\tilde{\ell}) \qquad \text{(III-14)}$$

where $A = P_1 v^1$, and the index $i=1,\ldots,f_\sigma$ labels the eigenvectors belonging to the eigenvalue λ_σ, where f_σ is the multiplicity of the eigenvalue λ_σ. Thus, any linear combination of the f_σ vectors $\Psi^{(\sigma_i)}$ is also a solution of (III-14) with eigenvalue λ_σ.

Applying S to both sides of equation (III-14), and using the fact that $SS^\dagger=1$, equation (III-14) can be expressed as

$$\sum_{\tilde{\ell}',\beta} A_{\alpha',\beta'}(\tilde{L},\tilde{L}')\Psi_{\beta'}^{\prime(\sigma_i)}(\tilde{L}') = \lambda_\sigma \Psi_{\alpha'}^{\prime(\sigma_i)}(\tilde{L}) \qquad \text{(III-15)}$$

where
$$\Psi_{\alpha'}^{\prime(\sigma_i)}(\tilde{L}) = \sum_{\alpha} S_{\alpha',\alpha}\Psi_{\alpha}^{(\sigma_i)}(\tilde{\ell})$$

or
$$\Psi_{\alpha}^{\prime(\sigma_i)}(\tilde{\ell}) = \sum_{\alpha} S_{\alpha',\alpha}\Psi_{[S^{-1}\alpha]}^{(\sigma_i)}([S^{-1}\tilde{\ell}]) \qquad \text{(III-16)}$$

Because S is a symmetry operation of the defect space, then as $(\tilde{\ell}',\beta)$ run over the atoms of the space, so do $S^{-1}(\tilde{\ell}',\beta)$ although in a different order. Because of (III-16), equation (III-15) may be written as

$$\sum_{\tilde{\ell}',\beta} A_{\alpha\beta}(\tilde{\ell},\tilde{\ell}')\Psi'^{(\sigma_i)}_{\beta}(\tilde{\ell}') = \lambda_{\sigma}\Psi'^{(\sigma_i)}_{\alpha}(\tilde{\ell}) \qquad \text{(III-17)}$$

From (III-17), it is observed that if the vector $\Psi^{(\sigma_i)}$ is an eigenvector of A, with eigenvalue λ_σ, then so is $\Psi'^{(\sigma_i)}$. This means that $\Psi'^{(\sigma_i)}$ must be a linear combination of the vectors $\Psi^{(\sigma_i)}$. Consequently, under all operations of the group which take the molecule, defined by the defect space, into itself, the f_σ vectors $\Psi^{(\sigma_i)}$ transform only among themselves, and therefore form a proper basis for the group.

The connection between $\Psi^{(\sigma_i)}$ and the theory of group representation can now be made. It is said that $\Psi^{(\sigma_i)}$ belongs to the i^{th} row of the σ^{th} irreducible representation of the group. If the σ^{th} representation appears more than once, say m_σ times, then $\Psi^{(\sigma^j_i)}_{\alpha}(\tilde{\ell})$ connects the i^{th} row of the $\sigma^{j\,th}$ irreducible representation to $(\tilde{\ell},\alpha)$ in the defect space. Therefore, the matrix M of (III-10) can be constructed out of the vectors $\Psi^{(\sigma^j_i)}$.

The reduction of Q now lies in finding the vectors $\Psi^{(\sigma^j_i)}$. The means by which $\Psi^{(\sigma^j_i)}$ are found is now outlined, starting with the character table for the irreducible representations of the group. This table, if not listed, can be found using the following rules:

1) All the complete classes of the group (i.e., n_c) can be found from a knowledge of the group elements.

2) The number of irreducible representations, n_r is equal to n_c.

3) The dimensionalities f_σ of the irreducible representations of the group can be found by using rule (2) and

$$\sum_{\sigma=1}^{n_r} f_\sigma^2 = g \tag{III-18}$$

where g is the order of the group. Rule (3) determines the first column of the character table, because

$$\chi^{(\sigma)}(e) = f_\sigma \tag{III-19}$$

where e is the identity element.

4) On the basis that:

a) the rows of the character table must be orthogonal and normalized to g, with a weighting factor N_k (the number of elements in the k^{th} class $\underline{\underline{C}}_k$), i.e.,

$$\sum_R \chi^{(\sigma)}(R)^* \chi^{(\sigma 1)}(R) = \sum_{k=1}^{n_c} N_k \chi^{(\sigma)}(\underline{\underline{C}}_k)^* \chi^{(\sigma 1)}(\underline{\underline{C}}_k) = g\delta_{\sigma,\sigma_1} \tag{III-20}$$

where R are the elements of the group G;

b) the columns of the character table must be orthogonal vectors normalized to g/N_k, i.e.,

$$\sum_{\sigma=1}^{n_r} \chi^{(\sigma)}(\underline{\underline{C}}_k)^* \chi^{(\sigma)}(\underline{\underline{C}}_{k'}) = \frac{g}{N_k}\delta_{k,k'} \tag{III-21}$$

all the other elements of the character table may be worked out.

Once these elements of the table have been found, it is easy to find out how many times the σ^{th} irreducible representation occurs in a given representation of the group. If $\chi(R)$ is the character of a given representation of G, associated with $R \varepsilon G$, then,

$$m_\sigma = \frac{1}{g}\sum_R \chi^{(\sigma)}(R)^* \chi(R) = \frac{1}{g}\sum_{k=1}^{n_c} N_k \chi^{(\sigma)}(\underline{\underline{C}}_k)^* \chi(\underline{\underline{C}}_k) \quad \text{(III-22)}$$

gives the number of times m_σ, the σ^{th} irreducible representation $\Gamma^{(\sigma)}(R)$, is found in the given representation $\Gamma(R)$ of the group.

Having found the types of irreducible representations and the number of times they appear, it is now necessary to define them explicitly. By inspection, (of literature or of the symmetry of the representation), a set of basis functions $\phi_j^{(\sigma)}$, that belong to the j^{th} row of the σ^{th} irreducible representation, is found, such that these functions, under the operation of the group operators P_R, transform among themselves. P_R is the operator which corresponds to R and requires the following to be satisfied:

$$P_R q(\tilde{x}) = q(R^{-1}\tilde{x})$$

where q is some function of $\tilde{x}=(x,y,z)$. These set of f_σ basis functions are then listed alongside the appropriate representations in the character table.

With this information, the irreducible representation $\Gamma^{(\sigma)}(R)$ can be found from

$$P_R\phi_j^{(\sigma)} = \sum_{j'=1}^{f_\sigma} \phi_{j'}^{(\sigma)}\Gamma_{j'j}^{(\sigma)}(R) \qquad \text{(III-23)}$$

Having obtained the irreducible representations $\Gamma^{(\sigma)}(R)$, the projection operator, defined by

$$\underline{\underline{P}}_{ij}^{(\sigma)} = \frac{f_\sigma}{R}\sum_R \Gamma_{ij}^{(\sigma)}(R)^*P_R \qquad \text{(III-24)}$$

is applied to Ψ, an arbitrary vector in the defect space, and in so doing, produces the eigenvector $\Psi^{(\sigma i)}$, which transforms according to the ith row of the σth irreducible representation.

$$\Psi^{(\sigma_i)} = \underline{\underline{P}}_{ii}^{(\sigma)}\,\Psi \qquad \text{(III-25)}$$

This is the desired result.

In general, since the character table and basis functions for most symmetry groups, can be found in the literature, only the last few steps need be attempted to find $\Psi^{(\sigma i)}$. In Appendix II, the procedure is briefly outlined for a first nearest neighbour defect space in the f.c.c. lattice. The results of Appendix II are used in Appendix III, to find the reduced P_1 and v^1 (for the same lattice and space).

SECTION C

INTERATOMIC POTENTIALS AND THE DEFECT LATTICE

This section contains a brief description of pair potentials. In the first part of the section a short motivative type discussion is given for using an effective pair potential between atoms in a crystal lattice. The ideas of this part, which were stimulated by the treatment of liquids in Hirschfelder (1967), also allow for a pair potential view of the effective lattice. Parts 2 (Morse potential), 3 (Lennard Jones potential) and 4 (Ionic crystals) are shorts on three effective pair potentials which prove useful in the next chapter, Application.

1. The Crystal Potential

Consider the perfect crystal system of N_s identical atoms, whose total potential energy function $\Phi((\tilde{\ell},\alpha)_1,(\tilde{\ell},\alpha)_2, \ldots,(\tilde{\ell},\alpha)_{N_s})$ may be expanded as a sum of two, three,...,n-body potentials:

$$\Phi^\circ = \frac{1}{2!}\sum_{i=1}^{N_s}\sum_{\substack{j=1 \\ i\neq j}}^{N_s}\phi_{ij} + \frac{1}{3!}\sum_{i-1}^{N_s}\sum_{\substack{j=1 \\ i\neq j\neq k}}^{N_s}\sum_{k=1}^{N_s}T_{ijk} + \ldots + \frac{1}{n!}\sum_{\substack{i_1 \\ i_1\neq\ldots\neq i_n}}^{N_s}\cdots\cdots\sum_{i_n}^{N_s}T_{i_1,\ldots,i_n} \qquad \text{(III-26}_a\text{)}$$

where

$$\left(\frac{d\Phi^\circ}{da}\right)_{a=a_o} = 0 \qquad \text{(III-26}_b\text{)}$$

Equation (III-26) may be rewritten as

$$\Phi^{\circ} = \frac{1}{2!} \sum_{i=1}^{Ns} \sum_{\substack{j=1 \\ i \neq j}}^{Ns} \phi_{ij}^{eff} \qquad \text{(III-27)}$$

where ϕ_{ij}^{eff} is related to the "bare" two-body potential by

$$\phi_{ij}^{eff} = \phi_{ij} \left\{ 1 + \frac{1}{3} \sum_{k \neq i,j}^{Ns} \left(\frac{T_{ijk}}{\phi_{ij}} \right) + \cdots\cdot \right\} \qquad \text{(III-28)}$$

Therefore, in a crystal, if vibrations are neglected

$$\phi_{ij}^{eff} = \phi_{ij}^{eff}\left((\tilde{\ell},\alpha)_i, (\tilde{\ell},\alpha)_j ; \underline{\underline{B}} \right) \qquad \text{(III-29)}$$

where $\underline{\underline{B}}$ symbolizes a dependence on some bulk properties of the solid. It is easily seen that the separation between nearest neighbours in a crystal is not given by r_o--the separation at which the interatomic potential has a minimum. This difference on the separation distance is the result of the attraction of an atom to atoms beyond its nearest neighbour. Below, the form of the pairwise potential ϕ_{ij}^{eff}, in the crystal, is taken to be the same as ϕ_{ij} with a change only in the potential parameters.

In a crystal with N_σ substitutional defect atoms a, and $N_b = (N_s - N_\sigma)$ remaining perfect lattice atoms b, the effective interatomic potentials depend on the type of pairing aa, ab, or bb. Care is needed to avoid overcounting the interactions, while still defining physically meaningful effective potentials. For a random distribution of N_σ and N_b atoms,

$$\Phi_c = \frac{1}{2!}\sum_{\substack{m \\ m\neq n}}^{N_\sigma}\sum_{n}^{N_\sigma}\phi_{mn}^{aa}+\frac{1}{2!}\sum_{\substack{i \\ i\neq j}}^{N_b}\sum_{j}^{N_b}\phi_{ij}^{bb}+\sum_{m}^{N_\sigma}\sum_{i}^{N_b}\phi_{mi}^{ab}$$

$$+\frac{1}{3!}\sum_{\substack{m_1 \\ m_1\neq m_2\neq m_3}}^{N_\sigma}\sum_{m_2}^{N_\sigma}\sum_{m_3}^{N_\sigma}T_{m_1m_2m_3}^{aaa}+\frac{1}{3!}\sum_{\substack{i_1 \\ i_1\neq i_2\neq i_3}}^{N_b}\sum_{i_2}^{N_b}\sum_{i_3}^{N_b}T_{i_1i_2i_3}^{bbb}$$

$$+\frac{1}{2!}\sum_{m}^{N_\sigma}\sum_{\substack{i \\ i\neq j}}^{N_b}\sum_{j}^{N_b}T_{ijm}^{bba}+\frac{1}{2!}\sum_{i}^{N_b}\sum_{\substack{m \\ m\neq n}}^{N_\sigma}\sum_{n}^{N_\sigma}T_{imn}^{baa}+\cdots \qquad \text{(III-30)}$$

If

$$\Phi_c = \frac{1}{2!}\sum_{\substack{i \\ i\neq j}}^{N_b}\sum_{j}^{N_b}\phi_{ij}^{bb\ \mathrm{eff}}+\frac{1}{2!}\sum_{\substack{m \\ m\neq n}}^{N_\sigma}\sum_{n}^{N_\sigma}\phi_{mn}^{aa\ \mathrm{eff}}+\sum_{i}^{N_b}\sum_{m}^{N_\sigma}\phi_{im}^{ba\ \mathrm{eff}} \qquad \text{(III-31)}$$

then the definition of the effective pair potential is ambigious, since the environment of a given pair contains some a and some b atoms. It is desirable to define the interatomic effective potential as the effective potential of a pair, immersed in a medium of a given bulk composition

$$c = \frac{N_\sigma}{N_s} \qquad \left(\frac{d\Phi_c}{da}\right)_{a=a_c} = 0$$

This is possible if a and b are quite similar and/or if the properties of a and b are completely randomly distributed in the crystal.

At "low enough" concentration c of a in b, where no a is aware of any other a, the situation may be simplified, since the environment of the aa pair is essentially all b. This is only reasonable if already the forces are "short enough" ranged. The same is true for an ab or a bb pair. Consistent with this picture, all the T^{bba}_{ijm} terms are assigned to the ϕ^{ba}_{im} pair, the T^{baa}_{imn} terms to ϕ^{aa}_{mn} and so on. Thus, (III-30) becomes

$$\Phi_c = \frac{1}{2!}\sum_{\substack{i \\ i\neq j}}^{N_b}\sum_{j}^{N_b}\phi^{bb}_{ij}\left\{1+\frac{1}{3}\sum_{k\neq i,j}^{N_b}(T^{bbb}_{ijk}/\phi^{bb}_{ij}) + \cdots\right\} \qquad (\text{III-32}_a)$$

$$+\sum_{i}^{N_b}\sum_{m}^{N_\sigma}\phi^{ba}_{im}\left\{1+\frac{1}{2!}\sum_{j\neq i}^{N_b}(T^{bba}_{ijm}/\phi^{ba}_{im}) + \cdots\right\} \qquad (\text{III-32}_b)$$

$$+\frac{1}{2!}\sum_{\substack{m \\ m\neq n}}^{N_\sigma}\sum_{n}^{N_\sigma}\phi^{aa}_{mn}\left\{1+\sum_{i}^{N_b}(T^{baa}_{imn}/\phi^{aa}_{mn})+\frac{2!}{3!}\sum_{m_1\neq m,n}^{N_\sigma}(T^{aaa}_{m_1mn}/\phi^{aa}_{mn})+\cdots\right\}$$

$$(\text{III-32}_c)$$

The sums inside the curly brackets of (III-32$_a$) are over N_b atoms found in a given volume, whereas the similar sum in (III-28), for the perfect crystal, covers all N_s atoms of the crystal. At "low enough" concentration that is being considered, the difference between these two sums for the terms inside the curly brackets is negligible. Thus, for the same separation of i and j

$$\phi^{bb\ \text{eff}}_{ij} \simeq \phi^{\text{eff}}_{ij} \qquad (\text{III-33})$$

Clearly, in this case, the effective lattice would only be defined by

$$\Phi^{eff} = \frac{1}{2!} \sum_{\substack{i \\ i \neq j}}^{N_s} \sum_{j}^{N_s} \phi_{ij}^{eff}(a=a_c) \qquad \text{(III-34)}$$

where a_c is the lattice constant of the crystal lattice with a concentration c of random substitutional impurity atoms a. Because of equation (III-26_b)

$$\left(\frac{d\Phi^{eff}}{da}\right)_{a=a_c} \neq 0 \qquad \text{(III-35)}$$

The placing of the impurities in this lattice results in

$$\left(\frac{d\Phi_c}{da}\right)_{a=a_c} = 0 \qquad \text{(III-36)}$$

or the stable defect lattice, which is observed.

If the concentration of impurities is not "low enough", the equation for $\phi_{ij}^{bb\ eff}$ has some information about the properties of atoms a. Thus, if the form of ϕ_{mn}^{aa} is the same as ϕ_{ij}^{bb}, the parameters of $\phi_{ij}^{bb\ eff}$ are different from those of ϕ_{ij}^{eff}, but the form of the potential remains the same. Here again, the symmetry about any atom b, in a lattice of atoms b, with an interatomic potential $\phi_{ij}^{bb\ eff}$, is the same as that of the perfect lattice. Therefore (Section E, Chapter II), the effective lattice energy is given by

$$\phi^{eff} = \frac{1}{2!}\sum_{\substack{i \\ i\neq j}}^{N_s}\sum_{j}^{N_s}\phi_{ij}^{bb\ eff}(a=a_c) \qquad \text{(III-37)}$$

where, except for mass defects, the relation given by (III-35) still holds.

In a real crystal, both central and non-central forces contribute to the lattice energy. Although the non-central contributions to the lattice energy may be sizeable, the change in lattice energy, due to the non-central contributions, may be negligible in most cases (Christian and Vitek (1970)). Assuming this is the case for all the substances that are treated in this thesis, even where non-centrality may be of particular importance, central potentials can be used to describe crystal lattices, and they are said to give a good representation of force changes, but not necessarily of the forces themselves.

The description of interatomic forces is restricted here to central potentials

$$\phi(r_{ij}) = \phi_{ij}(|(\tilde{\ell},\alpha)_i-(\tilde{\ell},\alpha)_j|) \qquad \text{(III-38)}$$

which, irrespective of their form, depend on certain parameters. For such potentials, there are four important properties that require parametrization; they are

a) δ, the distance, toward the origin, beyond which the repulsive forces become very large, (a measure of"hardness");

b) ε, the potential's energy depth (a measure of the strength of binding);

c) r_o, the distance from any origin atom, where the potential has its minimum;

d) r_e, the extent of the potential.

Using these properties, the potential of (III-38) may be written as

$$\phi\ (\delta,\varepsilon,r_o,r_e;r_{ij})$$

If $\phi_{AA}(\delta_A,\varepsilon_A,r_{oA},r_{eA};r_{ij})$, $\phi_{BB}(\delta_B,\varepsilon_B,r_{oB},r_{eB};r_{ij})$ and $\phi_{AB}(\delta_{AB},\varepsilon_{AB},r_{oAB},r_{eAB};r_{ij})$ are interatomic potentials of the same form, connecting the atomic pairs AA, BB and AB respectively, then the following empirical combining laws may be valid:

$$\delta_{AB} = \frac{\delta_A+\delta_B}{2} \qquad \text{(III-39)}$$

and

$$\varepsilon_{AB} = \frac{D_{AB}}{\sqrt{D_A D_B}}\sqrt{\varepsilon_A \varepsilon_B} \qquad \text{(III-40)}$$

where D_{AB}, D_A, and D_B, are the dissociation energies of the molecules AB, AA, and BB, respectively. Since the interatomic potentials have a "hard core" at $r \sim \delta$, the atoms appear, at this distance, as almost rigid spheres, and (III-39) is valid for such potentials. Equation (III-40) is a more general form of the molecular result, suggested by Hirschfelder, Curtiss and Bird (1954), i.e.,

$$D_{AB} = \sqrt{D_A D_B} \tag{III-41}$$

to the crystal state. If (III-41) does not hold, then the relationship will be out by a factor of

$$\frac{D_{AB}}{\sqrt{D_A D_B}}$$

Since D_{AB}, D_A and D_A are easily found, it was thought that if the same type of forces determine the major part of the binding energy in the crystal, as in the molecule, then (III-40) may be a good approximation. From crystal information (i.e., Cu_3Au), it is seen in Chapter IV that this relation does not hold for the Cu/Au crystal system. It seems obvious that

$$\min(r_{oA}, r_{oB}) \leq r_{oAB} \leq \max(r_{oA}, r_{oB}) \tag{III-42}$$

and

$$\min(r_{eA}, r_{eB}) \leq r_{eAB} \leq \max(r_{eA}, r_{eB}) \tag{III-43}$$

but nothing more precise can be stated about these parameters.

In Chapter IV, the Morse potential, the Lennard-Jones, and the Born-Mayer plus Coulomb potentials are used in treating metallic, rare gas and alkali halide crystals, respectively. A brief discussion of these potentials is now given.

2. The Morse Potential

The Morse potential, which found general use in the problem of molecular vibrations, has also been used as an interatomic potential for metallic crystals by Girifalco and Wiezer

(1959), Cotterill and Doyama (1967) and De Wette, Cotterill and Doyama (1966). This potential takes the form

$$\phi(r) = \varepsilon(e^{-2\alpha(r-r_o)}-2e^{-\alpha(r-r_o)}) \qquad \text{(III-44)}$$

and has a depth of ε at $r=r_o$. This potential is rather physical as is seen from

$$r\to\infty \qquad \phi(r)\to 0 \qquad \text{(III-45}_a\text{)}$$

$$r\to 0 \qquad \phi(r)\to\varepsilon e^{\alpha r_o}(e^{\alpha r_o}-2)>>\varepsilon \qquad \text{(III-45}_b\text{)}$$

$$\text{since} \qquad e^{\alpha r_o}>>1$$

For small r

$$\phi(r) \sim \varepsilon((1-2\alpha r)e^{2\alpha r_o}-2(1-\alpha r)e^{\alpha r_o})$$

$$\sim \varepsilon e^{2\alpha r_o}(1-2\alpha r) \qquad \text{(III-46)}$$

and therefore the "hard core"

$$\frac{\varepsilon e^{2\alpha r_o}}{e} = \varepsilon e^{2\alpha r_o}(1-2\alpha\delta)$$

or

$$\delta \sim \frac{1-e^{-1}}{2\alpha}$$

is associated with $\frac{1}{\alpha}$. For large r, very roughly

$$\phi(r) \sim -2\varepsilon e^{-\alpha(r-r_o)} \qquad \text{(III-47)}$$

and the extent of the potential r_e,

$$\frac{-2\varepsilon}{e} \sim -2\varepsilon e^{-\alpha(r_e-r_o)}$$

or
$$r_e \sim r_o + \frac{1}{\alpha}$$

is associated with r_o and $\frac{1}{\alpha}$

For a pair of atoms in a crystal lattice, the Morse potential parameters ε, α, and r_o, are calculated by solving three independent equations that are related to the three necessary and sufficient conditions for crystal stability. These conditions are:

a) a crystal that neither explodes nor implodes

b) a crystal that is stable under infinitesimal dilution or compressive deformation and infinitesimal shear deformation

c) a crystal whose cohesive energy is finite.

If the total energy of the crystal containing N_s atoms A is

$$\Phi^\circ = \frac{N_s}{2} \sum_{j=1}^{n_s} n_j \phi(\varepsilon, \alpha, r_o; r_{ij}) \qquad \text{(III-48)}$$

where n_j are the number of atoms in the j^{th} nearest neighbour shell, and n_s are the number of shells included in the sum, then condition (a) means

$$\left(\frac{d\Phi^\circ}{da}\right)_{a=a_o} = 0 \qquad \text{(III-49)}$$

where a_o is the lattice constant of the stable lattice and (III-49) is the first equation which must be satisfied. Generally, the evaporation of a neutral atom from the crystal requires, first, the localization of an electron at the atom to be removed. This implies an electron redistribution, and thus the energy per atom, (Φ°/N_s), cannot, in general, be equated with the energy of sublimation per atom, but rather is associated with the energy of vacancy formation E_v^f (Cotterill and Doyama (1967)). Therefore, the second equation to be satisfied is

$$\frac{\Phi^\circ}{N_s} = E_v^f \qquad \text{(III-50)}$$

The third equation, related to condition (b), is given by

$$B_{oo} = V_{oo}\left(\frac{d^2\Phi^\circ}{dV_o^2}\right)_{a=a_o} \qquad \text{(III-51)}$$

where $B_{oo} = 1/K_{oo}$, and K_{oo} is the zero temperature and pressure compressibility, while V_o is the zero temperature and V_{oo} is zero temperature and pressure crystal volume. Using (III-49),

$$V_{oo} = \frac{N_s a_o^3}{n_a} \quad \text{and} \quad v = \frac{a_o^3}{n_a}$$

where n_a is the number of atoms per unit cell, equation (III-51) becomes

$$B_{oo} = \frac{n_a}{18a_o}\sum_{j=1}^{n_s} n_j\left(\frac{d^2\phi(\varepsilon,\alpha,r_o;r_{ij})}{da^2}\right)_{a=a_o} \qquad \text{(III-52)}$$

and therefore, ε, α, and r_o may be determined.

3. The Lennard-Jones Potential

A complete discussion of this potential is presented in Hirschfelder, Curtiss and Bird (1954); only a brief sketch is presented here. The Lennard-Jones potential is given by

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad \text{(III-53)}$$

The depth of this potential is ε at $r=2^{\frac{1}{6}}\sigma$. As $r\to 0$ the potential becomes infinite, while as $r\to\infty$ the potential tends to a constant value, zero. It is obvious that the extent of this potential is governed by the attractive term $\left(\frac{\sigma}{r}\right)^{6}$. Thus, the potential drops to a depth of $\left(\frac{1}{n}\right)\varepsilon$ in

$$r_e \sim (4n)^{\frac{1}{6}}\,\sigma$$

On the other hand, the "hard core" is determined by the repulsive term $\left(\frac{\sigma}{r}\right)^{12}$. Thus, the potential feels an n-fold increase in energy ε at

$$\delta \sim \left(\frac{4}{n}\right)^{\frac{1}{12}}\sigma$$

Therefore, in this potential, σ gives a measure of the "hard core", extent and also position of the minimum.

4. Ionic Crystals

In order to discuss the lattice dynamics of alkali halides, the perfect lattice Green's functions are required. The lattice vibrations of the alkali halides have been represented by the shell model, introduced by Dick and Overhauser (1958), which considers the ions as consisting of rigid charged shells bound to cores by harmonic restoring forces; this thesis is not concerned with any more sophisticated model than the rigid ion model. Thus, it should be noted that all perfect lattice information for KBr has been obtained as input data from Timusk (1970).

The rigid ion model is required in this thesis so that a crude estimation of the distortion of the defect space about an Na^+ impurity in KBr can be made.

An excellent treatment of ionic crystals from the rigid ion point of view is contained in Seitz (1940), and only a brief discussion of the interatomic potential for these crystals is presented here.

Ionic crystals are composed of positively charged metal atom ions and negatively charged electro-negative atom ions. The main interaction is the ordinary electrostatic one. The electrostatic forces in these crystals are balanced by repulsive forces which, on the basis of quantum mechanics, are the result of ion-ion exchange, and take the form of a Born-Mayer potential

$$\lambda\ e^{-r/\rho} \qquad \text{(III-54)}$$

therefore, the total potential is given by

$$\phi(r_{ij}) = \lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}} \qquad \text{(III-55)}$$

where the + sign is taken between like charges q of atoms i,j and the - sign is taken between unlike charges q.

SECTION D

NEUTRON SCATTERING

The scattering of neutrons by nuclei bound in crystals has been discussed by many authors (e.g., Van Hove (1954), Brockhouse (1964),(1966)). The approximations, used by these authors, make the scattering valid for thermal neutrons, whose energies are so low that only s-wave scattering is of importance. With these approximations, the neutron scattering cross section can be found by using the Born approximation (Van Hove (1954)). Thus, in a monatomic lattice (for simplicity), the scattering cross section, written in terms of the correlation functions for the scattering particles is

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_1}{2\pi\hbar k_o} S(\tilde{k},\omega) \qquad \text{(III-56)}$$

where

$$S(\tilde{k},\omega) = \frac{1}{N_s} \sum_{\tilde{\ell}} \sum_{\tilde{\ell}'} A_{\tilde{\ell}} A^*_{\tilde{\ell}} e^{i\tilde{k}.(\tilde{\ell}-\tilde{\ell}')} \int_{-\infty}^{\infty} dt\ e^{i\omega t} \exp(<\tilde{k}.\tilde{u}(\tilde{\ell},t)\tilde{k}.\tilde{u}(\tilde{\ell}',0)>) \qquad \text{(III-57)}$$

$\tilde{k}_o$ and $\tilde{k}_1$ are the initial and final wave vectors of the neutron, $\hbar k=\hbar(\tilde{k}_o-\tilde{k}_1)$ is the momentum transfer to the crystal, and $\hbar\omega$ is the energy transfer to the crystal. It is noted that equation (III-57) is the simplified form of the general expression for $S(\tilde{k},\omega)$, which is valid in the harmonic approximation. The quantity $A_{\tilde{\ell}}$, in (III-57) can be considered as an effective temperature dependent scattering length

$$A_{\tilde{\ell}} = a_{\tilde{\ell}} e^{-\frac{1}{2}\langle(\tilde{k}.\tilde{u}(\tilde{\ell}))^2\rangle} \qquad \text{(III-58)}$$

where $a_{\tilde{\ell}}$ is the neutron scattering length of the $\tilde{\ell}^{th}$ atom. In the perfect crystal, the exponential factor of (III-58), known as the Debye Waller factor, is independent of $\tilde{\ell}$, but in an imperfect crystal, this is not the case.

For one phonon inelastic scattering, the exponential in (III-57) can be expanded as follows:

$$e^{\langle\tilde{k}.\tilde{u}(\tilde{\ell},t)\tilde{k}.\tilde{u}(\tilde{\ell}',0)\rangle} \simeq 1+\langle\tilde{k}.\tilde{u}(\tilde{\ell},t)\tilde{k}.\tilde{u}(\tilde{\ell}',0)\rangle \qquad \text{(III-59)}$$

where the first term of (III-59) gives the elastic scattering, and the second term the one phonon process. By looking at the form of the second term of (III-59), it is clear that all the information required for its evaluation is contained in the displacement-displacement Green's function.

Now the term of interest in equation (III-57) is

$$S(\tilde{k},\omega) = \frac{1}{N_s}\sum_{\tilde{\ell}\,\tilde{\ell}'} A_{\tilde{\ell}}A^*_{\tilde{\ell}'}e^{i\tilde{k}.(\tilde{\ell}-\tilde{\ell}')}\int_{-\infty}^{\infty} dt\; e^{i\omega t}\langle\tilde{k}.\tilde{u}(\tilde{\ell},t)\tilde{k}.\tilde{u}(\tilde{\ell}',0)\rangle \qquad \text{(III-60)}$$

Using equations (II-8), (II-13), and the fact that ω can be positive or negative, since neutrons can gain or lose $|\hbar\omega|$,

$$\int_{-\infty}^{\infty} dt\; e^{i\omega t}\langle u_\alpha(\tilde{\ell},t)u_\beta(\tilde{\ell}',0)\rangle = \hbar\eta(\omega)\ \mathrm{Im}\ G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) \qquad \text{(III-61)}$$

where

$$\left.\begin{aligned} \eta(\omega) &= \frac{1}{e^{\beta\omega}-1} && \text{(gain)} \\ \eta(\omega) &= \frac{1}{1-e^{-\beta\omega}} && \text{(loss)} \end{aligned}\right\} \qquad \text{(III-62)}$$

and therefore, (III-60) becomes

$$S(\tilde{k},\omega) = \frac{\hbar}{N_s}\eta(\omega)\sum_{\tilde{\ell}\ \tilde{\ell}'} A_{\ell}A_{\ell}^{*}\ e^{i\tilde{k}.(\ell-\ell')}\sum_{\alpha\beta} k_{\alpha}k_{\beta}\mathrm{Im}\ G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) \qquad \text{(III-63)}$$

The scattering cross section is now defined by equations (III-56) and (III-63) and can be separated into two parts, a "coherent" part and an "incoherent" part. The incoherent scattering can be classified as that part which depends on the magnitude of $\tilde{k}$, and the coherent scattering as that part which depends also on the direction of $\tilde{k}$. Simply speaking, the contribution that comes from the average behaviour of the host atoms is the coherent part, and the incoherent part of the scattering is the contribution due to deviations from this average.

Elliott and Taylor (1967) have shown that the different weighting given to host and defect sites by A_h and A_d respectively results in

$$S(\tilde{k},\omega) = S_{inc}(\tilde{k},\omega)+S_{coh}(\tilde{k},\omega) \qquad \text{(III-64)}$$

where

$$S_{inc}(\tilde{k},\omega) = \mathrm{Im}\ \eta(\omega)\hbar\ \frac{(A_d-A_h)^2c(1-c)}{1-(1-c)M\varepsilon\omega^2P(0;\omega)}\ k^2P(0;\omega) \qquad \text{(III-65)}$$

and

$$S_{coh}(\tilde{k},\omega) = \mathrm{Im}\ \eta(\omega)\hbar\left(A_h+\frac{c(A_d-A_h)}{1-(1-c)M\varepsilon\omega^2P(0,\omega)}\right)^2\sum_{\alpha\beta\ j}k_{\alpha}\sigma_{\alpha}^{j}(\tilde{k})$$

$$\times\ k_{\beta}\sigma_{\alpha}^{j}(k)<G_j(\tilde{k},\omega)> \qquad \text{(III-66)}$$

for mass defects treated in the low concentration theory.

For a low concentration of impurities, randomly distributed in the host crystal lattice, Lakatos and Krumhansl (1968) have shown that the coherent and incoherent contribution to $S(\tilde{k},\omega)$ may be expressed as

$$S_{inc}(\tilde{k},\omega) = \hbar\eta(\omega)\sum_{\alpha\beta} k_\alpha k_\beta \sum_{\tilde{\ell}} \Delta_{\tilde{\ell}}^2 \mathrm{Im}\ G_{\alpha\beta}(\tilde{\ell},\tilde{\ell};\omega) \qquad \text{(III-67)}$$

and

$$S_{coh}(\tilde{k},\omega) = \frac{\hbar}{N_s}\eta(\omega)\overline{H}^2\sum_{\alpha\beta} k_\alpha k_\beta \sum_{\tilde{\ell}\ \tilde{\ell}'} e^{i\tilde{k}\cdot(\tilde{\ell}-\tilde{\ell}')}\mathrm{Im}\ G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) \qquad \text{(III-68)}$$

where $\Delta_{\tilde{\ell}}$ is the deviation of the effective scattering length from the average effective coherent scattering length $\overline{H}$

It is obvious from both (III-65) and (III-67) that the incoherent scattering is related to a modified density of states, while from both (III-66) and (III-68) it is seen that the coherent scattering is related to the individual excitations--the phonons.

SECTION E

IMPURITY INDUCED INFRARED ABSORPTION

The impurity induced infrared absorption in crystals has been treated by Klein (1968) for ionic and neutral crystals with charged impurities, Davies and Healey (1968) for rare gas crystals, and Maradudin (1966_b), Elliott and Taylor (1967) for general crystals.

In perfect crystals, the frequencies of phonons excited or de-excited by light, must equal the frequency of the light, and the sum of the wave vectors of these phonons must equal the wave vector of light. If the wave length of light is "large enough" (compared to the size of the unit cell), as in the case for infrared absorption, then only those modes, whose $\tilde{k}$ (wave vector) add up to zero, can interact with the light incident on the crystal. For a perfect alkali-halide crystal, the light can interact only with $\tilde{k}=0$ phonons in the one phonon absorption process. When impurities are introduced into such a crystal, the crystal loses its translational symmetry, and $\tilde{k}=0$ restriction is relaxed, so that light can now interact with all vibrational modes.

The absorption constant $\alpha(\omega)$ is given by

$$\alpha(\omega) = \frac{2\omega\kappa}{c'} \qquad \text{(III-69)}$$

where c' is velocity of light and κ is the imaginary part of the complex index of refraction $n'=n-i\kappa$. The complex dielectric constant

$$\varepsilon' = \varepsilon_1 - i\varepsilon_2$$

is related to the complex index of refraction as follows:

$$n'^2 = \varepsilon'$$

$$\varepsilon_1 = n^2 - \kappa^2$$

$$\varepsilon_2 = 2n\kappa$$

and therefore (III-69) may be written as

$$\alpha(\omega) = \frac{\omega}{n(\omega)c'}\,\varepsilon_2$$

From Jackson (1962) one finds that

$$\varepsilon' = 1+4\pi\,\frac{\tilde{E}\cdot\chi\cdot\tilde{E}}{|\tilde{E}^2|} = 1+4\pi\tilde{t}\cdot\chi\cdot\tilde{t} \qquad \text{(III-70)}$$

where χ is the general susceptibility of the medium and $\tilde{E}$ is the electric field applied and may be written as

$$\tilde{E} = |\tilde{E}|\tilde{t}$$

Using (III-70), the absorption constant may be written as

$$\alpha(\omega) = -\frac{4\pi\omega}{n(\omega)c'}\,\mathrm{Im}\sum_{\substack{\alpha\ \beta\\ \tilde{\ell}\ \tilde{\ell}'}} t_\alpha\chi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega)t_\beta \qquad \text{(III-71)}$$

If the total electric dipole moment of the crystal is

$$\mu = \sum_{\alpha} \sum_{\tilde{\ell}} e_{\alpha}(\tilde{\ell}) u_{\alpha}(\tilde{\ell})$$

where $e_{\alpha}(\tilde{\ell})$ is the effective charge of the a^{th} atom in the $\tilde{\ell}^{th}$ cell, then from the fact that the Green's function is related to the response function of the crystal the electric susceptibility is (Kubo (1958)) given in terms of the Zubarev type displacement-displacement Green's function as follows:

$$\chi_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) = - \frac{e_{\alpha}(\tilde{\ell}) e_{\beta}(\tilde{\ell}') G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega)}{V} \qquad \text{(III-72)}$$

Therefore (III-71) becomes

$$\alpha(\omega) = + \frac{4\pi\omega}{n(\omega) c' V} \operatorname{Im} \sum_{\substack{\alpha\ \beta \\ \tilde{\ell}\ \tilde{\ell}'}} t_{\alpha} e_{\alpha}(\tilde{\ell}) G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) e_{\beta}(\tilde{\ell}') t_{\beta} \qquad \text{(III-73}_a\text{)}$$

Klein (1968) showed that the optical absorption constant for a monovalent impurity in an alkali halide lattice may be written as

$$\alpha(\omega) = \frac{(n\ (\infty)+2)^2}{9n(\omega)} \frac{4\pi e\omega}{c' m_R} \frac{N}{V} \operatorname{Im} G_{To,To}(\tilde{k}=0;\omega) \qquad \text{(III-73}_b\text{)}$$

where $n(\infty)$ is the index of refraction in the high frequency limit, and m_R the reduced mass of the crystal pair of atoms. Here, $n(\omega)$ can be regarded as a constant.

SECTION F

THE LOCAL MODE

An important property of the Green's function for a crystal with impurities is the location of its poles. The Dyson equation has the formal solution of

$$G = (I-PV)^{-1}P \qquad \text{(III-74)}$$

This solution establishes that the poles of G occur at

$$\det(I-PV) = 0 \qquad \text{(III-75)}$$

or where P has poles. The latter refers to the perfect crystal, whereas the former (III-75), describes the effect of the defect and its related modes.

For a frequency less than the maximum frequency of vibration in the perfect crystal (monatomic), equation (III-75) has a finite imaginary part

$$(\text{Im } P)V \qquad \text{(III-76)}$$

and so, there can be no pole due to (III-75). However, there can be a residual effect, called a resonance, in the neighbourhood of the frequencies, given by the vanishing of the real part of equation (III-75). If on the other hand, the frequency considered is greater than the maximum frequency of vibration of the perfect lattice, then

$$\mathrm{Im}\ P = 0 \qquad \text{(III-77)}$$

and there can be a pole at distance $i\delta$ from the real axis. This pole is called a local mode and the vibrations are localized to a region around the defect.

At "low enough" concentration c, where there is no overlap of any two defect spaces v^i and v^j $(i\neq j)$, the local mode problem can be reduced into the one defect form

$$\det(I-P_1v^1) = 0 \quad , \quad \omega>\omega_m \qquad \text{(III-78)}$$

Apart from the frequency of the local mode, which may be found from (III-78), it is of interest to find an expression for the strength of the local mode. Experimentally, any quantity which is determined is related to

$$\mathrm{Im}\ G_{ij}(\omega) \qquad \text{(III-79)}$$

where the i and j labels refer to the particular representation which satisfies (III-78). If the local mode occurs at $\omega=\omega_0$, then the strength of the pole at $\omega=\omega_0$ is related to

$$s = \int_{\omega_0-\varepsilon}^{\omega_0+\varepsilon} \mathrm{Im}\ G_{ij}(\omega)\ d\omega \quad , \quad \varepsilon>0 \qquad \text{(III-80)}$$

which, within the one defect approach, may be expressed as

$$s = \int_{\omega_0-\varepsilon}^{\omega_0+\varepsilon} d\omega \sum_{k_1k_2} P_{ik_1}(\omega)(\mathrm{Im}\ t_{k_1k_2}(\omega))P_{k_2j}(\omega) \qquad \text{(III-81)}$$

where t is the scattering matrix of the one defect problem.

$$t = v^1(I-P_1v^1)^{-1} = v^1X \tag{III-82}$$

and
$$(I-P_1v^1)X = I \tag{III-83}$$

Therefore, using Cramers rule, X may be written as

$$X = \frac{D}{\det(I-P_1v^1)} \tag{III-84}$$

and (III-81) becomes

$$s = \sum_{k_1k_2k_3} \int_{\omega_o-\varepsilon}^{\omega_o+\varepsilon} d\omega\ P_{1_{ik_1}}(\omega)v^1_{k_1k_2}(\omega)D_{k_2k_3}(\omega)P_{1_{k_3j}}(\omega)\ \mathrm{Im}\left(\frac{1}{\det(I-P_1v^1)}\right) \tag{III-85}$$

where if

$$I = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & & \cdot \\ \cdot & \cdot & \ddots & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ 0 & 0 & \cdots & 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{pmatrix}, \ldots, \begin{pmatrix} 0 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ 1 \end{pmatrix} = (\tilde{I}_1, \ldots, \tilde{I}_n)$$

and
$$Y = (\tilde{Y}_1, \ldots, \tilde{Y}_n) = I-P_1v^1$$

then
$$D_{ij} = \det(\tilde{Y}_1, \ldots, \tilde{Y}_{i-1}, \tilde{I}_j, \tilde{Y}_{i+1}, \ldots, \tilde{Y}_n)$$

If $P_1(\omega)v^1(\omega)D(\omega)P_1(\omega)$ is analytical in $(\omega_o-\varepsilon) \leq \omega \leq (\omega_o+\varepsilon)$, for $\varepsilon > 0$, and

$$\det(I-P_1v^1) = \sum_{n=i_o}^{n_f} (\omega-\omega_o)^n f_n(\omega)$$

$$= (\omega-\omega_o)^{i_o} \sum_{n=0}^{n_f-i_o} (\omega-\omega_o)^n f_{n+i_o}(\omega)$$

$$= (\omega-\omega_o)^{i_o}\underline{\underline{g}}(\omega) \qquad \text{(III-86)}$$

then, by Cauchy's integral formula, (III-85) becomes

$$s = \frac{2\pi}{(i_o-1)!} F_{ij}^{(i_o-1)}(\omega_o) \qquad \text{(III-87)}$$

where

$$F_{ij}^{(n)}(\omega_o) = \frac{d^n}{d\omega_o^n}\left\{\left[\sum_{k_1k_2k_3} P_{1_{ik_1}}(\omega_o)v^1_{k_1k_2}(\omega_o)D_{k_2k_3}(\omega_o)P_{1_{k_3j}}(\omega_o)\right]\underline{\underline{g}}(\omega)\right\} \qquad \text{(III-88)}$$

Generally, for a local mode, $i_o=1$, and so (III-80) may be expressed as

$$s = 2\pi\sum_{k_1k_2k_3}\left\{P_{1_{ik_1}}(\omega_o)v^1_{k_1k_2}(\omega_o)D_{k_2k_3}(\omega_o)P_{1_{k_3j}}(\omega_o)\right\}\underline{\underline{g}}(\omega_o) \qquad \text{(III-89)}$$

Another property of interest is the r.m.s. displacement of the defect in the crystal

$$\sqrt{\langle u^2\rangle} \qquad \text{(III-90)}$$

This will be considered only for a mass impurity. What is required here is the $\tilde{\ell}=\tilde{\ell}'=0$ Green's function

$$G_{\alpha\beta}(0;\omega) = g(\omega)\delta_{\alpha\beta} \qquad \text{(III-91)}$$

where clearly

$$g(\omega) = \frac{p(\omega)}{1-m\varepsilon\omega^2 p(\omega)} \qquad \text{(III-92)}$$

m = the mass of the host atom and

$$p(\omega) = P_{\alpha\alpha}(0;\omega)$$

Using equations (II-13), (III-6) and (III-92), the square of (III-90) may be written as

$$\langle u^2\rangle = 3\langle u_\alpha(0,t)u_\alpha(0,t)\rangle = \frac{3i\hbar}{2}\int_{-\infty}^{\infty} d\omega \frac{1}{e^{\beta\omega}-1}\,(g(\omega+i\delta)-g(\omega-i\delta))$$

$$= \frac{3\hbar}{2m}\int_0^{\omega_m} d\omega \frac{\nu(\omega)\ \coth(\beta\omega/2)}{\omega\left[\left(1-\epsilon\omega^2 \underline{\underline{P}}\int \frac{\nu(\omega')d\omega'}{\omega^2-\omega'^2}\right)^2+\left(\frac{\pi\epsilon\omega\nu(\omega)}{2}\right)^2\right]} \qquad \text{(III-93)}$$

This, however, is not the complete picture, since for

$$0<\epsilon<1$$

the defect atom has a lighter mass than the host atom, and therefore, there is an $\omega=\omega_o>\omega_m$ for which

$$1-\epsilon\omega_o^2\int_0^{\omega_m}\frac{\nu(\omega')d\omega'}{\omega_o^2-\omega'^2} = 0 \qquad \text{(III-94)}$$

(i.e., the local mode condition for a mass impurity) and another pole appears in the integral for the correlation function. This is dealt with in the usual way, by using a small imaginary part $i\delta$ where $\delta\to 0^+$. It can be shown (Taylor (1964)), that there is an extra contribution to (III-93), i.e.,

$$\frac{3\hbar}{2m}\,\frac{\coth\ (\beta\omega/2)}{\epsilon^2\omega_o^3\left[\int \frac{\omega'^2\nu(\omega')d\omega'}{(\omega_o^2-\omega'^2)^2}\right]} \qquad \text{(III-95)}$$

due to the pole at $\omega=\omega_o$.

CHAPTER IV

APPLICATION

"If you want to find out anything from the theoretical physicists about the methods they use, I advise you stick closely to one principle: don't listen to their words, fix your attention on their deeds."

--A. Einstien

SECTION A

A CALCULATION OF THE FREQUENCIES AND WIDTHS OF PHONONS IN $Cu_{0.97}Au_{0.03}$

The phonon frequencies and widths in the random alloy $Cu_{0.97}Au_{0.03}$ are found in this section by using the low concentration theory and are compared with experimental observation. In order to achieve an appropriate description of the alloy system it is essential to include the effects of volume change on alloying using the effective lattice. Morse potentials, discussed in Section C of Chapter IV, are used to attempt to describe these effects as well as to estimate the force constant changes associated with the gold impurities.

Svensson and Brockhouse (1967) measured the phonon dispersion curve in an alloy containing 3% gold, for the $T_1(\zeta,\zeta,0)$ branch halfway out to the zone boundary. They found their experimental results to be in substantial agreement with the mass defect theory. However, the more recent experiments of Svensson and Kamitakahara (1971), with which this section is concerned, on the 3% Cu/Au alloy, although in substantial agreement with the earlier work, are not in agreement with the mass defect theory further out towards the zone boundary along the T_1 $(\zeta,\zeta,0)$ branch and along most of the T $(0,0,\zeta)$ branch. At this concentration the low concentration theory should be reasonable.

The c^2 corrections to the low concentration mass defect theory have been calculated using (II-122) for the random defect lattice and it is found (Figure (F-9A)) that no appreciable effects occur at c=0.03, while at c=0.093 the effects are appreciable. However, this calculation can only serve as a guide when extended defects are considered. Furthermore, Hartmann (1968) has investigated the effect of short range order within the low concentration theory for c=0.093 and found corrections of the order of 10% in the resonance region. For c=0.03 it is not expected that these corrections would amount to more than a few percent. Hence, the assumption of perfect randomicity in this calculation is adequate.

The experimental results, even for c=0.03, do not agree with the calculations of Elliott and Maradudin (1965), and therefore, this suggests that the differences between copper/gold and copper/copper force constants must be taken into account. However, it is important to notice the 1.6% expansion of the lattice, due to the addition of the impurities. The use of 2.0 as an average Gruneisen parameter for copper (Daniels and Smith (1958)) gives a frequency shift of 0.08Thz in the neighbourhood of the supposed resonance. As the maximum experimental shift is 0.12THz, this volume effect cannot be ignored.

The changes in the force constants on addition of gold to copper are complicated by this change in volume. The approximation which is made, is to regard the alloy as being represented by an effective lattice of copper atoms at the experimental lattice spacing of the alloy, into which the gold atoms have been placed substitutionally. This effective lattice described by a set of effective lattice force constants, uniform throughout the crystal, can be obtained from the interatomic potential for copper by using the observed volume change. There are then local force constant changes around each impurity atom placed in this effective lattice. The lattice sites affected by force constant changes due to a particular impurity are called the defect space of that impurity. In Part 1 of this section the use of Morse potentials to estimate these various changes is described.

To obtain, in a manner similar to experiment, the change of the dispersion curves upon alloying, it is necessary to calculate the neutron differential scattering cross section for the alloy as a function of energy transfer for different momentum transfers. Thus, the distortion of the phonon dispersion curves is obtained by examining the frequency shift of these cross sections from those for copper. This procedure also allows for taking into account the effects of the rather considerable experimental broadening.

1. Effective Lattice and Local Force Constants

As mentioned above, a description of the change of the copper phonon frequencies with volume is necessary, i.e., the mode Gruneisen parameters are needed. It is not satisfactory to just take the experimental elastic constant Gruneisen parameters and apply them to the phonon modes at non-zero wave vectors. The elastic constant Gruneisen parameters for the $T(0,0,\zeta)$ and $T_1(\zeta,\zeta,0)$ branches are quite different (See (F-1A)) yet $T(0,0,1)$ and $T_1(1,1,0)$ are the same mode.

Interatomic potentials are required to obtain this description and for a lack of a more sophisticated choice, the Morse potential form is taken. This potential has been applied with various degrees of success to elastic constants (Girifalco and Weizer (1959)), line defects (Cotterill and Doyama (1967)), and copper phonon frequencies (De Wette, Cotterill and Doyama (1966)). However, here it is necessary to use the Morse potential to calculate a volume dependent property. As the potential is volume independent it cannot include such volume dependent effects as those due to changes in the electron screening. The importance of this contribution to the phonon frequencies depends on the degree of overlap between the copper ions. As the screening decreases with increasing volume, it can be expected that the use of the Morse potential will overestimate the magnitude of the Gruneisen parameters. This error should be worse for the longitudinal modes which are far more dependent upon screening than are the transverse modes.

The input data and the resulting Morse potential parameters are given in Table (T-1A) and are the same as those of Cotterill and Doyama (1967). The force constants calculated from this potential are compared with the experimental values of Svensson, Brockhouse and Rowe (1967) in Table (T-2A). It is seen that they are larger and of a somewhat shorter range than the experimental force constants. In fact, they lead to values for the phonon frequencies that are about 10% too high. This comparison also indicates a second failing of the Morse potential in that the experimental results suggest that there is a non-central contribution to the interatomic potential as (1XX-1XY) differs from 1ZZ. The data on which De Wette, Cotterill and Doyama (1966) base their potential for copper is not clear although the potential does give better values for the phonon frequencies.

However, both the potentials referred to above overestimate the elastic constant Gruneisen parameters by amounts ranging from 10% to 100%, the potential of Cotterill and Doyama (1967) being the worse offender. To rescue the situation, it is necessary to resort to the procedure of applying the percentage force constant changes (See page 95, Thesis) given by the Morse potential, to the experimental force constants. This procedure results in much better Gruneisen values. Whether this improvement is due to an approximate inclusion of non-central potential features and/or to an enhancement of the effects of the "long range" forces is not clear. The resulting mode Gruneisen parameters, $\gamma_j(\bar{k})$, for the various symmetry directions are shown in Figure (F-1A) with the experimental elastic constant values (Daniels and Smith (1958)) indicated by arrows. The remaining discrepancy for $T_1(\zeta,\zeta,0)$ is rather unfortunate as this is one of the branches to be investigated. It will also be seen that the structure obtained for this branch is essential in obtaining agreement with experiment. A similar structure was obtained using the Morse potentials directly. The evidence in Part 2 of this section further suggests that the longitudinal Gruneisen parameters are grossly overestimated at the zone boundary, whereas the discrepancy for the transverse branches is probably small. The effective lattice force constants, resulting from the above calculation, are given in Table (T-2A) while the change of frequency for the dispersion curves for $T_1(\zeta,\zeta,0)$ and $T(0,0,\zeta)$ due to the effective lattice is given in Figure (F-10A).

The method of obtaining the interatomic potentials between unlike atoms has been described in Section C of Chapter III. The first requirement is the interatomic potential for gold. Again a Morse potential is used, the parameters being determined in the same matter that Cotterill and Doyama (1967) determined those for copper (See Part 2, Section C, Chapter III). The input data and results are given in Table (T-1A).

To obtain the radius of the repulsive part of the potential for Cu/Au it is natural to take the mean of the radii for copper and gold potentials. If r_o(CuAu) is also determined as the mean of r_o(Cu) and r_o(Au) it is found that

$$r_o(\text{CuAu}) = \frac{1}{2}\,(r_o(\text{Cu})+r_o(\text{Au})) \qquad \text{(IV-1)}$$

and

$$\alpha(\text{CuAu})^{-1} = \frac{1}{2}(\alpha(\text{Cu})^{-1}+\alpha(\text{Au})^{-1}) \qquad \text{(IV-2)}$$

The molecular procedure suggests taking the geometric mean to obtain the energy parameter ε(cuAu), i.e.

$$\varepsilon(\text{CuAu}) = \sqrt{\varepsilon(\text{Cu})\ \ (\text{Au})} \qquad \text{(IV-3)}$$

It can be seen immediately, from Table (T-1A) that this would lead to a weakening of the force constants between copper and gold atoms as compared to those between copper atoms. The evidence discussed in Part 2 of this section indicates the opposite effect. Indeed the procedure described by (IV-3) gives a similarly incorrect result when applied to the calculation of the dissociation energy of the CuAu molecule. A more useful approach is to use the information available for the ordered alloy Cu_3Au and compare it with the result obtained by (III-40). As the heats of vacancy formation are not available for CuAu system, only the stability condition and the bulk modulus could be used to determine the CuAu parameters. Being in a position to determine two parameters, ε(CuAu) and r_o(CuAu) were chosen, since (IV-2) is the more reasonable approximation (See Part 1 and 2, Section C, Chapter III). For the interactions between copper atoms and between the gold atoms the previously determined potentials were used. The results for ε(CuAu) and

r_o(CuAu) and α(CuAu) are given in Table (T-1A).

Since the nearest neighbour local force constants are the force constants of interest, it is natural to work with those forces that refer to motion parallel and transverse to the nearest neighbour bond. The force constants for the motion along $(\zeta,\zeta,0)$, $(\zeta,\bar{\zeta},0)$ and $(0,0,\zeta)$, are called A, B_1, and B_2 respectively. They are related to the conventional force constants, which refer to motion with respect to the crystal axes, by

$$\begin{aligned} A &= 1XX+1XY \\ B_1 &= 1XX-1XY \\ B_2 &= 1ZZ \end{aligned} \qquad \text{(IV-4)}$$

If no relaxation of the atomic positions about the defect is assumed, then the changes in these local force constants are easily calculated. Following the spirit of the discussion of Gruneisen parameters the percentage changes of the Morse potential force constants are applied to the effective lattice force constants. It is these changes in the latter force constants (ΔA, ΔB_1, ΔB_2) that are given in Table (T-3A).

Some relaxation (∿0.0043Å, 1st n.n.) of the atomic positions is to be expected and with information on the interatomic potentials an estimate of the effects of such a relaxation can be made. As this information is not too reliable, it is only worthwhile doing a one-dimensional calculation, taking the dimension as the direction of a nearest neighbour. If all but the impurity atom and its nearest neighbours are held fixed, a relaxation of the nearest neighbour of 0.15% (expansion) is found. This hardly changes if the second nearest neighbours in this line (fourth nearest neighbours in three dimensions) are released. Consistent with these results is the assumption that the effective Cu potential for the CuAu lattice is the same as that of the perfect Cu lattice (See Part 1, Section C, Chapter III). The resulting nearest neighbour local force constant changes, between the gold impurity and its nearest neighbour (ΔA, ΔB_1, ΔB_2), and between the nearest and fourth nearest neighbours ($\Delta A'$, $\Delta B_1'$, $\Delta B_2'$), are given in Table (T-3A). It is seen that ΔA, ΔB_1 and ΔB_2 are somewhat smaller due to relaxation, but the addition of $\Delta A'$, $\Delta B_1'$, and $\Delta B_2'$ numerically compensate for this change. No examination of changes in any of the more long range force constants has been attempted as the force constants themselves are much smaller than those considered above. Consistent with the relaxation model, the changes in force constants between, say, the nearest neighbour atoms of a gold impurity or one of these nearest neighbour atoms and a third nearest neighbour atom, have not been examined. As is mentioned in Part 2 of this section, this omission could be significant.

2. Comparison with Experiment

The elastic one phonon cross section for the coherent scattering of neutrons by lattice vibrations is given by

$$\frac{d^2\sigma}{d\Omega dE} = \frac{a^2 k_2 e^{\beta\omega}}{2\pi k_1 (e^{\beta\omega}-1)} \sum_{\substack{\alpha\ \beta \\ \tilde{\ell}\ \tilde{\ell}'}} k_\alpha k_\beta \ \mathrm{Im}\ G_{\alpha\beta}(\tilde{\ell},\tilde{\ell}';\omega) e^{i\tilde{k}.(\tilde{\ell}-\tilde{\ell}')} \tag{IV-5}$$

where the neutron is scattered from $\tilde{k}_1$ to $\tilde{k}_2$ with $\tilde{k}=\tilde{k}_1-\tilde{k}_2$, with an energy change $E=\hbar\omega$ at a temperature $T=\hbar/k_B\beta$. This result has been specialized from (III-63) to the case of identical coherent scattering lengths for the atomic species, which is an excellent approximation of a copper/gold alloy. The scattering length and the Debye Waller factor, whose variation with atomic species is also neglected, have, as well as the the appropriate constants, been absorbed in the constant a in (IV-5).

The experimentalist is able to examine the scattering by the j^{th} phonon branch if he arranges his scattering geometry such that, approximately,

$$\tilde{k}.\tilde{\sigma}^{j'}(\tilde{q}) = 0 \qquad \text{for} \quad j' \neq j \tag{IV-6}$$

where $\tilde{q}$ is a wave vector in the first Brillouin zone, differing from $\tilde{k}$ by a reciprocal lattice vector. In this case and on using

$$U(j,\tilde{k};\alpha,\tilde{\ell}) = \frac{1}{\sqrt{N_s M_{Cu}}} \exp(i\ \tilde{k}.\tilde{\ell})\sigma_\alpha^j(\tilde{k}) \tag{IV-7}$$

the scattering cross section (IV-5) becomes

$$\frac{d^2\sigma}{d\Omega dE} = \frac{a^2 k_2 e^{\beta\omega}}{2\pi M_{Cu} k_1 (e^{\beta\omega}-1)} \text{Im } G_j(\tilde{q},\omega)(\tilde{k}.\tilde{\sigma}^j(\tilde{q}))^2 \qquad \text{(IV-8)}$$

This form applies for both the disordered and ordered crystals as the host lattice eigenvectors enter only via the transformation (IV-7). Since these eigenvectors are independent of $|\tilde{q}|$, for $\tilde{q}$ along a symmetry direction, and since the interest here is only in the shape of the cross section as a function of ω for a given $\tilde{k}$ (Constant Q method, Brockhouse (1961)) it is only necessary to calculate

$$J(j,\tilde{k},\omega) = \frac{k_2}{k_1} \frac{e^{\beta\omega}}{e^{\beta\omega}-1} \text{Im } G_j(\tilde{q},\omega) \qquad \text{(IV-9)}$$

The experimental resolution can be taken into account, approximately by folding $J(j,\tilde{k},\omega)$ with a Gaussian of appropriate width W,

$$J_b(j,\tilde{k},\omega) = \int \exp\left[-\left(\frac{\omega-\omega'}{2W}\right)^2\right] J(j,\tilde{k},\omega')d\omega' \qquad \text{(IV-10)}$$

Values for W were obtained by noting the width of the experimental cross section at very low $\tilde{q}$ where the effects of alloying should be small. This is a further approximation, as both theory and experiment (for pure crystals) indicate that the resolution is a function of $\tilde{k}$ and ω. The value, taken for W, was that equivalent to a width (FWHM) of 0.22 THz (Svensson and Kamitakahara (1971)).

Following the experimental method (Svensson and Kamitakahara) the centre of the peak in $J_b(j,\tilde{k},\omega)$ was defined to be the centre of the half maximum points. Although $J(j,\tilde{k},\omega)$ tends to develop a shoulder to the main peak in the resonance region (Re $\Sigma_j(\tilde{q},\omega_j(\tilde{q})) \sim 0$), the values of W are sufficiently large as to reduce this structure to a slightly assymmetric peak (See for instance Elliott and Taylor (1967)). The shift $\Delta\omega$, due to the addition of the impurities, is then the frequency difference between the peak centre and the frequency of the copper phonon, $\omega_j(\tilde{q})$, due allowance having been made for the volume effect described in Part 1 of this section.

To carry out these calculations numerical values for the effective lattice Green's function, G^o are needed. These were obtained in the standard way using the method of Gilat and Raubenheimer (1966)(Sec.A,Chap.III). Re G^o was then obtained from Im G^o via equation (III-9).

With only nearest neighbour force constant changes in an f.c.c. lattice, v^s--and hence t^s and x^s--are 39×39 matrices. If M is the orthogonal transformation matrix (A-13), then, denoting the irreducible forms of the matrices by a prime,

$$x' = Mx^sM^\dagger = v'(I-(1-c)G^{o}{}'v')^{-1} \qquad \text{(IV-11)}$$

At worst, it is necessary to invert a complex 4×4 matrix, (See Appendix III for v' and $G^{o}{}'$), which is easily done on the computer. These steps are obviously not necessary when x^s is given by (II-85), with the mass defect treated exactly.

The neutron cross section involves a Fourier transform of G. It is also convenient to transform from the Cartesian coordinates, α, to the phonon mode labels, j. The transformation is effected by the matrix (IV-7). Using this transformation, (II-75) becomes

$$G_{jj'}(\tilde{k},\omega) = \delta_{jj'}G^{0}_{j}(\tilde{k},\omega)+\sum_{j_1} G^{0}_{j}(\tilde{k},\omega)\Sigma_{jj_1}(\tilde{k},\omega)G_{j_1j'}(\tilde{k},\omega) \qquad \text{(IV-12)}$$

where

$$\Sigma(\omega) = cUM^{\dagger}X'MU^{\dagger} \qquad \text{(IV-13)}$$

or

$$\Sigma\ (\omega) = cU\,X\,U^{\dagger} \qquad \text{(IV-14)}$$

The fact that the configuration average renders the Green's function, G , diagonal on $\tilde{k}$ is used above. The effective lattice Green's functions, G^{0}, are automatically diagonal on j and $\tilde{k}$.

If $\tilde{k}$ is along a symmetry direction, Σ becomes diagonal on j, as well as on $\tilde{k}$, and (IV-12) is trivial to solve. The result is

$$G_{j}(\tilde{k},\omega) = (\omega^2-\omega^2_j(\tilde{k})-\Sigma_j(\tilde{k},\omega))^{-1} \qquad \text{(IV-15)}$$

having used

$$G^{0}_{j}(\tilde{k},\omega) = (\omega^2-\omega^2_j(\tilde{k}))^{-1} ,$$

$\omega_j(\tilde{k})$ being the frequency of the phonon mode $(j,\tilde{k})$ in the effective lattice.

For only nearest neighbour force constant changes it is easy to check (II-76) against (II-86). The spectral functions have been calculated using each of these expressions. For the mass change appropriate to gold in copper, no discernable difference (i.e., less than .008 THz) for changes in A up to 80% and for B_1, B_2 up to 150% were found for $1\text{THz} \leq \omega \leq \omega_{max}$.

The differences in the frequency shift, obtained by examining the peak in $J_b(j,\tilde{k},\omega)$ and by using the self energy on the energy shell, $\Sigma_j(\tilde{q},\omega_j(\tilde{q}))$, can be quite considerable. These two procedures are compared in Figure (F-2A) using the fitted force constant changes described below. Although the differences are quite small for $T_1(\zeta,\zeta,0)$, they become significant for $T(0,0,\zeta)$.

Attempting to fit all the experimental points involves too much labour to be worthwhile. Instead, a fit to the clearly defined features of the experimental results is done. The only such feature common to the two branches examined experimentally is the maximum negative frequency shift. During preliminary investigation it was found that this shift depends, in a natural way, on the total force constant changes. The $T(0,0,\zeta)$ branch is three times as dependent on ΔB_2 as on ΔA or ΔB_1. The $T_1(\zeta,\zeta,0)$ branch, whose polarization vector is $(1/\sqrt{2}, -1/\sqrt{2}, 0)$, is most dependent on ΔB_1, being only half as dependent on the other transverse force constant change, ΔB_2, and a third as dependent on ΔA. In general this branch is twice as dependent on the force constant changes as the $T(\zeta,0,0)$ branch. In all cases, an increase in force constant decreases the above shift. The third condition chosen to determine ΔA, ΔB_1 and ΔB_2 is the minimization of the sum of the squares of the percentage changes in the force constants.

The resulting fit is shown in Figures (F-3A), (F-4A) with the fitted force constant changes being given in Table (T-3A). The circles in Figure (F-3A) are the experimental results of Svensson add Kamitakahara (1971). The open and filled circles refer to different incident energies. Kamitakahara (private communication) suggests that the closed circles may be more reliable, particularly at the higher frequencies and it is to these closed circles that the fit was made. In Figure (F-4A) the open circles are the earlier results of Svensson and Brockhouse (1967) and the filled circles, to which the theory was fitted, are the results of Svensson and Kamitakahara. Although the fit is good it does need qualifying as it depends on the use of the calculated Gruneisen parameters. Before analysing it further, Figures (F-5A), (F-6A), which give the shifts, without the volume effect included are examined. These figures show the shifts for the mass defect, the fitted force constant changes and the calculated force constant changes. For completeness the shifts appropriate to force constant changes of opposite signs to those calculated are also included.

It is observed for the $T(0,0,\zeta)$ branch that the frequency shifts obtained from the fitted and calculated local force constant changes are in reasonable agreement. The mass defect result gives too large a negative shift. For the $T_1(\zeta,\zeta,0)$ branch it is the mass defect and fitted force constant changes that give similar results while the calculated force constants give too small a frequency shift. The large magnitude of the fitted value of ΔB_1 arises from the need to maintain approximate agreement with the mass defect result for the $T_1(\zeta,\zeta,0)$ branch but at the same time decrease the shift for the $T(0,0,\zeta)$ branch.

Both the positive sign of ΔB_2 and the large magnitude of ΔB_1 are rather surprising but to some extent must be due to the use of unreliable mode Gruneisen parameters. However, near the zone boundary for the $T(0,0,\zeta)$ branch and to some extent for the $T_1(\zeta,\zeta,0)$ branch, the calculated volume effect appears to be fairly reliable. By comparing Figures (F-3A) and (F-5A), and Figures (F-4A) and (F-6A), it is seen that the shift due to the volume effect is dominant near the zone boundary. For the $T(0,0,\zeta)$ branch, there is good agreement with experiment, but the effect for the $T_1(\zeta,\zeta,0)$ branch may be overestimated. Since the calculated value of the $T(0,0,\zeta)$ elastic constant Gruneisen parameter is in good agreement with the experimental value, and the calculated Gruneisen parameter is a simple function of frequency (See Figure (F-1A)), the inclination is to accept the calculated shift, due to the volume change, for the whole of this branch.

The very poor calculated value for the $T_1(\zeta,\zeta,0)$ elastic constant Gruneisen parameter, the large magnitude value of ΔB_1, and the conclusions of the above two paragraphs, indicate that the lack of reliability for the two branches under consideration is confined to the $T_1(\zeta,\zeta,0)$ branch in frequency region 0 to 3 THz. The evidence indicates that the actual shift, due to the volume effect, is greater than that calculated. However, any reasonable guess for the mode Gruneisen parameter is not sufficient to bring the frequency shift, obtained from the calculated force constant changes, into even fair agreement with experiment, although the correction is in the right direction. Such a guess leads to a fitted value of ΔB_1 of about -1,100 dynes cm^{-1},which is becoming reasonable, but ΔB_2 remains positive at around 300 dynes cm^{-1} with ΔA essentially unchanged. These values of ΔB_1 and ΔB_2 still require an appreciable non-central contribution to the copper/gold interatomic potential.

However, a comparison between the experimental and calculated widths (FWHM), Γ, shown in Figures (F-7A) and (F-8A) does support the fitted force constant changes. Although there is little to choose between the widths of the $T(0,0,\zeta)$ phonon modes obtained from the fitted and calculated values of the force constant changes (Figure (F-7A)) there is a considerable difference for the $T_1(\zeta,\zeta,0)$ branch (Figure (F-8A)). In this comparison, the effects of the volume change enter only in a very minor way, corresponding, approximately, to a scaling of P of about 2%. Hence, the evidence is quite strong. A readjustment of ΔB_1 of the kind mentioned in the previous paragraph should not seriously affect the agreement, according to the results of some preliminary calculations.

Also, a comparison was made of the frequency shifts calculated using the derived force constant changes obtained with and without relaxation (See Table (T-3A)). This comparison showed that there was little to be gained in obtaining agreement with experiment by allowing for such relaxation. The difference is not worth illustrating as it amounts to less than 0.004 THz at the most. In view of the lack of reliability in the calculations of the frequency shift due to the volume change it is not worthwhile attempting to fit six force constant changes. However, the results in Table (T-3A) indicate that if such a procedure were carried out it should lead to somewhat lower values of ΔA, ΔB_1 and ΔB_2, in particular making the magnitude of ΔB_1 more reasonable.

Before completely dismissing the effects of relaxation, it should be noted that some force constant changes that could be important have been omitted. Focussing on a nearest neighbour atom of a gold impurity, it is seen that changes in only two of its nearest neighbour force constants have been taken into account. Relaxation would change all of them to some degree. Simple geometric considerations suggest that only the longitudinal changes (ΔA) should be important since they are of the same magnitude as $\Delta A'$ (Table (T-1A)). Further, it would seem that they should have effects similar to those due to the nearest neighbour (of the gold impurity) transverse force constant changes. The omission of the possibility of these effects could be a reason for the large magnitude of the fitted

ΔB_1. It is possible to allow for these effects, if the calculated values of the appropriate force constant changes are accepted, by using the perturbative approach given in Part 2, Section B of Chapter II, but the labour required is somewhat more than that required to include just $\Delta A'$, $\Delta B_1'$ and $\Delta B_2'$. The performance of such a calculation is intended in the near future.

There has been no systematic investigation of any of the other phonon branches in the alloy containing 3% gold. However, Kamitakahara (1971) has investigated a few modes in each branch and finds no frequency shift less than that given by a line drawn between the origin and a shift of -0.15 THz at 7 THz. Unfortunately, the zone boundary Gruneisen parameters give shifts of nearly -0.3 THz for the longitudinal modes. The calculated zone boundary shift, neglecting the volume effect, is negative with a lower bound of -0.04 THz being given by the mass defect case, and about +0.06 THz with the calculated force constants. Obtaining any kind of agreement with the results of Kamitakahara requires values for the longitudinal zone boundary Gruneisen parameters that are half those that have been calculated here. That the situation would be worse for the longitudinal modes as compared to the transverse modes, was anticipated in Part 1 of this section. However, the amount of disagreement is rather disappointing. It may also be a reflection on the use of the mode Gruneisen parameters found from the Morse potential, to calculate the effects of the volume change.

In conclusion it can be stated that the experimental results can be understood in the light of the low concentration defect theory plus a correction due to the change in volume on adding impurities. The resonance, whose possibility started the experimental investigation, in fact does occur although modified by local force constant changes and masked by the volume effect. The lack of a detailed knowledge of the interatomic forces in an alloy, and thus a lack of a systematic method of including the volume effect, renders quantitative understanding difficult.

TABLE (T-1A)

Morse Potential Data

	E_v^f eV	a_o Å	B dynes $cm^{-2} \times 10^{12}$	ε eV	r_o Å	α $Å^{-1}$	D kcal $mole^{-1}$
Cu	1.17(±0.11) (a)	3.614(7) (b)	1.371	0.1700	2.5924	2.3216	47.0 (d)
Au	0.94(±0.09) (a)	4.0781	1.728	0.1563	2.8855	2.8395	52.5 (d)
CuAu	-	3.7426	1.523 (c)	0.217 (c) 0.1818 (d)	2.597 (c) 2.7389 (IV-1)	2.5546 2.5546	55.4 (d)

(a) Simmons and Balluffi (1963) [Other experimental results indicate variations in E_v^f of up to ±.5]

(b) Svensson and Kamitakahara (1971)

(c) Cu_3Au data; Flinn, McManus and Rayne (1960)

(d) Weast and Selby (1966)

TABLE (T-2A)

Copper Force Constants

dynes cm^{-1}

	Experiment	Morse Potential	Effective Lattice[(a)]
1XX	13,160±192	18,548	12,064
1ZZ	-1,489±330	-474	-880
1XY	14,880±337	19,022	13,520
2XX	453±295	296	434
2YY	-345±170	-2,225	-334
3XX	573±228	255	544
3YY	321±117	34	306
3YZ	252±154	74	242
3XY	342± 77	147	326
4XX	99± 89	39	94
4ZZ	-190±154	-7	-179
4XY	424±301	46	422
5XX	-121±195	-19	-113
5YY	15± 86	-2	14
5ZZ	32±114	2	30
5XY	-51± 97	-7	-48

(a) appropriate to a lattice constant of 3.634(1) Å (Svensson and Kamitakahara (1971))

TABLE (T-3A)

	Effective Lattice Force Constants dynes cm^{-1}		Changes in Local Force Constants dynes cm^{-1}		
			Calculated		Fitted
			no relaxation	with relaxation	
A	25,584	ΔA	9,808	9,293	6,780
B_1	-1,456	ΔB_1	-552	-499	-2,080
B_2	-880	ΔB_2	-310	-155	550
		ΔA'	-	731	-
		$\Delta B_1'$	-	-77	-
		$\Delta B_2'$	-	-155	-

FIGURE (F-1A) The mode Gruneisen parameter $\gamma_j(\tilde{k})$ for the longitudinal modes (———), transverse modes (except for $T_2(\zeta,\zeta,0)$) (-----) and the transverse mode $T_2(\zeta,\zeta,0)$ (—•—•—) are shown for the $(0,0,\zeta)$, $(\zeta,\zeta,0)$ and (ζ,ζ,ζ) symmetry directions. The arrows indicate the appropriate $\tilde{q}=0$ experimental results.

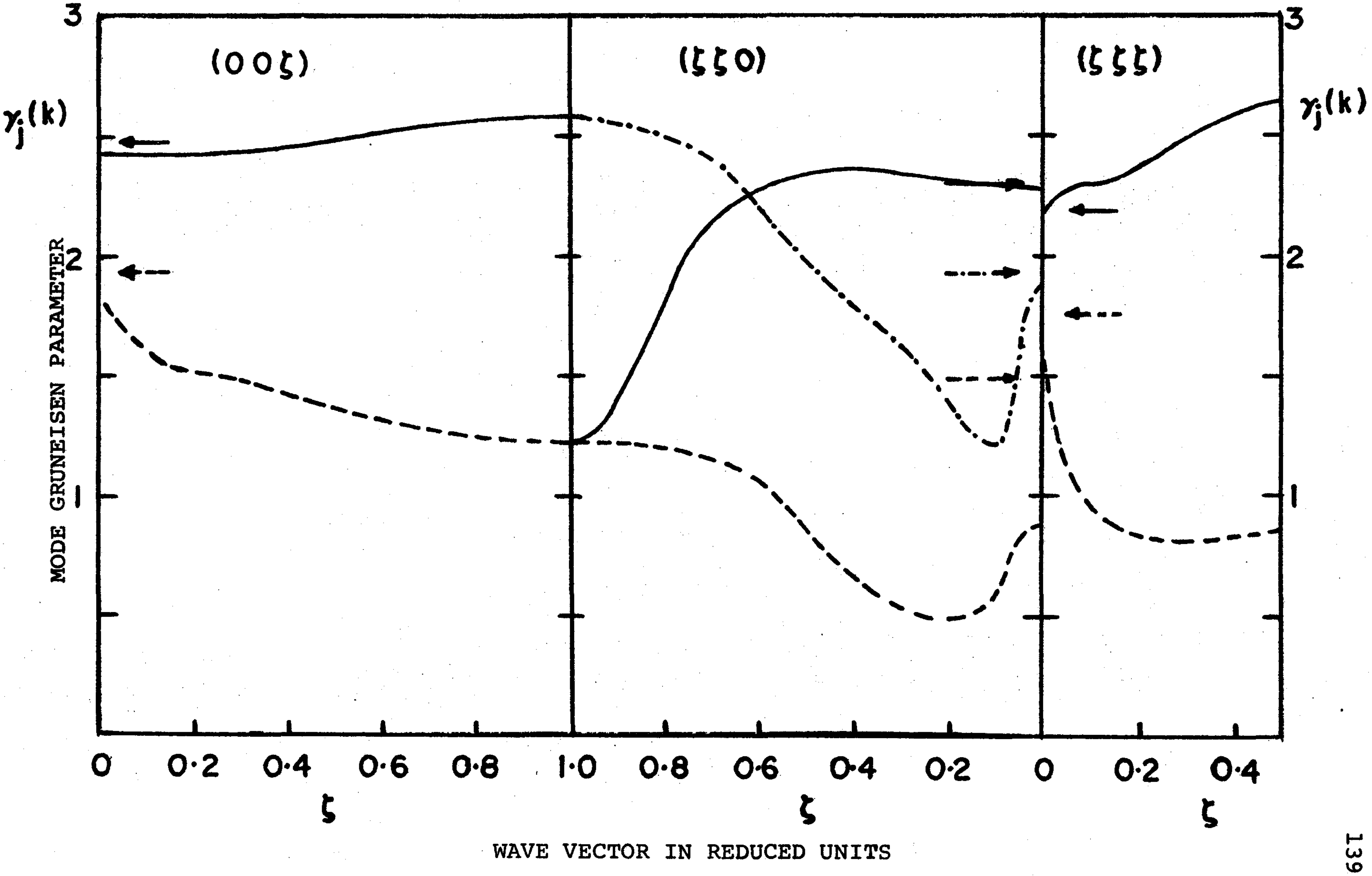

3
(00ζ)
(ζζ0)
(ζζζ)
3
$\gamma_j(k)$
$\gamma_j(k)$
2
2
1
1
MODE GRUNEISEN PARAMETER
0
0·2
0·4
0·6
0·8
1·0
0·8
0·6
0·4
0·2
0
0·2
0·4
ζ
ζ
ζ
WAVE VECTOR IN REDUCED UNITS

FIGURE (F-1A)

FIGURE (F-2A) The frequency shifts for (a) $T(0,0,\zeta)$ (b) $T_1(\zeta,\zeta,0)$ using the fitted force constant changes of Table (T-3A) (no volume effect), where (———) was obtained from the scattering cross section while + was obtained from the self energy, $\Sigma_{ij}(\tilde{k},\omega_j(\tilde{k}))/2\omega_j(\tilde{k})$.

FIGURE (F-2A)

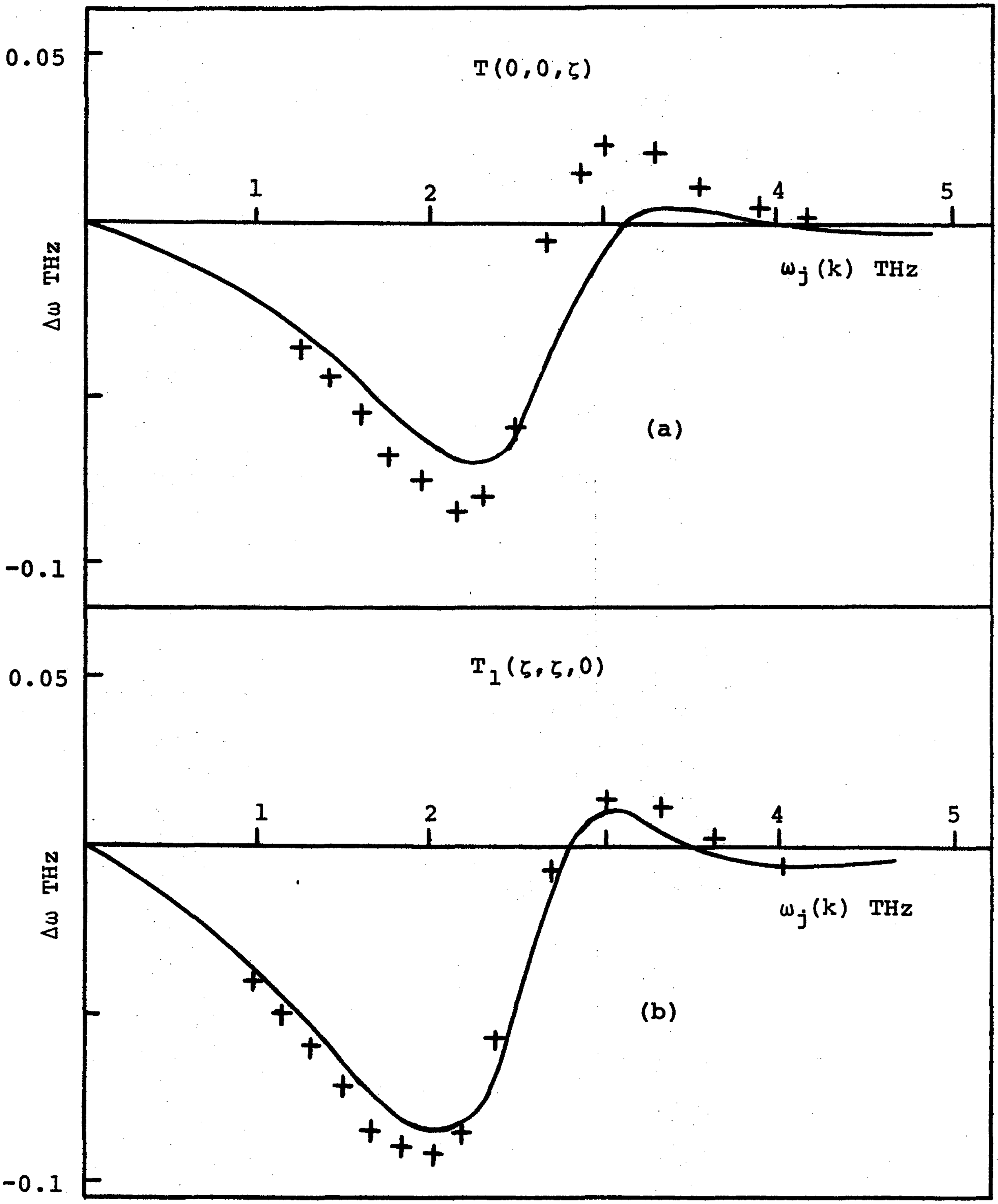

T(0,0,ζ)
0.05
-0.1
1
2
4
5
$\Delta\omega$ THz
$\omega_j(k)$ THz
(a)
$T_1(\zeta,\zeta,0)$
0.05
-0.1
1
2
4
5
$\Delta\omega$ THz
$\omega_j(k)$ THz
(b)

FIGURE (F-3A) The fitted frequency shift for the $T(0,0,\zeta)$ branch. The theoretical curve (———) is fitted to the filled circles. The open and closed circles are experimental values. Kamitakahara (1971) indicated the closed circles to be more reliable past ∿2.5 THz.

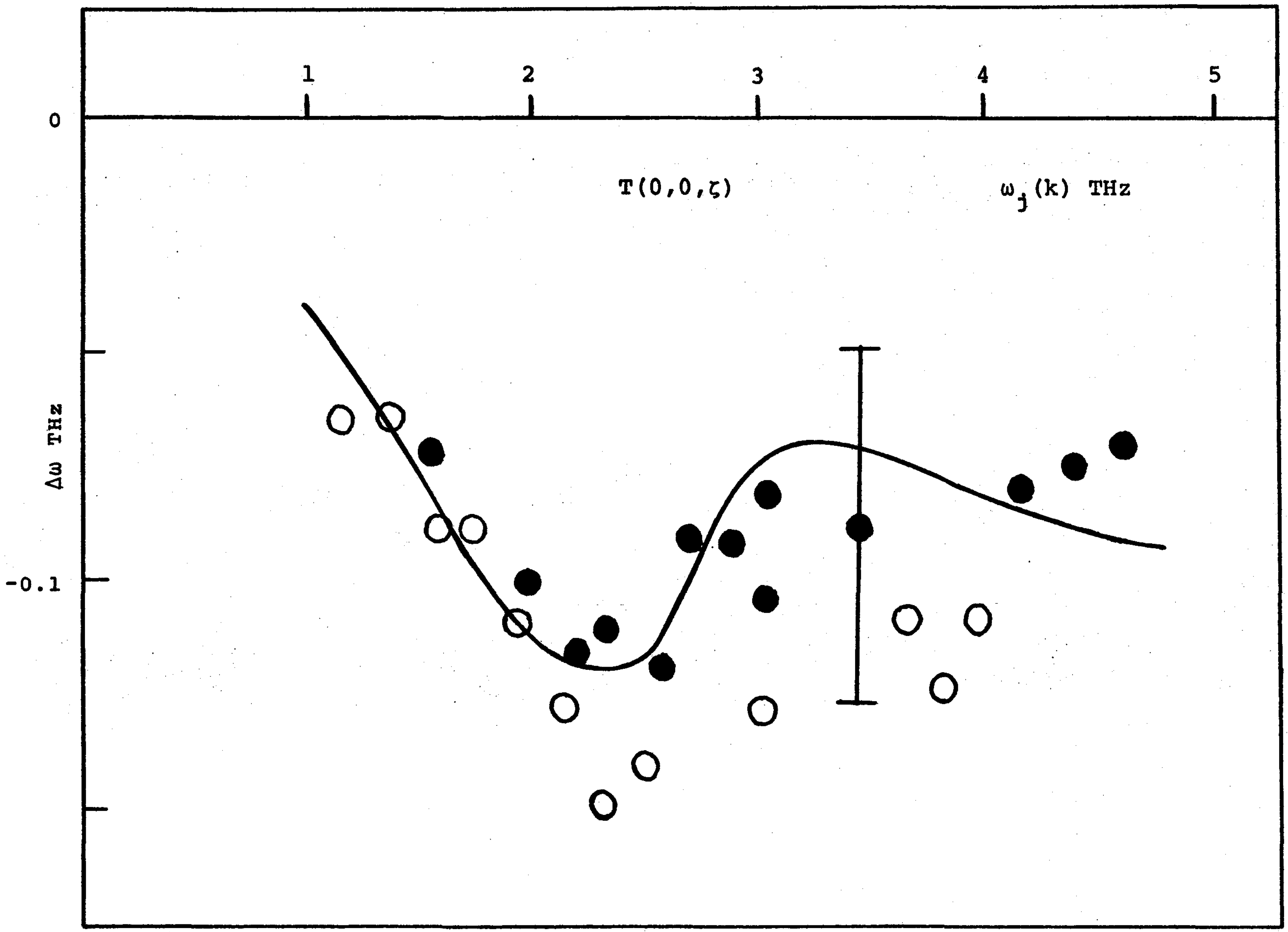


FIGURE (F-3A)

FIGURE (F-4A) The fitted (to closed circles) frequency shift for $T_1(\zeta,\zeta,0)$ phonon branch. The open and closed circles indicate the experimental values.

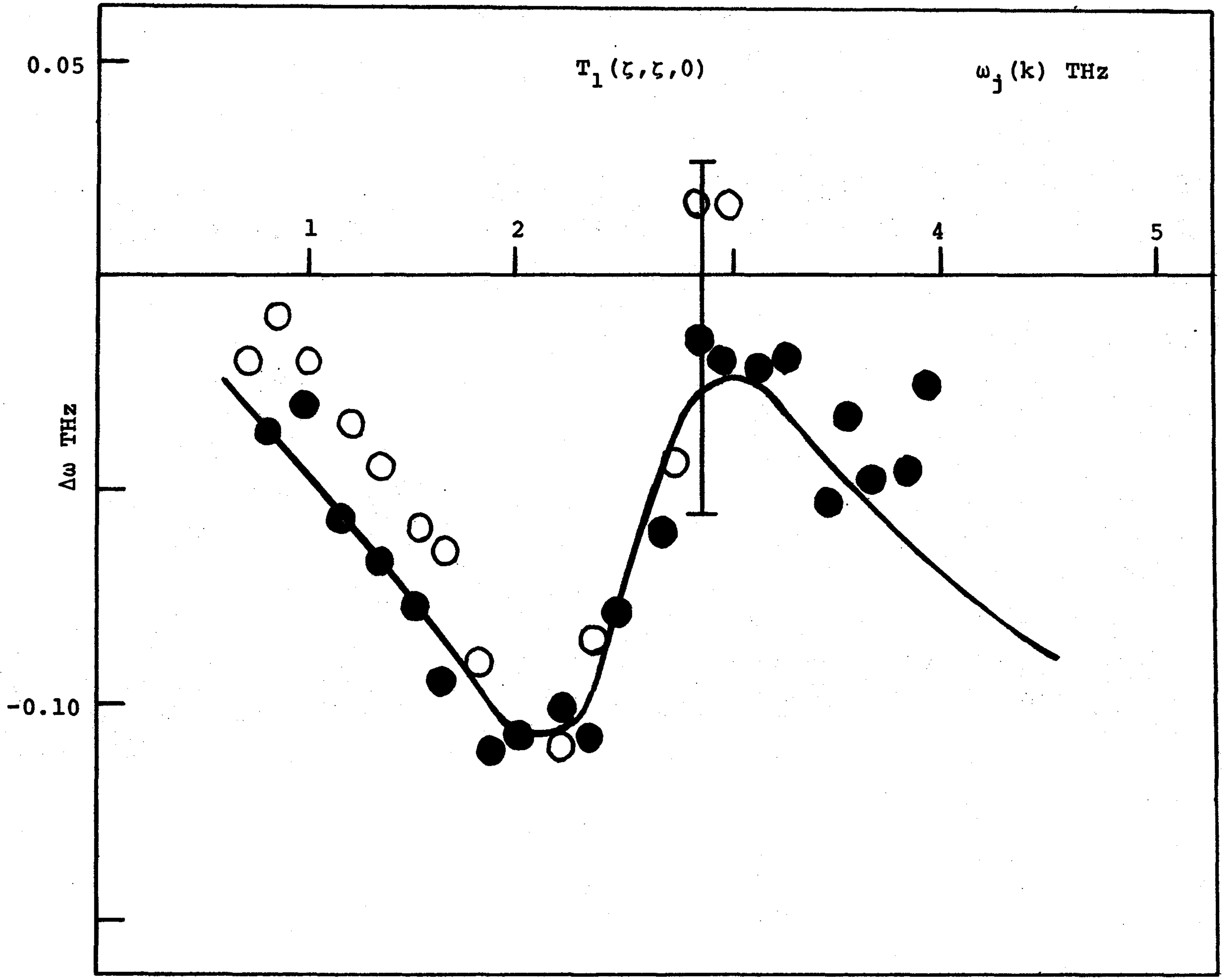


FIGURE (F-4A)

FIGURE (F-5A) Comparison of the frequency shifts with no volume effect for the T(0,0,ζ) branch; (———) mass defect, (-----) fitted force constant changes, (—•—•—) calculated force constant changes, (•••••) force constant changes of opposite sign to the calculated ones.

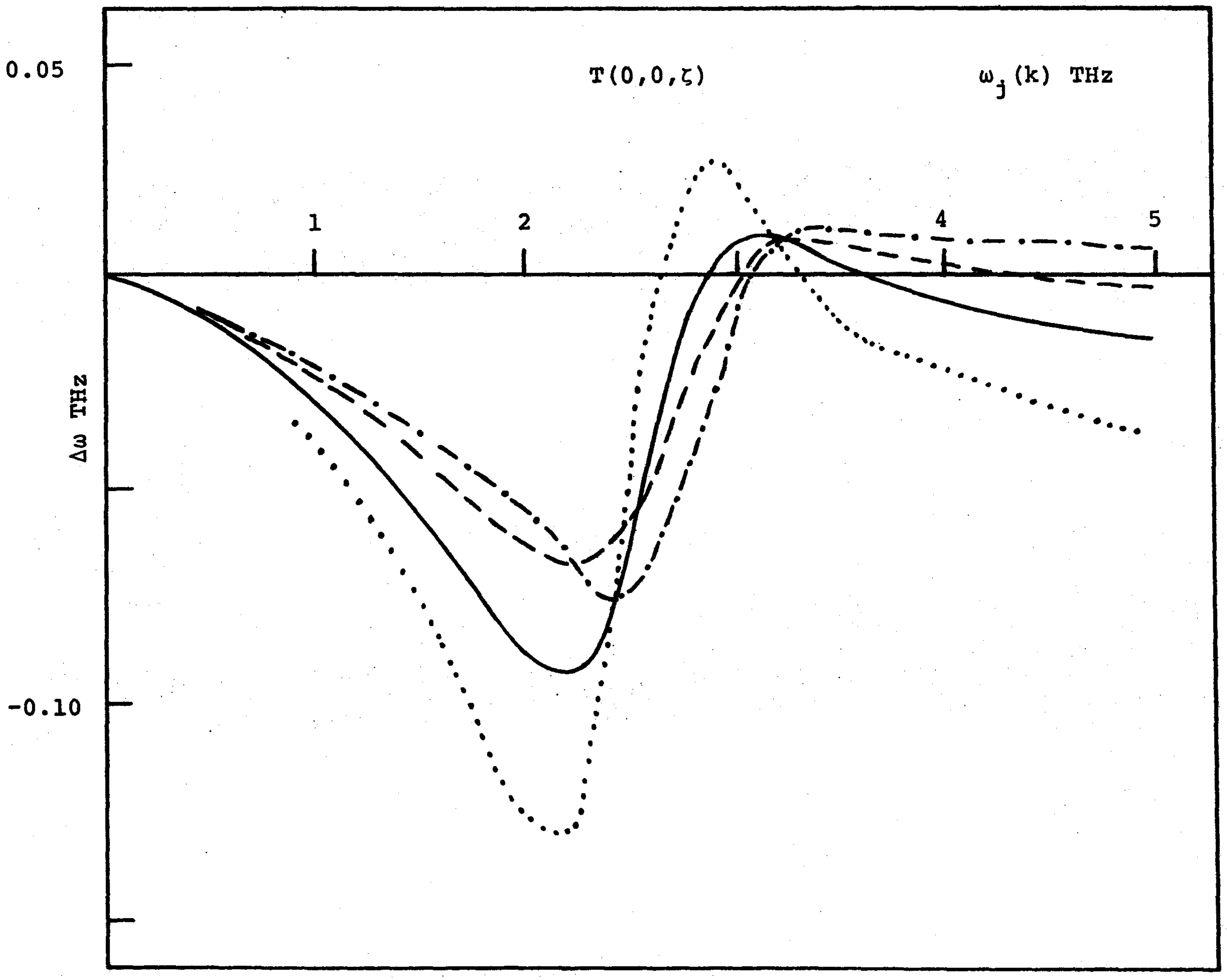


FIGURE (F-5A)

FIGURE (F-6A) Comparison of the frequency shifts with no volume effect for the $T_1(\zeta,\zeta,0)$ branch; (———) mass defect, (-----) fitted force constant changes, (—•—•—) calculated force constant changes, (•••••) force constant changes of the opposite sign to those calculated.

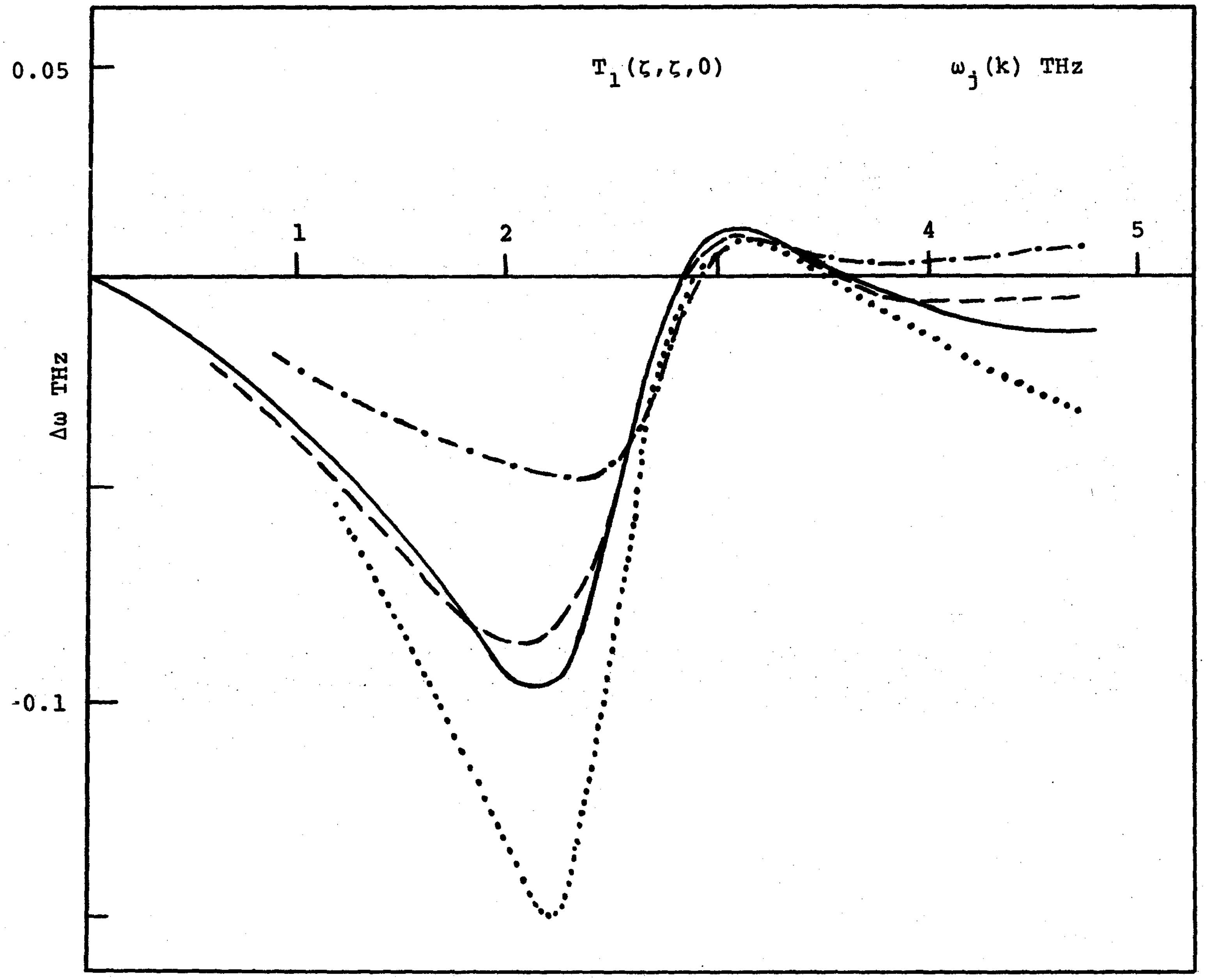


FIGURE (F-6A)

FIGURE (F-7A) Comparison of the experimental and theoretical neutron cross section widths of the T(0,0,ζ) branch; (———) mass defect, (-----) fitted force constant changes, (—•—•—) the calculated force constant changes, and the closed circles are the experimental results.

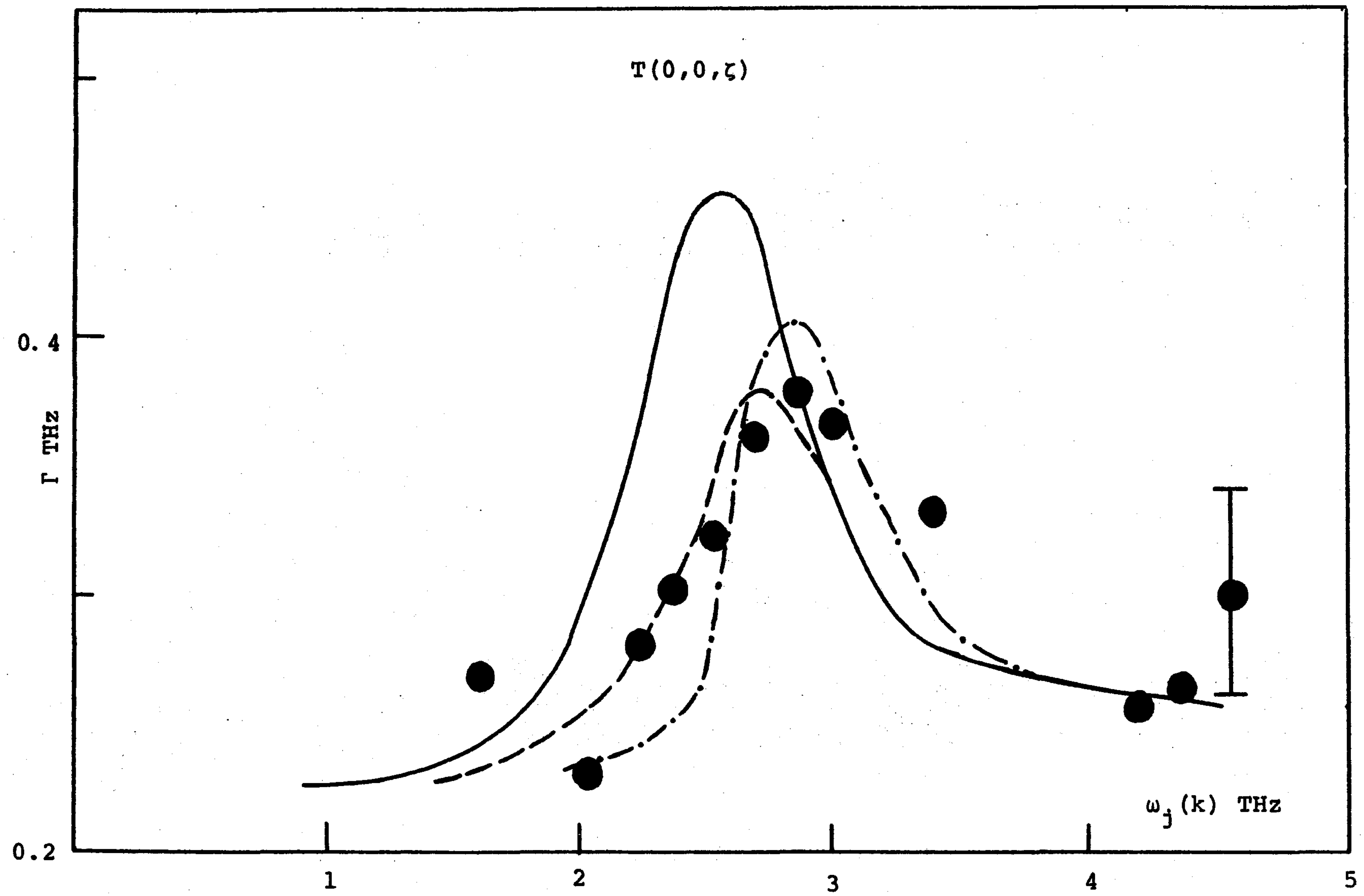


FIGURE (F-7A)

FIGURE (F-8A) Comparison of the experimental and theoretical neutron cross section widths for the $T_1(\zeta,\zeta,0)$ branch; (———) mass defect, (-----) fitted force constant changes, (—•—•—) the calculated force constant changes, and the closed circles indicate the experimental results.

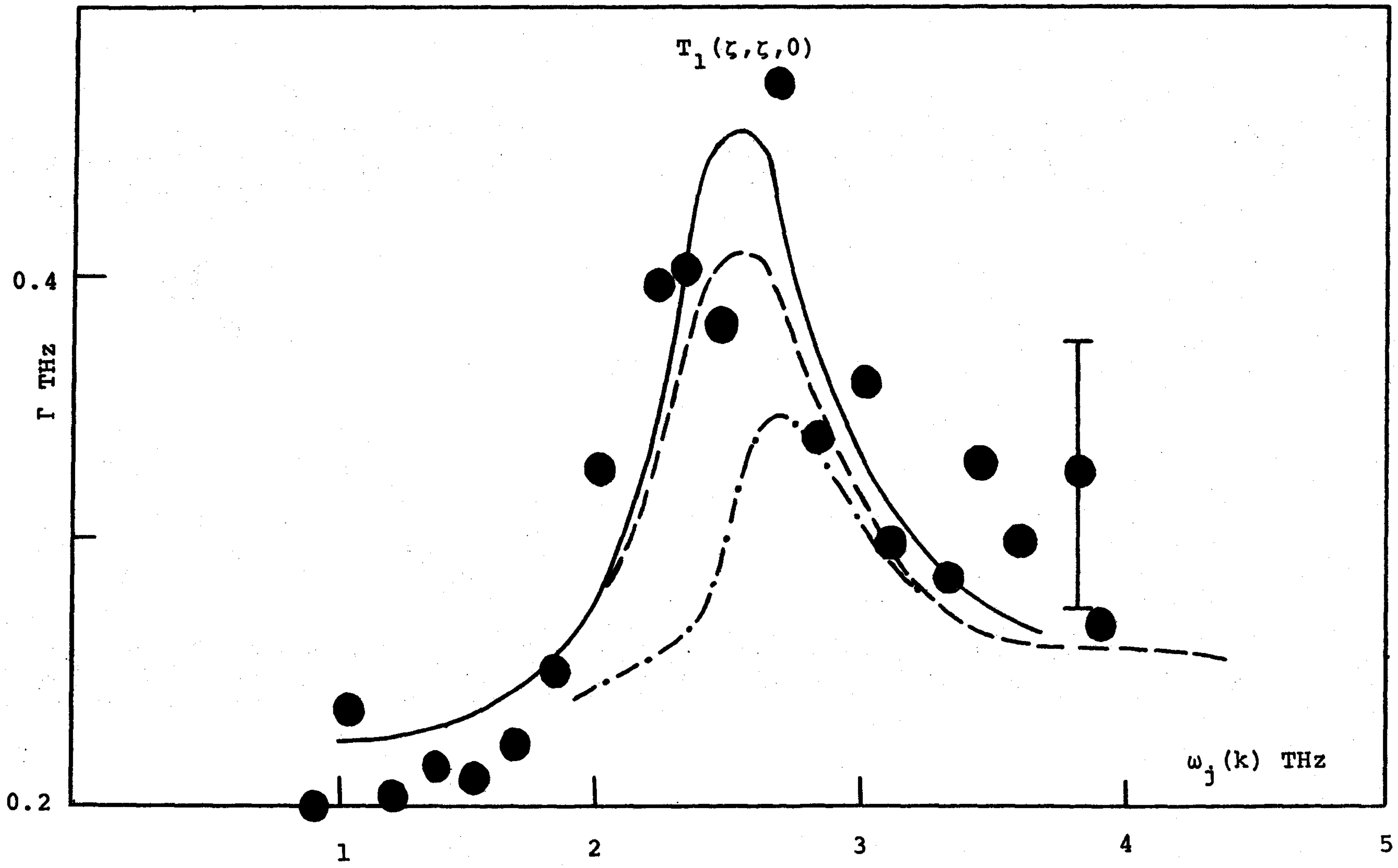


FIGURE (F-8A)

FIGURE (F-9A) Comparison of pair calculation for mass defects (-----) with the low concentration theory result for mass defects (———) frequency shifts for the $T(0,0,\zeta)$ branch at (a) 9.3% and (b) 3% gold in copper.

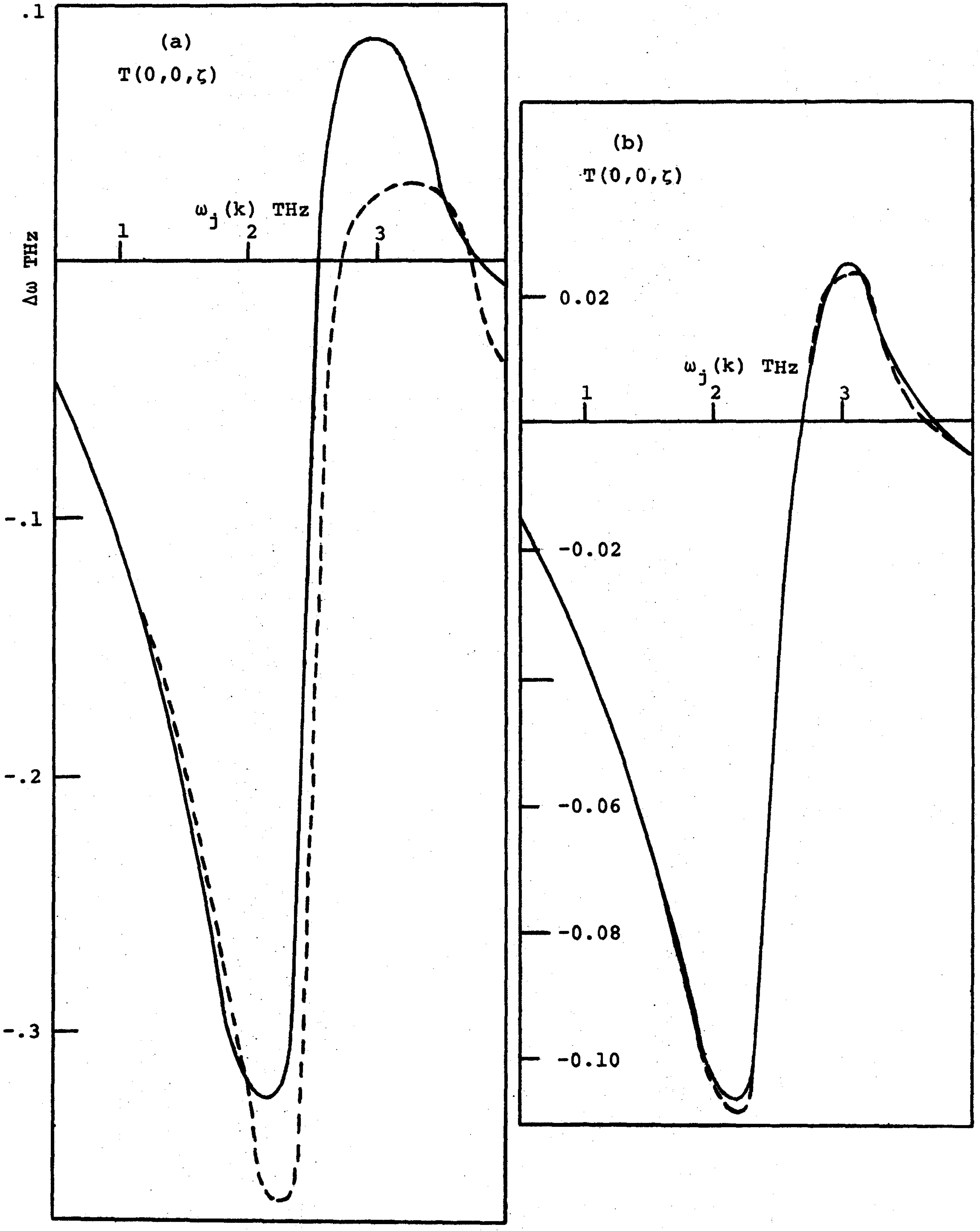

.1
-.1
-.2
-.3
Δω THz
(a)
T(0,0,ζ)
$\omega_j(k)$ THz
1
2
3
(b)
T(0,0,ζ)
$\omega_j(k)$ THz
1
2
3
0.02
-0.02
-0.06
-0.08
-0.10

FIGURE (F-9A)

FIGURE (F-10A) The change of frequency in (a) $T_1(\zeta,\zeta,0)$ and (b) $T(0,0,\zeta)$ branches resulting from the expansion of the perfect copper lattice to the effective lattice for 3% gold in copper.

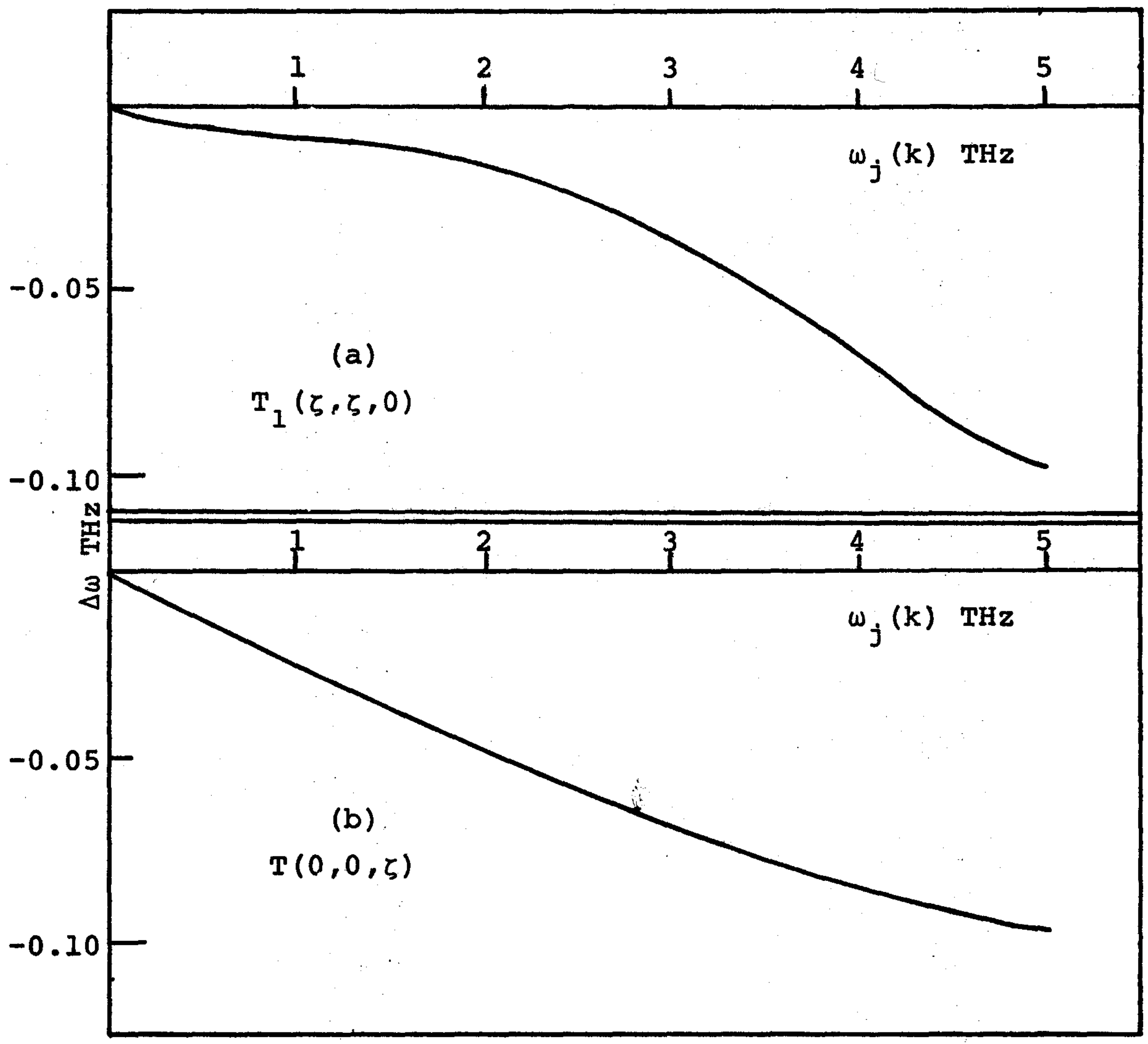

1
2
3
4
5
$\omega_j(k)$ THz
-0.05
(a)
$T_1(\zeta,\zeta,0)$
-0.10
$\Delta\omega$ THz
1
2
3
4
5
$\omega_j(k)$ THz
-0.05
(b)
$T(0,0,\zeta)$
-0.10

FIGURE (F-10A)

> "the decision to employ a particular piece of
> apparatus and to use it in a particular way
> carries an assumption that only certain sorts
> of circumstances will arise"
>
> --T.S. Kuhn

SECTION B

SINGULAR POINTS IN Na^+ AND Sm^{++} INDUCED INFRARED SPECTRA OF KBr

In this section the low concentration theory is applied to the experimental work of Timusk and Ward (1969,1970). These authors present a set of high resolution results on the impurity induced absorption in several KBr crystals each containing different substitutional impurities. For each different impurity type in KBr, a continuous absorption spectrum, from 40 to 90 cm^{-1}, having several very sharp discontinuities was obtained. The authors identified these slope discontinuous points with van Hove singularities of the host crystal. For two of the impurities used (i.e., Na^+ and Sm^{++}) the authors obtained absorption spectra for several impurity concentrations. Using these absorption spectra, they were able to follow the shift in frequency of what they call singularities A and B (Timusk and Ward (1969,1970)) and singularity C (Timusk and Ward (1970)) as a function of concentration. It is these results, concerning the singularity movement as a function of impurity concentration in the absorption spectrum of Na^+ in KBr or Sm^{++} in KBr, that are considered here.

Timusk and Ward (1970) found, from an examination of the shell-model phonon dispersion surfaces, that singularity A could be associated with a saddle point on the (1,1,0) axis at (.5,.5,0) of the second highest acoustic branch. In a similar fashion (Timusk and Ward (1969,70)) singularity B was associated with the maximum at (.65,.35,.35) of the second highest acoustic branch, while singularity C was associated with the saddle point (.55,.35,0) in the highest acoustic branch.

The perfect crystal Green's functions are required in order to use the low concentration defect theory to obtain information about the frequency shift of these singularities. These functions were found by Timusk (1970) using a shell-model calculation and are used here as given input data. A shortcoming of the use of these functions arises from the fact that they have singularity A at 70.55 cm^{-1} instead of of 74.73 cm^{-1}, singularity B at 71.22 cm^{-1} instead of 75.23 cm^{-1}, and singularity C at 82.6 cm^{-1} instead of 85.3 cm^{-1} (Timusk and Ward (1970)). Since only the frequency shifts of these singularities are of interest here, the theoretical results have been raised appropriately so that they may be compared with experiment.

1. Single Phonon Approach

The lattice vibration frequency spectra of solids contains sharp slope discontinuities at points in the zone where the modulus of the gradient of frequency, as a function of wave vector $\tilde{k}$, vanishes. If the spectral function for a defect lattice is found by some perturbative expansion in terms of the perfect lattice, then from the discussion of Appendix IV, it is obvious that the imaginary part of this spectral function reflects only the unshifted singularities of the perfect crystal density of states. Thus, using the low concentration theory, the defect induced optical absorption spectrum, which depends directly on Im <G> (See (III-73)) will not show any shift of the singular points as a function of defect concentration. At most, such an approach can result in a metamorphosis of the singularities (See Okazaki et al. (1967)). Realizing this, another approach must be used for attempting this problem.

If the effective lattice approach is used, as in the previous section for the Cu/Au system, then the change in frequency of the singular points in the absorption spectrum can be found by using the appropriate mode Gruneisen parameters. Table (T-1B) gives these parameters for singularities A, B and C, and also compares the experimental frequency shift of A, B and C to that obtained by contraction of the lattice due to .1% Na^+ in KBr. Here, the change in nearest neighbour separation (i.e., volume change) is estimated to be

$$\Delta a = c(a_{NaBr} - a_{KBr})$$

where $a_{NaBr} = 2.989$ Å and $a_{KBr} = 3.298$ Å (Kittel (1968)).

Obviously this also provides an inadequate description.

For Na^+ in KBr it is seen from (III-73$_b$) that the absorption constant is proportional to Im $G_{To}(\tilde{k}=0;\omega)$. Thus, if the frequencies of the singularities are such that

$$|\mathrm{Im}\ \Sigma| \quad \text{and} \quad |\mathrm{Re}\ \Sigma| << |\omega^2 - \omega^2_{To}(0)|$$

then by equation (II-75)

$$\mathrm{Im}\langle G_{To}(\tilde{k}=0;\omega)\rangle \sim \frac{\mathrm{Im}\ \Sigma_{To}(\tilde{k}=0,\omega)}{(\omega^2-\omega^2_{To}(0))^2}$$

Furthermore, it is observed from (II-76) that, apart from a resonance denominator, Im $\Sigma_{To}(\tilde{k}=0,\omega)$ (in the low concentration defect theory), is directly proportional to the weighted densities of states. Therefore the observed singularities can be associated with specific spectral functions (phonons) in the region of the zone which gives rise to these various van Hove singularities. Realizing this, the low concentration theory is used to follow the appropriate features of these spectral functions as a function of defect concentration, and their movement is associated with the movement of the singular points of the absorption spectrum.

Because Sm is divalent and K is monovalent the case of Sm^{++} in KBr is not as simple as that of Na^+. Elliott and Taylor (1967) have shown (for the mass impurity), that for an impurity having a charge different to that of the host atom it replaces, the absorption constant is related to a linear combination of Im<G> and the imaginary part of the perfect lattice Green's function. Assuming this type of relation still holds for Sm^{++} in KBr, even with force constant changes, the absorption constant (apart from resonance type denominators) is proportional to weighted densities of states. Thus, for Sm^{++}, as in the case for Na^{+} in KBr, the appropriate spectral functions are followed with concentration. Furthermore, for Sm^{++} the effective lattice theory is not used, since there is no expansion data available, and the system is of a very complex nature (i.e., (1) unbalanced charge, (2) vacancy).

Briefly, the movement of singularities A, B and C of the Na^{+} or Sm^{++} induced absorption spectra of KBr is found by following the appropriate features of

$$\mathrm{Im}\,\langle G_{TA_2}(.5,.5,0)\rangle$$

$$\mathrm{Im}\,\langle G_{TA_2}(.65,.35,.35)\rangle$$

and

$$\mathrm{Im}\,\langle G_{LA}(.55,.35,0)\rangle$$

respectively, as a function of defect concentration. Only these three $\tilde{k}$ points are followed since the behaviour of points neighbouring these $\tilde{k}$'s is similar. Because the concentration of defects is small ($\sim$.1%), the low concentration theory is used.

Clearly, for a Na^{+} impurity in KBr the perturbation V^{s} due to the impurity at a site s does not lower the point symmetry of the problem from cubic. Furthermore, Fong and Wong (1967) have studied the system of Sm^{++} in KBr and have concluded that the K^+ vacancy (required to compensate for the double charge of this rare-earth impurity ion) was sufficiently far from the rare-earth ion that the immediate environment of the Sm^{++} was still cubic. Thus, for V^s having cubic symmetry, the lattice dynamics problem in the low concentration theory can be treated most easily by transforming the real $(\tilde{\ell},\alpha)$ space to a space spanned by motions corresponding to the representations of the cubic group (Buchanan (1969)). Using the same procedure as outlined in the previous section, $\mathrm{Im}\langle G_j(k)\rangle$ may be found. The full details of the block diagonalization and the explicite form of the matrices used is contained in Buchanan (1969) and is not repeated here.

Since $\tilde{k}$, associated with singularity A, is in a symmetry direction, Σ is diagonal on j as well as on k. As for singularities B and C Buchanan (1968) has found that the off diagonal elements of Σ (i.e., $\Sigma_{jj'}, j\neq j'$) are negligible. Thus, in deriving any spectral function of wave vector $\tilde{k}$, associated with singularities A, B or C (or any point in k-space immediately neighbouring these three points), the self energy has been assumed diagonal on j, and therefore, by (II-75)

$$\mathrm{Im}\langle G_j(k)\rangle = \frac{\mathrm{Im}\ \Sigma_j(\tilde{k})}{\left(\left(\omega^2-\omega_j^2(k)-\mathrm{Re}\ \Sigma_j(\tilde{k})\right)^2+\left(\mathrm{Im}\ \Sigma_j(\tilde{k})\right)^2\right)} \qquad \text{(IV-16)}$$

Before obtaining any explicit results, the defect space for either of these impurities in KBr must be defined. It is assumed that v^s, the matrix of the mass and force constant change due to the presence of one defect at s, can be described by a small number of changes localized about the impurity. Apart from the mass change, $m\varepsilon$, at the origin, the force constant model of Gethins, Timusk and Woll (1967) was used to describe the defect space. In this model, only the force constants connecting the impurity ion to its first nearest neighbours, f, and the force constants connecting these first nearest neighbours to their first nearest neighbours, g, (which are also the fourth nearest neighbours of the impurity ion), are changed. Furthermore, no change of the transverse force constants is allowed for in this model, since its effect is expected to be small, the transverse force constant being only about 10% of the longitudinal one. Buchanan and Woll (1969) applied this model to the study of the vibronic side bands of Sm^{++} in KBr and found

$$\Delta f = 14500 \text{ dynes cm}^{-1}$$
$$\Delta g = -1500 \text{ dynes cm}^{-1}$$

Their results are used in the present calculation for Sm^{++} in KBr since the increased Coulomb field due to the double charge on the Sm ion rules out any simple interatomic potential calculation. For Na^+ in KBr the Δf and Δg used are calculated from the appropriate interatomic potentials (See Part 4, Section C, Chapter III) by balancing the forces on Br in the one dimensional system

$$\text{Na} — \text{Br} — \text{K}$$

where both Na and K are held fixed. The result of this rather simple calculation gives

$$\Delta f = -6200 \text{ dynes cm}^{-1}$$

and $$\Delta g = -6000 \text{ dynes cm}^{-1}$$

2. Convolution Model

Although the spectral function approach may be a reasonable approximation, a proper self consistent treatment for a diatomic lattice would be better. Since such a self consistent procedure for a diatomic crystal with more than just mass impurities has not yet been properly formulated, a simulation of self consistency, using a convolution model, is attempted as a check.

If it is assumed that most of the information about the singularity position in the absorption spectrum comes from the weighted densities of states, and if the $\delta(\omega_j(\tilde{k})-\omega)$ of these functions are changed to $\mathrm{Im}\langle G_j(\tilde{k})\rangle$, as derived by the low concentration defect theory, then the singularities of $\alpha(\omega)$, determined in this way, will shift in frequency as a function of defect concentration. Basically, this is the idea of the convolution model, except that $\mathrm{Im}\langle G_j(\tilde{k})\rangle$ is taken to be either a Gaussian or a Lorentzian, whose width and shift are obtained from the low concentration theory results.

In this model the absorption spectrum is described by a background function and an envelope function

$$cD_o(\omega_j(\tilde{k}))$$

which depends directly on the phonons. Thus, if $\mathrm{Im}\langle G_j(\tilde{k})\rangle$ is approximated by a Gaussian

$$\alpha(\omega) \sim cB + c\int d\omega_j(\tilde{k})D_o(\omega_j(\tilde{k}))\frac{\exp\left[-\frac{[\omega-\omega_j(\tilde{k})-c(s_o+s_1\omega_j(\tilde{k}))]^2}{c^2[w_o+w_1\omega_j(\tilde{k})]^2\ln 2}\right]}{\sqrt{\pi\ln 2}\; c[w_o+w_1\omega_j(\tilde{k})]} \tag{IV-17}$$

whereas if it is approximated by a Lorentzian

$$\alpha(\omega) \sim cB + c\int d\omega_j(\tilde{k})\frac{D_o(\omega_j(\tilde{k}))}{\pi}\;\frac{[w_o+w_1\omega_j(\tilde{k})]}{[\omega-\omega_j(\tilde{k})-c(s_o+s_1\omega_j(\tilde{k}))]^2+c^2[w_o+w_1\omega_j(\tilde{k})]^2} \tag{IV-18}$$

where

$$\text{shift} = c(s_o+s_1\omega_j(\tilde{k}))$$

and

$$\text{FWHM} = 2c(w_o+w_1\omega_j(\tilde{k}))$$

are found from the low concentration theory results. The parameters w_o, w_1, s_o and s_1 are listed in Table (T-2B) for the three regions of the spectrum $D_o(\omega_j(\tilde{k}))$ (See Figure (F-1B)). B and $D_o(\omega_j(\tilde{k}))$ used here are given in Figure (F-1B). The motivation for (F-1B) arises from the absorption spectra of Timusk and Ward (1970) and from the density of states for KBr.

3. Results

Since singularities A and C are due to inband modes of vibration, their movement, in the single phonon approach, was obtained by following the center of the half maximum line of $\mathrm{Im}\langle G_j(\tilde{k};\omega)\rangle$. Singularity B, on the other hand is different from singularities A and C, since it is due to a maximum frequency point beyond which there are no more modes of vibration associated with the second highest accoustical branch. Therefore, the movement of singularity B must not only be associated with the shift of the spectral function but also with its width. The movement of singularity B is thus associated with some point on the high frequency tail of $\mathrm{Im}\langle G_j(\tilde{k};\omega)\rangle$. This point is taken, somewhat arbitrarily, to be that point on the high frequency side of $\mathrm{Im}\langle G_j(\tilde{k};\omega)\rangle$ which is 1/25 of $\max(\mathrm{Im}\langle G_j(\tilde{k};\omega)\rangle)$. A qualitative justification of this can be found from the convolution model, if $\mathrm{Im}\langle G_j(\tilde{k},\omega)\rangle$ is not too assymmetric. Using equations (A-37) and(A-38) and the results expressed by (F-8B) and (F-7B) it is found that the point to be followed on the high frequency tail of a Gaussian or a Lorenzian is $\sim$1/50 and 1/70 of their maximum respectively. In a single phonon approach, the 1/25 point is used to follow singularity B; but if instead, the 1/n point is used for $\begin{matrix} n<25 \\ n>25 \end{matrix}$ then it is found that the movement of this point is $\begin{matrix} \text{slower} \\ \text{faster} \end{matrix}$ than that for n=25.

The behaviour of the spectral function $\mathrm{Im}\langle G_{TA_2}(.65,.35,.35)\rangle$ for two concentrations of either Sm^{++} or Na^{+} in KBr is seen in figures (F-2B) and (F-3B) respectively. The vertical line on the high frequency tail indicates the frequency of

$$1/25\ \max(\mathrm{Im}\langle G_j(\tilde{k};\omega)\rangle)$$

It is observed for Sm^{++}in KBr (F-2B) that although the spectral functions are assymmetric there is no resonance, whereas for Na^{+} in KBr (F-3B) a distinct resonance appears. This resonance is almost independent of Δf but not of Δg. A value of Δg below $\sim$-7500 or above $\sim$-4500 dynes cm^{-1} removes the resonance from this region of singularity A and B.

Figure (F-4B) compares the movement of the center point of the FWHM and the high frequency tail of $\mathrm{Im}\langle G_{TA_2}(.65,.35,.35)\rangle$ with the experimental results for either Na^{+} or Sm^{++}in KBr. For Na^{+} in KBr the broken line of Figure (F-4B) shows approximately the additional effect which can result from the effective lattice contribution. It is obvious from the results of (F-4B) that following the center point of the FWHM does not explain the experimentally observed shifts.

The results for the shift of singularity A are presented in Figure (F-5B). The theoretical curves (solid line) follow the center point of the FWHM of $\mathrm{Im}\langle G_{TA_2}(.5,.5,0)\rangle$and, for Sm^{++} in KBr, are in good agreement with experiment. Even with the addition of the effective lattice (broken line) in

(F-5B), the results obtained for Na^+ in KBr are in rather poor agreement with experiment. Figure (F-6B), which follows the movement of singularity C shows that the shift of the center point of the FWHM of $\mathrm{Im}\langle G_{LA}(.55,.35,0)\rangle$ for Na^+ in KBr is in very good agreement with experiment. In this region, for Na^+ in KBr, the spectral functions are found to be symmetric and show no signs of resonance behaviour.

Because of the appearance of a resonance in the Na^+ results, the convolution model presented in Figures (F-7B) and (F-8B) was only attempted for Sm^{++} in KBr. The results of this model tend to favour a Lorentzian representation of the spectral function for Sm^{++} in KBr. This is not so surprising since the spectral function has a pseudo-Lorentzian form.

In conclusion, the experimental results, which indicate a faster movement of the singularities (A, B) for Na^+ than for Sm^{++} impurities in KBr, can be understood qualitatively (from the single phonon approach) to be a result of the resonance behaviour in the region of interest. Furthermore, the more rapid movement of singularity B, for either of these impurity systems, is a result of its being a maximum frequency singularity.

TABLE (T-1B)

Singularity	$\gamma_j(k)^{(a)}$	c %	$\Delta\omega$ in cm^{-1} effective lattice	$\Delta\omega$ in cm^{-1} experiment
A	2.79	.1	.059	.38
B	2.14	.1	.046	.72
C	2.11	.1	.051	.38

(a) Cowley (1971)

TABLE (T-2B)

Region	w_o $(cm^{-1}/\%conc)$	w_1 $(\%conc)^{-1}$	s_o $(cm^{-1}/\%conc)$	s_1 $(\%conc)^{-1}$
I	0.55	0.0	0.42	0.0
II	-21.37	0.288	-68.0	0.918
III	.27	0.0	1.1	0.0

FIGURE (F-1B) The envelope function $D_o(\omega_j(\tilde{k})$ used for the convolution model.

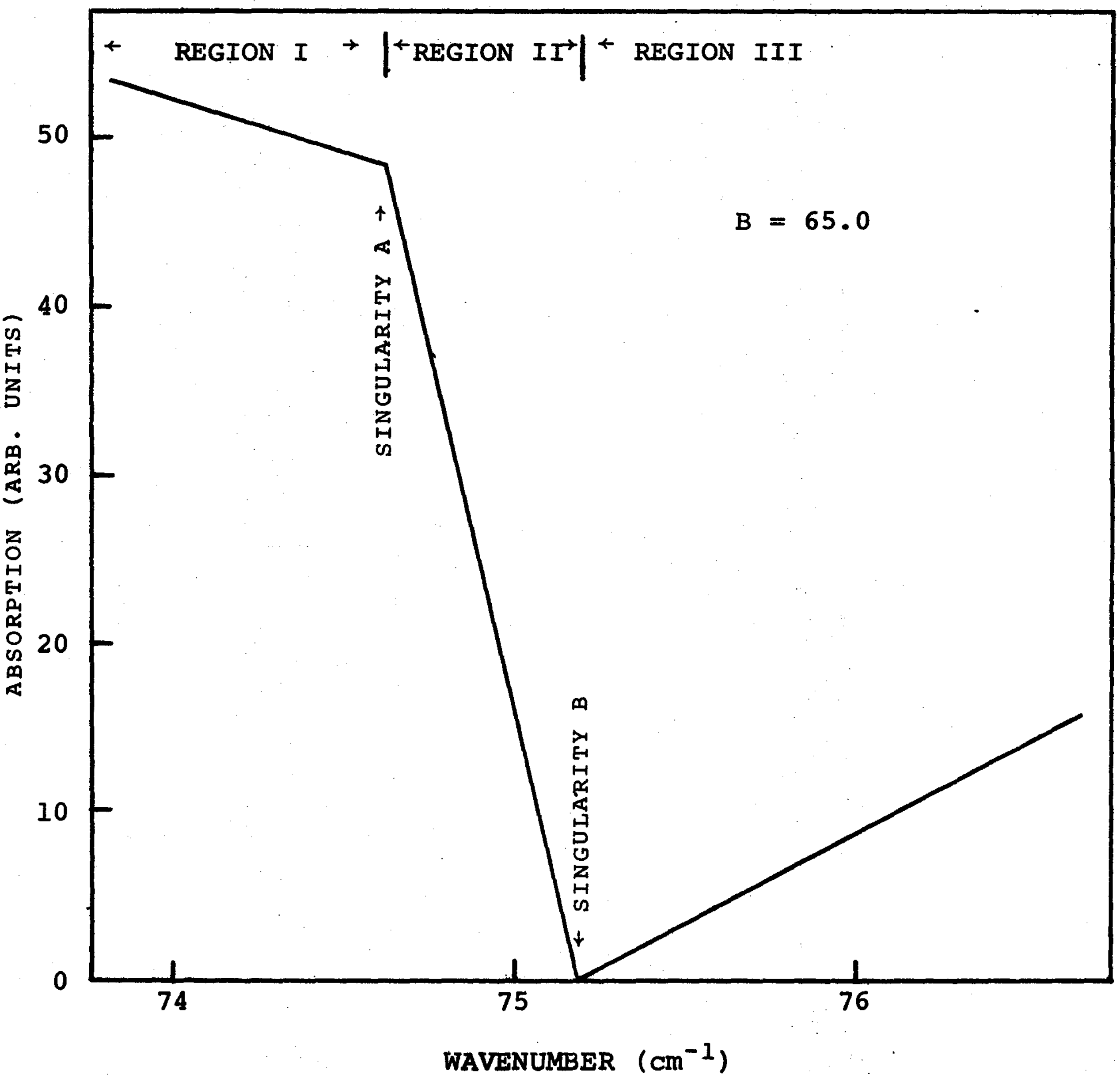

← REGION I →
←REGION II→
← REGION III
B = 65.0
SINGULARITY A →
SINGULARITY B →
ABSORPTION (ARB. UNITS)
0
10
20
30
40
50
74
75
76
WAVENUMBER (cm^{-1})

FIGURE (F-1B)

FIGURE (F-2B) The spectral functions appropriate to singularity B, for two concentrations of Sm^{++} in KBr are shown (———). The broken vertical line indicates $\omega_{TA_2}(.65, .35, .35)$ in KBr, while the vertical lines on the high frequency tails of the spectral functions indicate the position of $1/25 \max(\mathrm{Im}\langle G_{TA_2}((.65,.35,.35);\omega)\rangle)$.

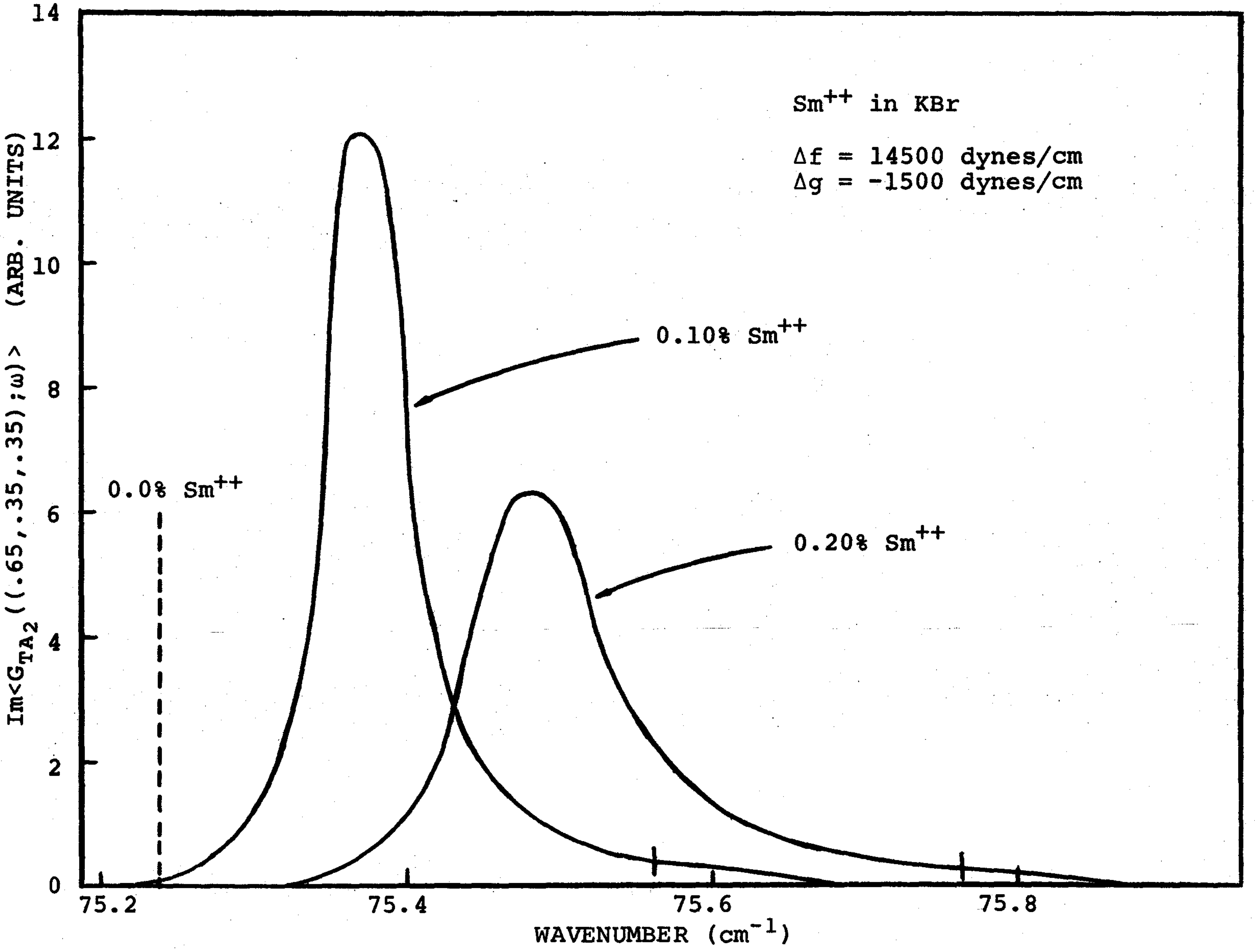

14
12
10
8
6
4
2
0
$\mathrm{Im}\langle G_{TA_2}((.65,.35,.35);\omega)\rangle$ (ARB. UNITS)
75.2
75.4
75.6
75.8
WAVENUMBER (cm^{-1})
Sm^{++} in KBr
Δf = 14500 dynes/cm
Δg = -1500 dynes/cm
0.10% Sm^{++}
0.20% Sm^{++}
0.0% Sm^{++}

FIGURE (F-2B)

FIGURE (F-3B) The spectral functions, appropriate to singularity B, for two concentrations of Na^+ in KBr are shown (———). The broken vertical line indicates $\omega_{TA_2}(.65, .35, .35)$ in KBr, while the vertical lines on the high frequency tails of the spectral functions indicate the position of $1/25\ \max(\mathrm{Im}\langle G_{TA_2}((.65,.35,.35);\omega)\rangle)$.

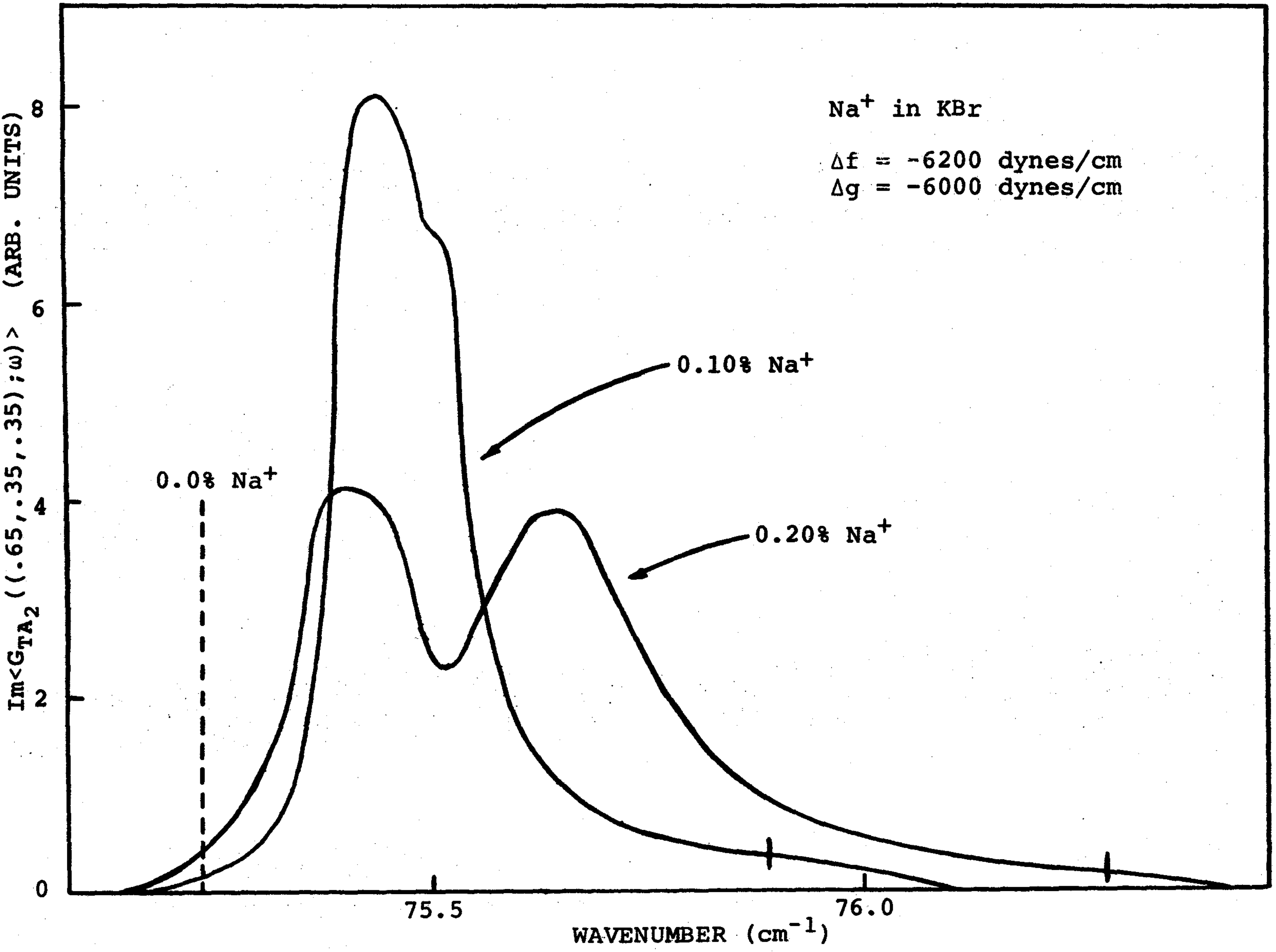

Na$^+$ in KBr
Δf = -6200 dynes/cm
Δg = -6000 dynes/cm
0.10% Na$^+$
0.20% Na$^+$
0.0% Na$^+$
8
6
4
2
0
75.5
76.0
Im<G_{TA_2}((.65,.35,.35);ω)> (ARB. UNITS)
WAVENUMBER (cm^{-1})

FIGURE (F-3B)

FIGURE (F-4B) Comparison of experimental and theoretical frequency shift of singularity B for (a) Sm^{++}, (b) Na^{+} in KBr. The (—•—•—) line indicates the movement of the center point of the FWHM of $Im<G_{TA_2}((.65,.35,.35);\omega)>$ while the (———) line indicates the movement of the high frequency tail. In (b) the broken line (-----) indicates the additional effect on the solid line as a result of including the volume change. The closed circles are the experimental results.

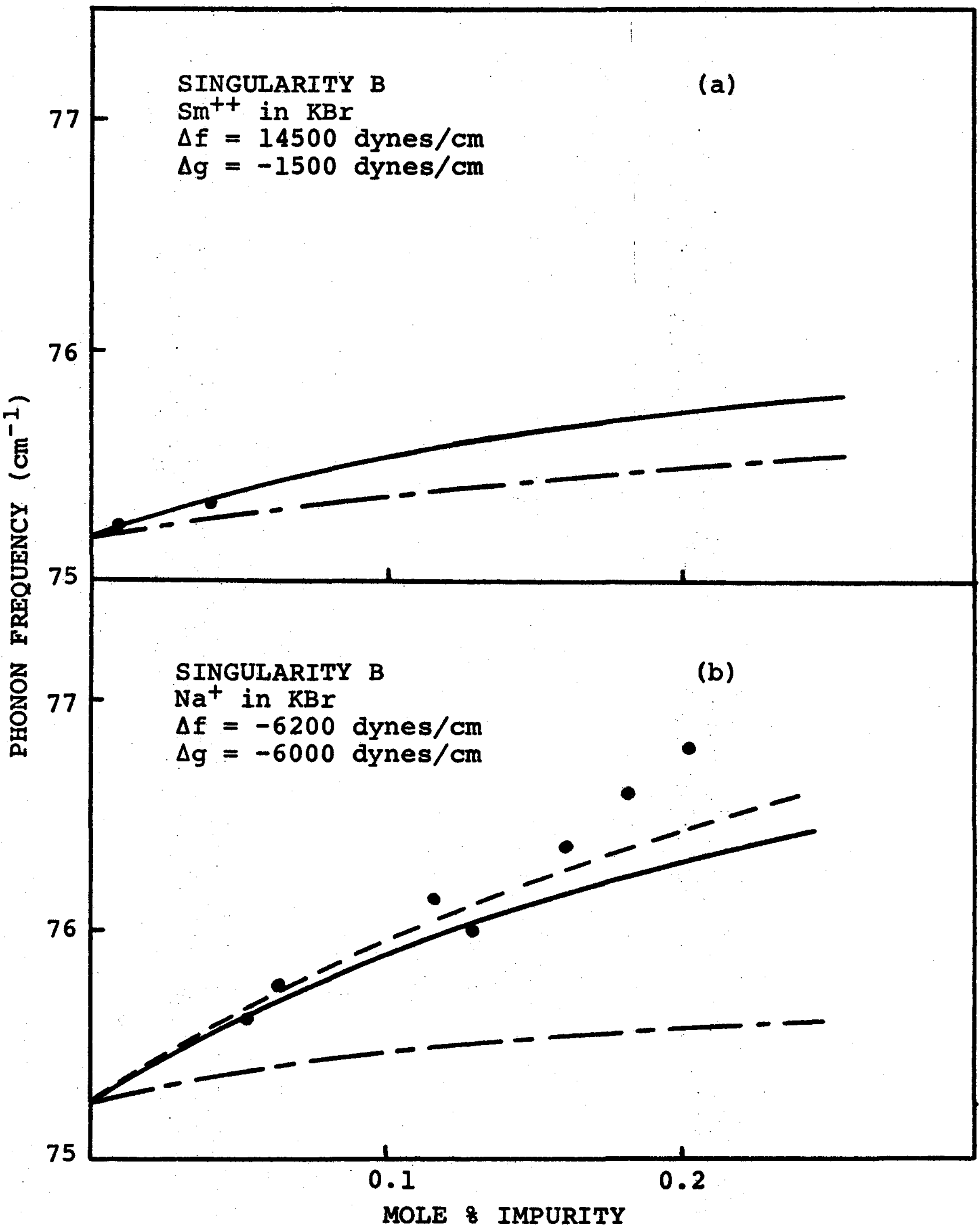

SINGULARITY B
(a)
Sm^{++} in KBr
Δf = 14500 dynes/cm
Δg = -1500 dynes/cm
SINGULARITY B
(b)
Na^{+} in KBr
Δf = -6200 dynes/cm
Δg = -6000 dynes/cm
77
76
75
PHONON FREQUENCY (cm^{-1})
0.1
0.2
MOLE % IMPURITY

FIGURE (F-4B)

FIGURE (F-5B) Comparison of experimental and theoretical frequency shift of singularity A for (a) Sm^{++}, (b) Na^{+} in KBr. The solid line(———) indicates the movement of the center point of the FWHM of $Im\langle G_{TA_2}((.5,.5,0);\omega)\rangle$. In (b) the broken line (-----) indicates the effect of including the volume change. The closed circles are the experimental results.

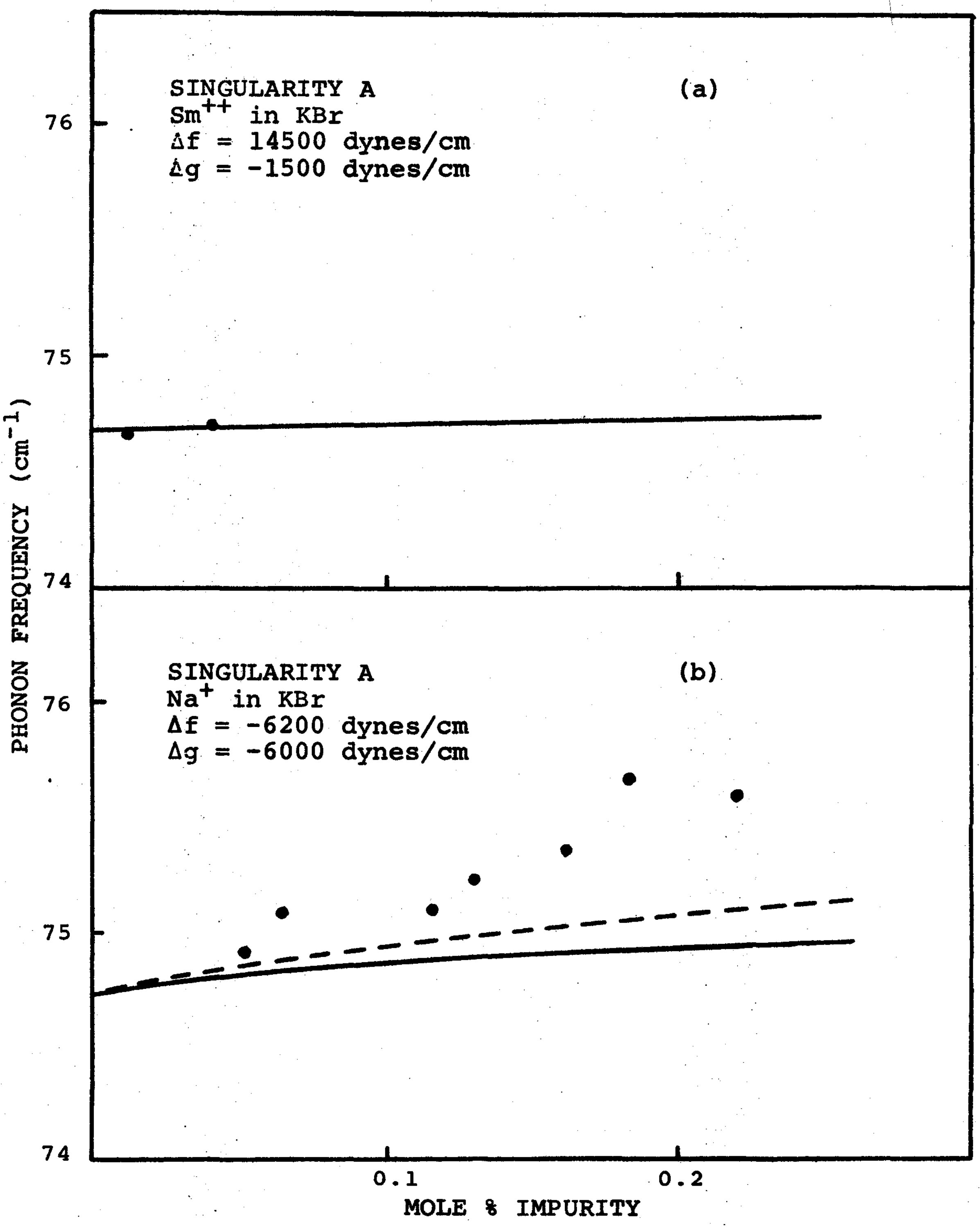

SINGULARITY A
(a)
Sm^{++} in KBr
Δf = 14500 dynes/cm
Δg = -1500 dynes/cm
76
75
74
SINGULARITY A
(b)
Na^{+} in KBr
Δf = -6200 dynes/cm
Δg = -6000 dynes/cm
76
75
74
0.1
0.2
PHONON FREQUENCY (cm^{-1})
MOLE % IMPURITY

FIGURE (F-5B)

FIGURE (F-6B) Comparison of experimental and theoretical frequency shift of singularity C for Na^+ in KBr. The solid line (———) indicates the movement of the center point of the FWHM of $Im\langle G_{LA}((.55,.35,0);\omega)\rangle$, while the broken line (-----) indicates the effect of including the volume change. The closed circles are the experimental results.

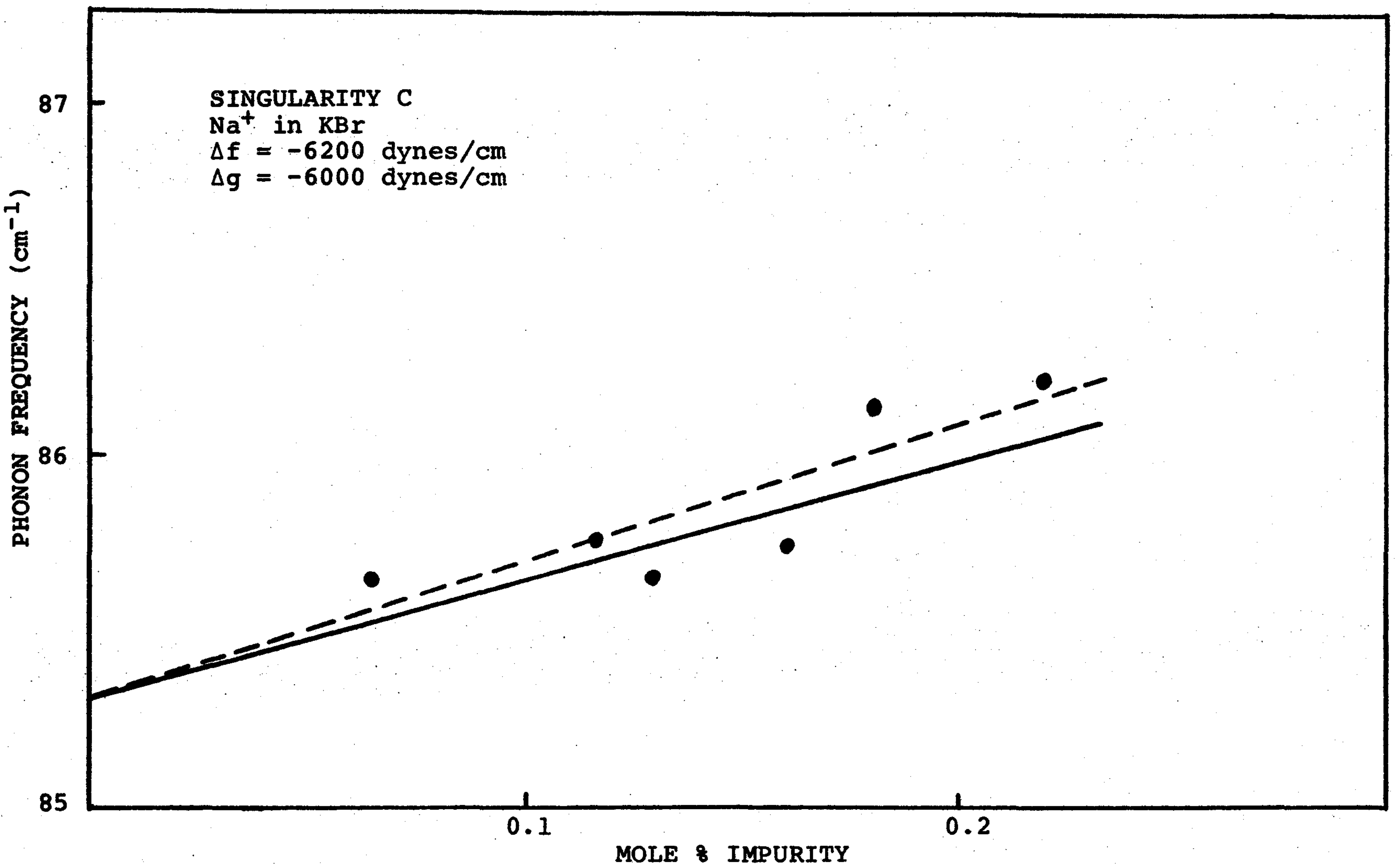

SINGULARITY C
Na^+ in KBr
Δf = -6200 dynes/cm
Δg = -6000 dynes/cm
87
86
85
PHONON FREQUENCY (cm^{-1})
0.1
0.2
MOLE % IMPURITY

FIGURE (F-6B)

FIGURE (F-7B) The convolution model using Lorentzian spectral function to follow the shift of singularities A and B for Sm^{++} in KBr.

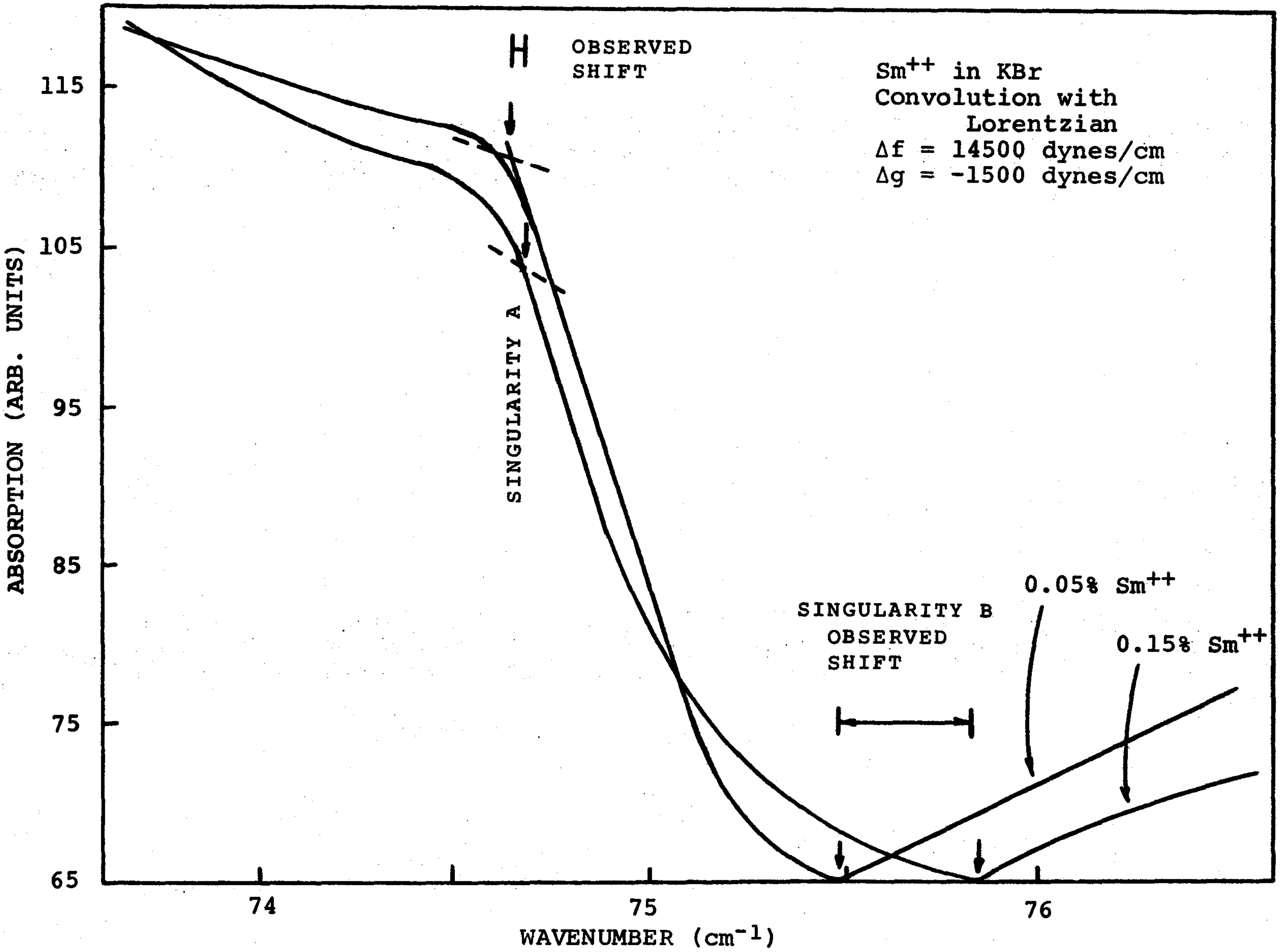

OBSERVED
SHIFT
Sm++ in KBr
Convolution with
Lorentzian
Δf = 14500 dynes/cm
Δg = -1500 dynes/cm
SINGULARITY A
SINGULARITY B
OBSERVED
SHIFT
0.05% Sm++
0.15% Sm++
115
105
95
85
75
65
74
75
76
ABSORPTION (ARB. UNITS)
WAVENUMBER (cm-1)

FIGURE (F-7B)

FIGURE (F-8B) The convolution model using Gaussian spectral function to follow the shift of singularities A and B for Sm^{++} in KBr.

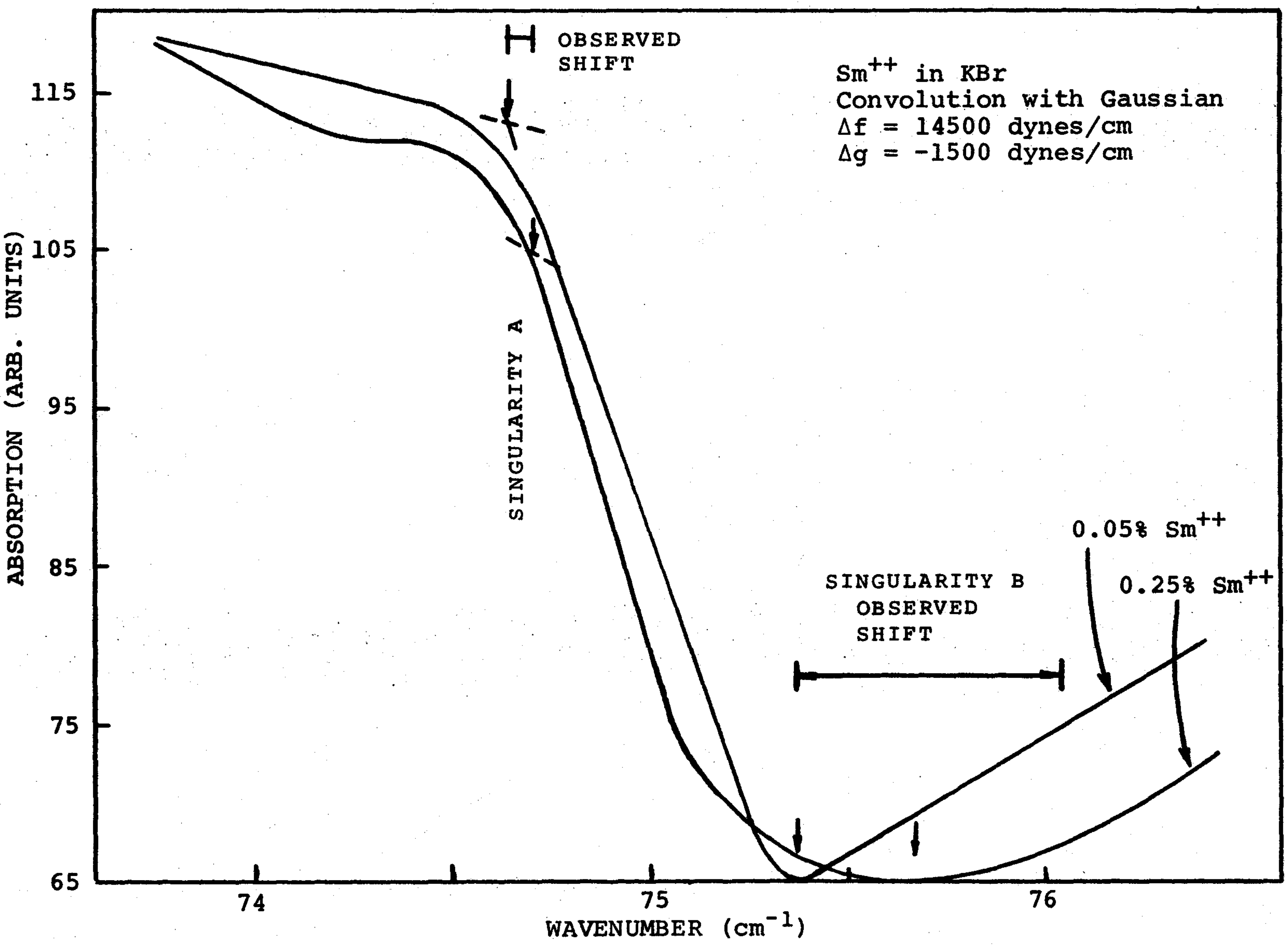

OBSERVED SHIFT
Sm^{++} in KBr
Convolution with Gaussian
Δf = 14500 dynes/cm
Δg = -1500 dynes/cm
SINGULARITY A
SINGULARITY B OBSERVED SHIFT
0.05% Sm^{++}
0.25% Sm^{++}
ABSORPTION (ARB. UNITS)
115
105
95
85
75
65
74
75
76
WAVENUMBER (cm^{-1})

FIGURE (F-8B)

"Most of our so-called reasoning consists in finding arguments for going on believing as we already do." --J.H. Robinson

SECTION C

CALCULATION OF PHONON SIDE BANDS OF H_2, D_2 AND N_2 IN SOLID ARGON

In this section the one phonon side band of the vibrational spectrum of a substitutional H_2, (D_2) molecule in an Ar crystal is formulated in terms of the displacement-displacement Green's functions. By considering the appropriate interatomic potentials, a considerable lattice relaxation is found about the H_2, (D_2) impurity. Using a one defect model and the low concentration defect theory these "long range" effects are crudely compensated for by introducing an effective lattice. The side bands are then calculated with the one defect theory in a harmonic approximation by using the temperature corrected experimental phonon frequencies. Also, a calculation of the position of the local mode side band for N_2 in Ar, as a function of temperature, is performed by adjusting the phonon frequencies appropriately.

Batchelder, Collins, Haywood and Sidney (1970) measured the phonon dispersion curves in solid Ar and found the force constants (to second nearest neighbour) by a least-squares fitting. Their first nearest neighbour force constants are listed in Table (T-1C). Later, Batchelder, Haywood and Saunderson (1970) measured the temperature dependence of phonon frequencies in solid Ar for the $T(0,0,\zeta)$ branch. Their results are used to scale the perfect Ar data to the appropriate temperature.

The induced infrared fundamental band of 1% H_2, (D_2) in solid argon was studied by Kriegler and Welsh (1968) (De Remigis and Welsh (1970)) at 82°K (80°K). Their results indicate a peak arising from a localized lattice vibration at about 112 cm^{-1} (79 cm^{-1}) and an inband peak at about 22 cm^{-1} (22 cm^{-1}) for H_2, (D_2) in solid Ar. Recently, De Remigis (1970) obtained results for the movement of the local mode side band peak for N_2 in Ar as a function of temperature. These results are indicated by the closed circles in Figure (F-1C). No results were obtained for the change of lattice constant in Ar as a result of the introduction of these impurities.

1. The Problems and Some Results

Although the melting point of argon is 83.8°K, it is assumed in this section that if the perfect argon vibrational properties are described by the temperature-corrected experimental phonon frequencies, then any additional effect, due to a low concentration (i.e., 1% for H_2 or D_2, 2% for N_2) of impurities, may be treated in the harmonic approximation.

From the Lennard-Jones potentials, using the data in Table (T-2C), it is found that the relaxation of the first nearest neighbour argon atoms about an N_2 impurity is less than 1% (expansion). Therefore, for 2% N_2 in Ar it is assumed that there will be no significant change in lattice spacing. Assuming this to be the case, and since Ar is f.c.c., the local mode frequency is calculated by using equation (III-78) and the information, contained in Appendix III, for the defect space defined by the impurity and its first nearest neighbours. Furthermore, from the data in Table (T-2C), the change of force constants due to the introduction of N_2 substitutionally into Ar is found to vary continuously from (in the notation of Section A, Chapter IV)

$$\Delta A = 640 \text{ dynes/cm}$$

$$\Delta B_1 = -72 \text{ dynes/cm}$$

$$\Delta B_2 = -72 \text{ dynes/cm}$$

at 55°K, to

$$\Delta A = 592 \text{ dynes/cm}$$

$$\Delta B_1 = -68 \text{ dynes/cm}$$

$$\Delta B_2 = -84 \text{ dynes/cm}$$

at 80°K. With these temperature dependent force constant change results and the temperature corrected phonons, the local mode frequencies, found by using (III-78) are compared with the experimental results in Figure (F-1C). This temperature dependence of the local mode position is thought to arise from the variation of the argon lattice constant and phonon frequencies as a function of temperature (De Remigis (1971)). Considering the approximations made, the agreement obtained with experimental results is reassuring.

Taylor (1971) has shown that in the harmonic approximation, the absorption spectrum due to the Q transition ($J=0 \rightarrow J=0$), of H_2, (D_2) in Ar is directly proportional to

$$\kappa(\omega) = \sum_{i=1}^{4} \sum_{j=1}^{4} q_i q_j \operatorname{Im} G_{ij}(\omega) \qquad \text{(IV-19)}$$

where i and j refer to the four orthonormal symmetry coordinates which transform as the first row of the F_{1u} representation of O_h, and the parameters q_i are given by

$$q_1 = w(e_1+8e_3+4e_2) \qquad \text{(IV-20}_a\text{)}$$

$$q_2 = 4u(-e_1+2e_3-e_2) \qquad \text{(IV-20}_b\text{)}$$

$$q_3 = 8n(2e_1+3e_3-5e_2) \qquad \text{(IV-20}_c\text{)}$$

$$q_4 = 8me_4 \qquad \text{(IV-20}_d\text{)}$$

The values of w, u, n and m for equation (IV-20) are found in (A-13) while the values of the e's are

$$e_1 = 157.2,\ e_2 = -11.1,\ e_3 = -14.1,\ e_4 = 3.0$$

(Taylor (1971)). Using the one defect approach, the G appropriate to this problem may be expressed as

$$G_{F_{1u}} = (I-P_{F_{1u}} v^{1}_{F_{1u}})^{-1} P_{F_{1u}} \qquad \text{(IV-21)}$$

where $P_{F_{1u}}$ and $v^{1}_{F_{1u}}$ are found in Appendix III. With only a longitudinal force constant change, $\Delta A = -270$ dynes/cm, for a first nearest neighbour's defect space,the local mode position for H_2 in Ar (82°K) and D_2 in Ar (80°K) can be fitted to 112 cm^{-1} and 79 cm^{-1} respectively. Although this perfect agreement with experiment may seem impressive, the same ΔA,used with (IV-21), (IV-20), and (IV-19) gives an inband mode peak at about 38 cm^{-1}. The fact that the local mode fit is so good is not surprising, since De Remigis and Welsh (1970) have already observed that 112/79 is practically equal to $(m_{D_2}/m_{H_2})^{\frac{1}{2}}$. Furthermore, the poor agreement of the inband peak is to be expected. Using the parameters of Table (T-2C), for the appropriate Lennard-Jones potentials, the one-dimensional relaxation model indicates a relaxation (contraction) of ∿5% for the first nearest neighbour, ∿2% for the second nearest neighbour, and ∿2% for the fourth nearest neighbour of the defect molecule. This indicates that even for 1% H_2, (D_2) in Ar, the defect spaces have a reasonably high probability of overlapping. This being the case, this simple one defect approach, using a first nearest neighbour defect space, is not expected to give very good agreement for the peak due to inband modes of vibration.

2. The Effective Lattice for H_2, (D_2) in Ar

Since no information is available on the change of lattice spacing for solid Ar, due to the substitutional H_2, (D_2) impurities, only a crude effective lattice can be considered. It has been seen (one-dimensional model) that the substitution of an H_2, (D_2) molecule in Ar causes a long range distortion. Since no method is available to calculate, three dimensionally, the distortion of the Ar atoms about a single H_2, (D_2), and then extend this procedure to consider 1% H_2, (D_2) randomly placed in Ar, only the simplest effective lattice is considered.

The effective lattice assumed in this calculation is the stable effective lattice (See Section C, Chapter III). Assuming that the effective lattice must be stable implies that the two conditions must be satisfied. The first is

$$\left(\frac{d\Phi^{eff}}{da}\right)_{a=a_C} = 0 \qquad \text{(IV-22)}$$

and the second is that the defects placed into this lattice must be mass defects.

From the work of Batchelder, Collines, Haywood and Sidney (1970) it is obvious that the first nearest neighbour transverse and second nearest neighbour force constants are between one and two orders of magnitude less than the first nearest neighbour longitudinal force constant. This being the case, it is further assumed that only first nearest neighbour force constants are important and need be considered. With this assumption, the first condition (IV-22) becomes

$$\frac{\sigma_{eff}}{r_{eff}} = \frac{\sigma_{Ar}}{r_{Ar}} \qquad (4.2°K) \qquad \text{(IV-23)}$$

while the second (only mass defect) implies

$$\varepsilon_{eff} = \varepsilon_{H_2,(D_2)\ Ar} \qquad \text{(IV-24}_a\text{)}$$

$$\sigma_{eff} = \sigma_{H_2,(D_2)\ Ar} \qquad \text{(IV-24}_b\text{)}$$

Since all these quantities are found from either Table (T-2C) or by using (IV-23) and (IV-24), the force constants for the effective lattice can be calculated. These are listed in Table (T-1C). Using (III-78), for the appropriate mass impurity in this effective lattice, the position of the local mode for H_2 in Ar at 82°K and D_2 in Ar at 80°K is found to be 113.6 cm^{-1} and 79.8 cm^{-1} respectively. Furthermore, using (IV-21), (IV-20) and (IV-19) the inband spectrum $\kappa(\omega)$ is found for the appropriate mass impurity in Ar. The results of this calculation are shown in Figures (F-2C) and F-3C) for H_2/Ar and D_2/Ar respectively. In these figures the position of the experimental peak is indicated by the vertical arrow and the theoretical peak at 24.5 cm^{-1} (82°K) can be identified with the 61.7 cm^{-1} ($\tilde{k}$=(.712,.212,.212)) critical point of solid Ar at 4.2°K. Because a mesh of .57 cm^{-1} was used in this calculation, most singularities are not observable in (F-2C) and (F-3C).

Considering the lack of sophistication of this theoretical approach and the fact that the observed experimental peaks have widths of roughly 20 cm^{-1}, the theoretically derived results seem quite reasonable.

TABLE (T-1C) (4.2°K)

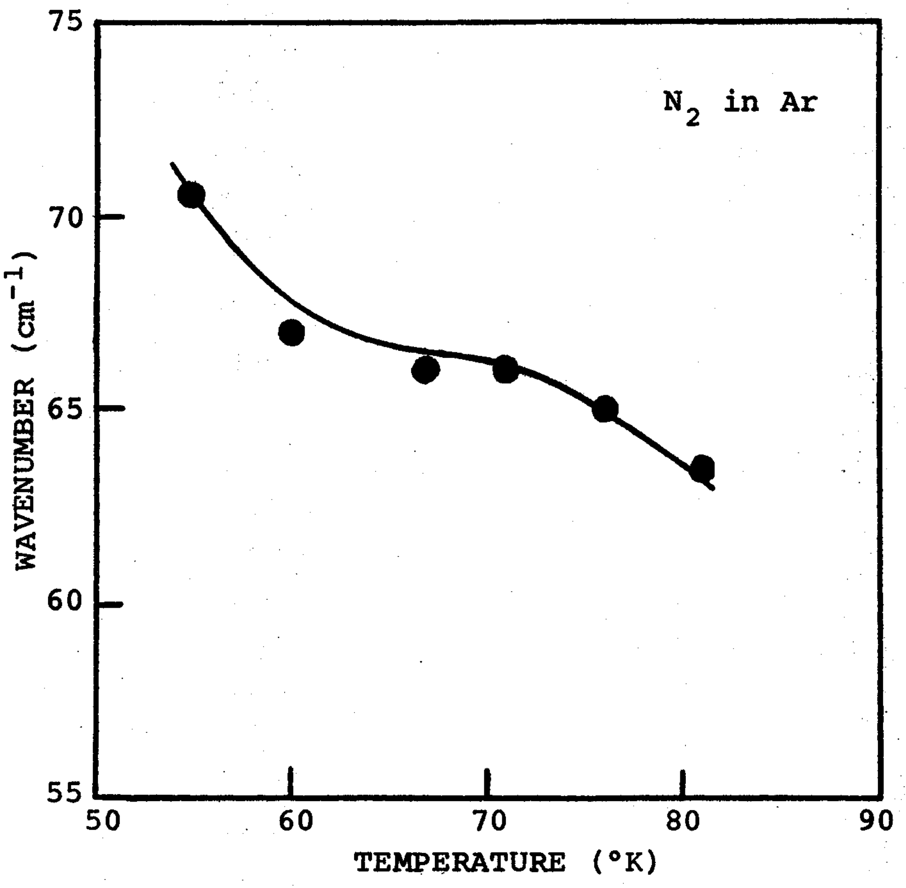
	Experimental Force Constants	Lennard-Jones Force Constants	Effective Lattice Force Constants
1XX	531	572	259
1XY	604	608	273
IZZ	- 7	-36	-14

TABLE (T-2C)

	ε°K	σÅ	Argon Temperature (°K)	r_{Ar} Nearest Neighbour Distance
N_2	95	3.7	4.2	3.748(a)
$H_2(D_2)$	37	2.93	55	3.796(a)
Ar	120	3.40	60	3.805(a)
N_2-A	107	3.55	65	3.814(a)
$H_2(D_2)$-A	67	3.17	70	3.822(a)
			75	3.833(a)
			80	3.845(a)

(a) Peterson, Batchelder and Simmons (1966)

FIGURE (F-1C) Comparison of experimental results (filled circles) and theoretical calculation (————) for the position of the local mode side band, of the N_2/Ar system, as a function of temperature.



75
70
65
60
55
50
60
70
80
90
WAVENUMBER (cm^{-1})
TEMPERATURE (°K)
N_2 in Ar

FIGURE (F-1C)

FIGURE (F-2C) The inband spectrum, $\kappa(\omega)$, corresponding to the H_2 vibrational-rotational transition, Q, with $J=0 \rightarrow J=0$ for 1% H_2 in solid Ar. The vertical arrow indicates the position of the experimental peak while the horizontal line (-----), and arrows, indicate the approximate width of the experimental peak. The (———) line is the theoretical result.

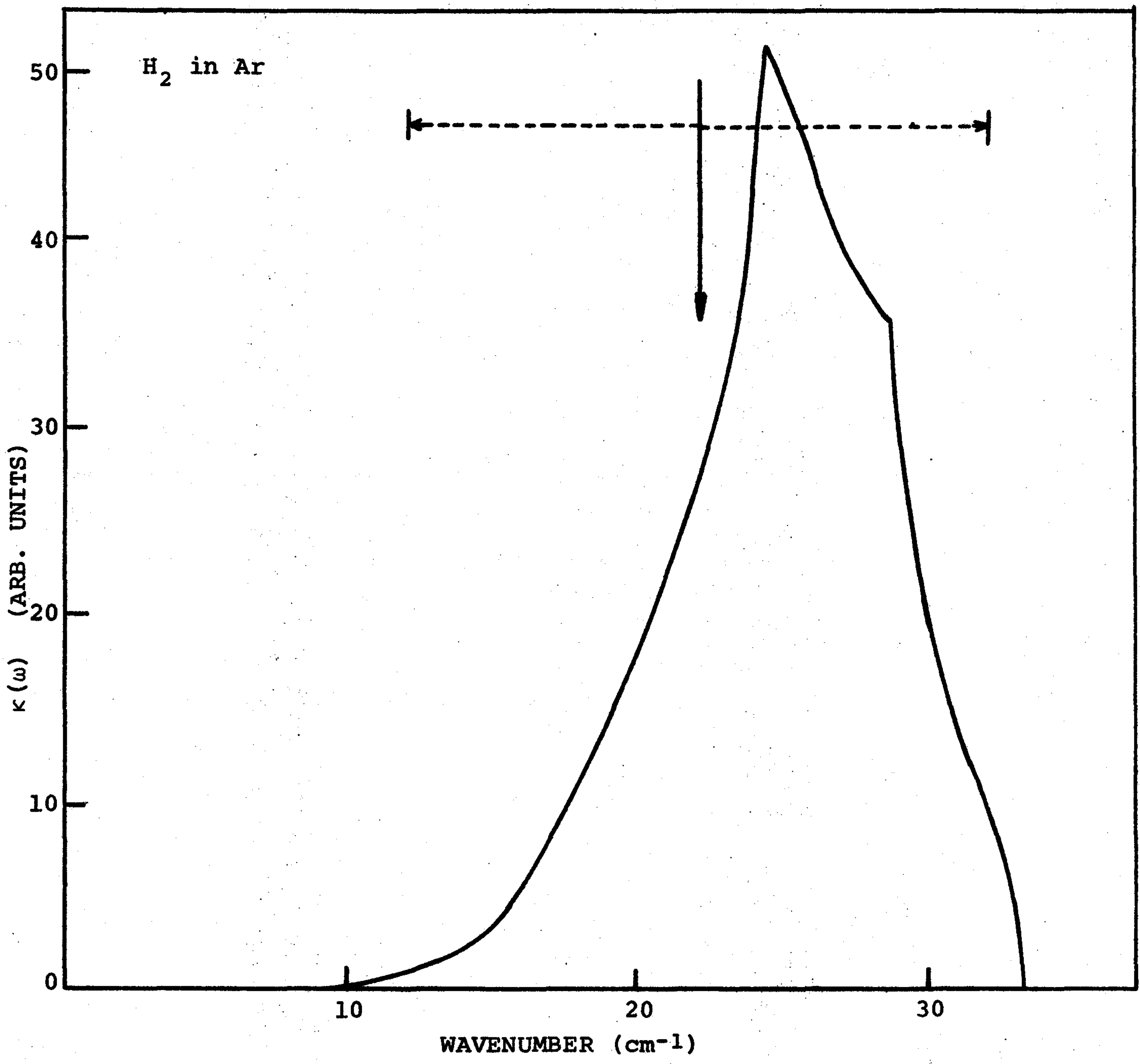

H$_2$ in Ar
50
40
30
20
10
0
$\kappa(\omega)$ (ARB. UNITS)
10
20
30
WAVENUMBER (cm^{-1})

FIGURE (F-2C)

FIGURE (F-3C) The inband spectrum, $\kappa(\omega)$, corresponding to the D_2 vibrational-rotational transition, Q, with J=0 → J=0 for 1% D_2 in solid Ar. The vertical arrow indicates the position of the experimental peak while the horizontal line (-----), and the arrows, indicate the approximate width of the experimental peak. The (———) line is the theoretical result.

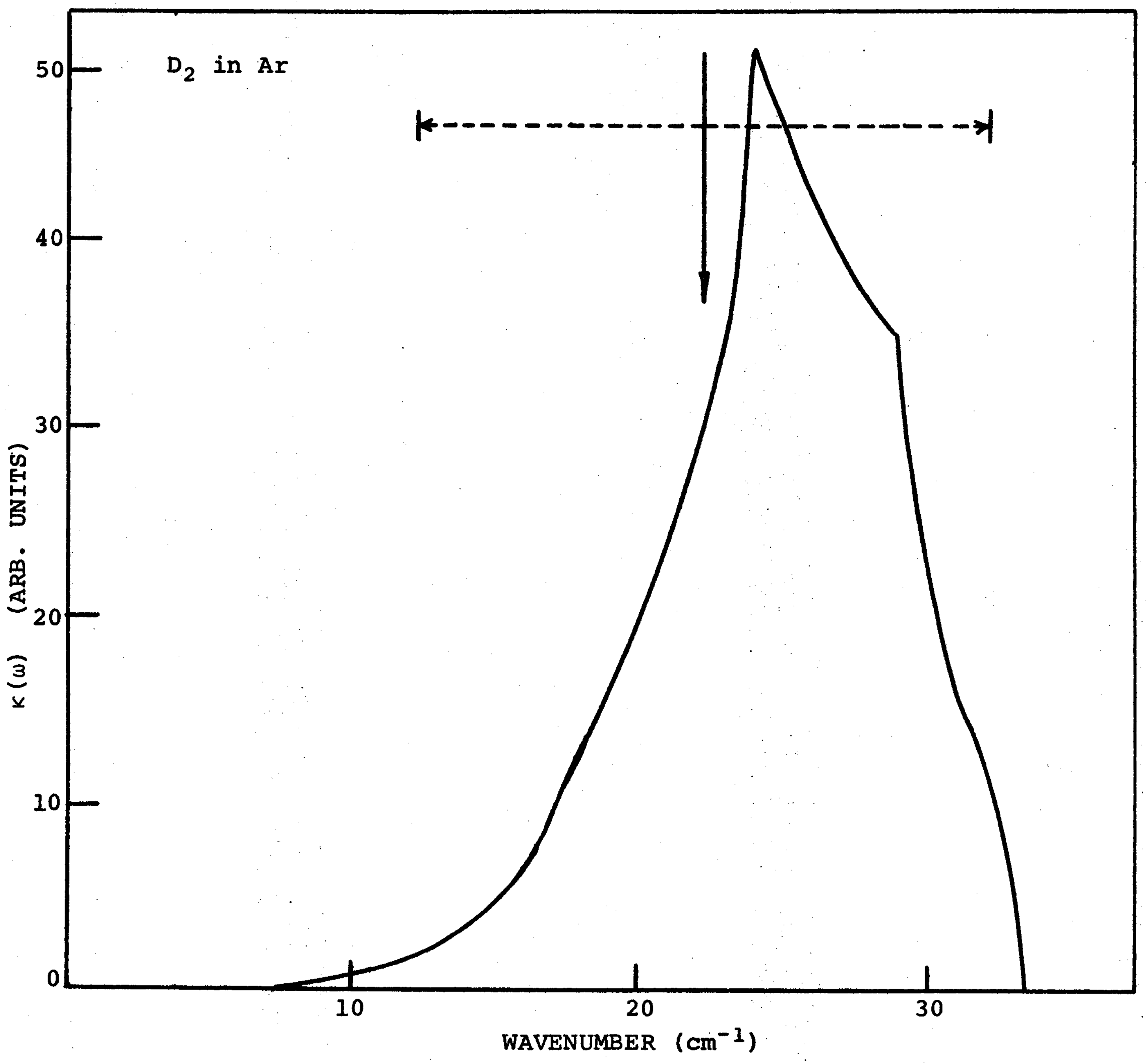

D_2 in Ar
50
40
30
20
10
0
$\kappa(\omega)$ (ARB. UNITS)
10
20
30
WAVENUMBER (cm^{-1})

FIGURE (F-3C)

"To the discoverer in this field the products of his imagination appear so necessary and natural that he regards them, and would have them regarded by others, not as creations of thought, but as given realities."

--A. Einstein

CHAPTER V

CONCLUSION

The broader aspects of a Conclusion Chapter are presented in the preface and afterword; however, there remain some points, associated with the body of this thesis, that require conclusion.

The application chapter indicates the usefulness of the effective lattice approach. Even though the use of this approach has been restricted to the low concentration defect theory it can, for mass impurities, be used for pairs with correlation or the n-tuple process. In Section A of Chapter IV is it seen that an understanding of the frequencies and widths of phonons in $Cu_{0.97}Au_{0.03}$ is found by taking into account the expansion of the lattice on alloying. Furthermore, Section C of the same chapter shows that even a crude model for the effective lattice (i.e., the stable effective lattice) provides a qualitatively satisfactory explanation of both the inband vibrational side band and the position of the corresponding local mode for the disordered $Ar_{0.99}H_2, (D_2)_{0.01}$crystal system.

The single phonon approach used in Section B of Chapter IV provides some useful information about the impurity concentration dependence of certain singular points in the defect induced far infrared absorption of KBr.

It is hoped, that the algebraic method formulated in Chapter II may, in the near future, provide some hints on how pair or n-tuple scattering may be used for more extended defect spaces than for just a mass defect.

Chapter IV indicates that in order to achieve a clearer understanding of substitutional defect crystal systems, a proper self consistent treatment of defect lattices, for extended defects,and a better three dimensional treatment of relaxation (beyond lattice statics) is required.

AFTERWORD

"La science a fait de nous des dieux avant même que nous méritions d'être des hommes."

--Jean Rostand
Pensée d'un Biologiste

APPENDIX I

THE INDEPENDENT GREEN'S FUNCTIONS FOR F.C.C.

For an f.c.c. lattice, it is easily shown that there are 13 independent "weighted" densities of states, $\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega)$ in the first nearest neighbour defect space.

The irreducible Brillouin zone in this lattice is 1/48th of the Brillouin zone, and any integral over such a zone will be indicated by $\int'$.

If $\tilde{q}=\tilde{k}a/2\pi$ (the wave vector in reduced units, where a is the lattice constant) and if

$$f^{j}_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\tilde{q}) = \frac{\sigma^{j}_{\alpha}(\tilde{q})\sigma^{j}_{\beta}(\tilde{q})e^{\frac{2\pi i}{a}\tilde{q}.(\tilde{\ell}-\tilde{\ell}')}}{n_A} \qquad \text{(A-1)}$$

in the Brillouin zone, then equation (III-7) is given by

$$\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega) = \sum_{j}\int d^3q\ f^{j}_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\tilde{q})\delta(\omega_j(\tilde{q})-\omega) \qquad \text{(A-2)}$$

where, for cubic lattices, σ is real.

If the independent, reduced $\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega)$ are defined as $\nu^{i}(\omega)$, then $\nu^{i}(\omega)$ can be written as

$$\nu^{i}(\omega)= \sum_{j}\int' d^3qF^{j}_{i}(\tilde{q})\delta(\omega_{j}(\tilde{q})-\omega) \qquad \text{(A-3)}$$

where $F^{j}_{i}(\tilde{q})$ is the ith independent function found by reducing $f^{j}_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\tilde{q})$ into the 1/48th Brillouin zone.

The 13 independent functions $F_j^i(\tilde{q})$ of the first nearest neighbour defect space are listed below:

$$F_1 = 48$$

$$\begin{aligned}F_2 = {} & 8(\sigma_x^j(\tilde{q})^2\cos(\pi q_x)(\cos(\pi q_y)+\cos(\pi q_z)) \\ & +\sigma_y^j(\tilde{q})^2\cos(\pi q_y)(\cos(\pi q_x)+\cos(\pi q_z)) \\ & +\sigma_z^j(\tilde{q})^2\cos(\pi q_z)(\cos(\pi q_x)+\cos(\pi q_y)))\end{aligned}$$

$$\begin{aligned}F_3 = {} & 16(\sigma_x^j(\tilde{q})^2\cos(\pi q_z)\cos(\pi q_y) \\ & +\sigma_y^j(\tilde{q})^2\cos(\pi q_x)\cos(\pi q_z) \\ & +\sigma_z^j(\tilde{q})^2\cos(\pi q_x)\cos(\pi q_y))\end{aligned}$$

$$\begin{aligned}F_4 = {} & -16(\sigma_x^j(\tilde{q})\sigma_y^j(\tilde{q})\sin(\pi q_x)\sin(\pi q_y) \\ & +\sigma_x^j(\tilde{q})\sigma_z^j(\tilde{q})\sin(\pi q_x)\sin(\pi q_z) \\ & +\sigma_y^j(\tilde{q})\sigma_z^j(\tilde{q})\sin(\pi q_y)\sin(\pi q_z))\end{aligned}$$

$$F_5 = 16(\sigma_x^j(\tilde{q})^2\cos(2\pi q_x)+\sigma_y^j(\tilde{q})^2\cos(2\pi q_y)+\sigma_z^j(\tilde{q})^2\cos(2\pi q_z))$$

$$\begin{aligned}F_6 = {} & 8(\sigma_x^j(\tilde{q})^2(\cos(2\pi q_y)+\cos(2\pi q_z)) \\ & +\sigma_y^j(\tilde{q})^2(\cos(2\pi q_x)+\cos(2\pi q_z)) \\ & +\sigma_z^j(\tilde{q})^2(\cos(2\pi q_x)+\cos(2\pi q_y)))\end{aligned}$$

$$\begin{aligned}F_7 = {} & 8(\sigma_x^j(\tilde{q})^2\cos(\pi q_x)(\cos(2\pi q_y)\cos(\pi q_z)+\cos(2\pi q_z)\cos(\pi q_y)) \\ & +\sigma_y^j(\tilde{q})^2\cos(\pi q_y)(\cos(2\pi q_x)\cos(\pi q_z)+\cos(2\pi q_z)\cos(\pi q_x)) \\ & +\sigma_z^j(\tilde{q})^2\cos(\pi q_z)(\cos(2\pi q_x)\cos(\pi q_y)+\cos(2\pi q_y)\cos(\pi q_x)))\end{aligned}$$

$$\begin{aligned}F_8 = {} & 16(\sigma_x^j(\tilde{q})^2\cos(2\pi q_x)\cos(\pi q_y)\cos(\pi q_z) \\ & +\sigma_y^j(\tilde{q})^2\cos(2\pi q_y)\cos(\pi q_x)\cos(\pi q_z) \\ & +\sigma_z^j(\tilde{q})^2\cos(2\pi q_z)\cos(\pi q_x)\cos(\pi q_y))\end{aligned}$$

$$\begin{aligned}F_9 = {} & -8(\sigma_x^j(\tilde{q})\sigma_y^j(\tilde{q})(\sin(\pi q_x)\sin(2\pi q_y)+\sin(2\pi q_x)\sin(\pi q_y))\cos(\pi q_z) \\ & +\sigma_x^j(\tilde{q})\sigma_z^j(\tilde{q})(\sin(\pi q_x)\sin(2\pi q_z)+\sin(2\pi q_x)\sin(\pi q_z))\cos(\pi q_y) \\ & +\sigma_y^j(\tilde{q})\sigma_z^j(\tilde{q})(\sin(\pi q_y)\sin(2\pi q_z)+\sin(2\pi q_y)\sin(\pi q_z))\cos(\pi q_x))\end{aligned}$$

$$\begin{aligned}F_{10} = {} & -16(\sigma_x^j(\tilde{q})\sigma_z^j(\tilde{q})\sin(\pi q_x)\sin(\pi q_z)\cos(2\pi q_y) \\ & +\sigma_x^j(\tilde{q})\sigma_y^j(\tilde{q})\sin(\pi q_x)\sin(\pi q_y)\cos(2\pi q_z) \\ & +\sigma_y^j(\tilde{q})\sigma_z^j(\tilde{q})\sin(\pi q_y)\sin(\pi q_z)\cos(2\pi q_x))\end{aligned}$$

$$\begin{aligned}F_{11} = {} & 8(\sigma_x^j(\tilde{q})^2\cos(2\pi q_x)(\cos(2\pi q_y)+\cos(2\pi q_z)) \\ & +\sigma_y^j(\tilde{q})^2\cos(2\pi q_y)(\cos(2\pi q_x)+\cos(2\pi q_z)) \\ & +\sigma_z^j(\tilde{q})^2\cos(2\pi q_z)(\cos(2\pi q_x)+\cos(2\pi q_y)))\end{aligned}$$

$$\begin{aligned}F_{12} = {} & 16(\sigma_x^j(\tilde{q})^2\cos(2\pi q_y)\cos(2\pi q_z) \\ & +\sigma_y^j(\tilde{q})^2\cos(2\pi q_x)\cos(2\pi q_z) \\ & +\sigma_z^j(\tilde{q})^2\cos(2\pi q_x)\cos(2\pi q_y))\end{aligned}$$

$$\begin{aligned}F_{13} = {} & -16(\sigma_x^j(\tilde{q})\sigma_y^j(\tilde{q})\sin(2\pi q_x)\sin(2\pi q_y) \\ & +\sigma_x^j(\tilde{q})\sigma_z^j(\tilde{q})\sin(2\pi q_x)\sin(2\pi q_z) \\ & +\sigma_y^j(\tilde{q})\sigma_z^j(\tilde{q})\sin(2\pi q_y)\sin(2\pi q_z))\end{aligned}$$

If P_i are the independent Green's functions associated with ν^i and F_i for $i=1,\ldots,13$, then the total Green's function matrix in the first nearest neighbour defect space is given by:

		0	1	2	3	4	5	6	7	8	9	10	11	12
		x y z	x y z	x y z	x y z	x y z	x y z	x y z	x y z	x y z	x y z	x y z	x y z	x y z
	x	1 0 0	2 4 0	2 0 4	3 0 0	2 -4 0	3 0 0	2 0 -4	2 4 0	2 0 4	3 0 0	2 -4 0	3 0 0	2 0 -4
0	y	0 1 0	4 2 0	0 3 0	0 2 4	-4 2 0	0 2 -4	0 3 0	4 2 0	0 3 0	0 2 4	-4 2 0	0 2 -4	0 3 0
	z	0 0 1	0 0 3	4 0 2	0 4 2	0 0 3	0 -4 2	-4 0 2	0 0 3	4 0 2	0 4 2	0 0 3	0 -4 2	-4 0 2
	x	2 4 0	1 0 0	3 0 0	2 0 -4	6 0 0	7 9 a	8 9 -9	b d 0	8 9 9	7 9 -a	5 0 0	2 0 4	3 0 0
1	y	4 2 0	0 1 0	0 2 -4	0 3 0	0 5 0	9 8 -9	9 7 a	d b 0	9 7 -a	9 8 9	0 6 0	0 3 0	0 2 4
	z	0 0 3	0 0 1	0 -4 2	-4 0 2	0 0 6	a -9 7	-9 a 7	0 0 c	9 -a 7	-a 9 7	0 0 6	4 0 2	0 4 2
	x	2 0 4	3 0 0	1 0 0	2 -4 0	3 0 0	2 4 0	5 0 0	8 9 9	b 0 d	7 -a 9	8 -9 9	7 a 9	6 0 0
2	y	0 3 0	0 2 -4	0 1 0	-4 2 0	0 2 4	4 2 0	0 6 0	9 7 -a	0 c 0	-a 7 9	-9 7 a	a 7 -9	0 6 0
	z	4 0 2	0 -4 2	0 0 1	0 0 3	0 4 2	0 0 3	0 0 6	9 -a 7	d 0 b	9 9 8	9 a 7	9 -9 8	0 0 5
	x	3 0 0	2 0 -4	2 -4 0	1 0 0	7 -9 a	6 0 0	2 4 0	7 9 -a	7 -a 9	c 0 0	2 0 4	6 0 0	7 a -9
3	y	0 2 4	0 3 0	-4 2 0	0 1 0	-9 8 9	0 5 0	4 2 0	9 8 9	-a 7 9	0 b d	0 3 0	0 6 0	a 7 9
	z	0 4 2	-4 0 2	0 0 3	0 0 1	a 9 7	0 0 6	0 0 3	-a 9 7	9 9 8	0 d b	4 0 2	0 0 5	-9 9 8
	x	2 -4 0	6 0 0	3 0 0	7 -9 a	1 0 0	2 0 -4	8 -9 -9	5 0 0	8 -9 9	2 0 4	b -d 0	7 -9 -a	3 0 0
4	y	-4 2 0	0 5 0	0 2 4	-9 8 9	0 1 0	0 3 0	-9 7 -a	0 6 0	-9 7 a	0 3 0	-d b 0	-9 8 -9	0 2 -4
	z	0 0 3	0 0 6	0 4 2	a 9 7	0 0 1	-4 0 2	-9 -a 7	0 0 6	9 a 7	4 0 2	0 0 c	-a -9 7	0 -4 2
	x	3 0 0	7 9 a	2 4 0	6 0 0	2 0 -4	1 0 0	2 -4 0	2 0 4	7 a 9	6 0 0	7 -9 -a	c 0 0	7 -a -9
5	y	0 2 -4	9 8 -9	4 2 0	0 5 0	0 3 0	0 1 0	-4 2 0	0 3 0	a 7 -9	0 6 0	-9 8 -9	0 b -d	-a 7 -9
	z	0 -4 2	a -9 7	0 0 3	0 0 6	-4 0 2	0 0 1	0 0 3	4 0 2	9 -9 8	0 0 5	-a -9 7	0 -d b	-9 -9 8
	x	2 0 -4	8 9 -9	5 0 0	2 4 0	8 -9 -9	2 -4 0	1 0 0	3 0 0	6 0 0	7 a -9	3 0 0	7 -a -9	b 0 -d
6	y	0 3 0	9 7 a	0 6 0	4 2 0	-9 7 -a	-4 2 0	0 1 0	0 2 4	0 6 0	a 7 9	0 2 -4	-a 7 -9	0 c 0
	z	-4 0 2	-9 a 7	0 0 6	0 0 3	-9 -a 7	0 0 3	0 0 1	0 4 2	0 0 5	-9 9 8	0 -4 2	-9 -9 8	-d 0 b
	x	2 4 0	b d 0	8 9 9	7 9 -a	5 0 0	2 0 4	3 0 0	1 0 0	3 0 0	2 0 -4	6 0 0	7 9 a	8 9 -9
7	y	4 2 0	d b 0	9 7 -a	9 8 9	0 6 0	0 3 0	0 2 4	0 1 0	0 2 -4	0 3 0	0 5 0	9 8 -9	9 7 a
	z	0 0 3	0 0 c	9 -a 7	-a 9 7	0 0 6	4 0 2	0 4 2	0 0 1	0 -4 2	-4 0 2	0 0 6	a -9 7	-9 a 7
	x	2 0 4	8 9 9	b 0 d	7 -a 9	8 -9 9	7 a 9	6 0 0	3 0 0	1 0 0	2 -4 0	3 0 0	2 4 0	5 0 0
8	y	0 3 0	9 7 -a	0 c 0	-a 7 9	-9 7 a	a 7 -9	0 6 0	0 2 -4	0 1 0	-4 2 0	0 2 4	4 2 0	0 6 0
	z	4 0 2	9 -a 7	d 0 b	9 9 8	9 a 7	9 -9 8	0 0 5	0 -4 2	0 0 1	0 0 3	0 4 2	0 0 3	0 0 6
	x	3 0 0	7 9 -a	7 -a 9	c 0 0	2 0 4	6 0 0	7 a -9	2 0 -4	2 -4 0	1 0 0	7 -9 a	6 0 0	2 4 0
9	y	0 2 4	9 8 9	-a 7 9	0 b d	0 3 0	0 6 0	a 7 9	0 3 0	-4 2 0	0 1 0	-9 8 9	0 5 0	4 2 0
	z	0 4 2	-a 9 7	9 9 8	0 d b	4 0 2	0 0 5	-9 9 8	-4 0 2	0 0 3	0 0 1	a 9 7	0 0 6	0 0 3
	x	2 -4 0	5 0 0	8 -9 9	2 0 4	b -d 0	7 -9 -a	3 0 0	6 0 0	3 0 0	7 -9 a	1 0 0	2 0 -4	8 -9 -9
10	y	-4 2 0	0 6 0	-9 7 a	0 3 0	-d b 0	-9 8 9	0 2 -4	0 5 0	0 2 4	-9 8 9	0 1 0	0 3 0	-9 7 -a
	z	0 0 3	0 0 6	9 a 7	4 0 2	0 0 c	-a -9 7	0 -4 2	0 0 6	0 4 2	a 9 7	0 0 1	-4 0 2	-9 -a 7
	x	3 0 0	2 0 4	7 a 9	6 0 0	7 -9 -a	c 0 0	7 -a -9	7 9 a	2 4 0	6 0 0	2 0 -4	1 0 0	2 -4 0
11	y	0 2 -4	0 3 0	a 7 -9	0 6 0	-9 8 -9	0 b -d	-a 7 -9	9 8 -9	4 2 0	0 5 0	0 3 0	0 1 0	-4 2 0
	z	0 -4 2	4 0 2	9 -9 8	0 0 5	-a -9 7	0 -d b	-9 -9 8	a -9 7	0 0 3	0 0 6	-4 0 2	0 0 1	0 0 3
	x	2 0 -4	3 0 0	6 0 0	7 a -9	3 0 0	7 -a -9	b 0 -d	8 9 -9	5 0 0	2 4 0	8 -9 -9	2 -4 0	1 0 0
12	y	0 3 0	0 2 4	0 6 0	a 7 9	0 2 -4	-a 7 -9	0 c 0	9 7 a	0 6 0	4 2 0	-9 7 -a	-4 2 0	0 1 0
	z	-4 0 2	0 4 2	0 0 5	-9 9 8	0 -4 2	-9 -9 8	-d 0 b	-9 a 7	0 0 6	0 0 3	-9 -a 7	0 0 3	0 0 1

(A-4)

a=10, b=11, c=12, d=13.

where the integers ±i indicate $\pm P_i$, and the atoms are given by:

$$\begin{array}{llll} 0 = (000), & 1 = \frac{a}{2}(110), & 2 = \frac{a}{2}(101), & 3 = \frac{a}{2}(011) \\ 4 = \frac{a}{2}(1\bar{1}0), & 5 = \frac{a}{2}(0\bar{1}1), & 6 = \frac{a}{2}(\bar{1}01), & 7 = \frac{a}{2}(\bar{1}\bar{1}0) \\ 8 = \frac{a}{2}(\bar{1}0\bar{1}), & 9 = \frac{a}{2}(0\bar{1}\bar{1}), & 10 = \frac{a}{2}(\bar{1}10), & 11 = \frac{a}{2}(01\bar{1}) \\ & 12 = \frac{a}{2}(10\bar{1}). & & \end{array} \qquad \text{(A-5)}$$

The other independent Green's functions that are considered, are those connecting the defect site to the 2nd, 3rd, 4th or 5th nearest neighbour shells. These Green's function matrices will only be considered to within a rotational transformation.

Following the method outlined above, it is found that the Green's function matrices connecting the defect to a second, third and fourth nearest neighbour shell atom are, respectively:

$$\begin{array}{ll|ccc|} \frac{a}{2} & & (200)\ x & (200)\ y & (200)\ z \\ (000) & x & P_5 & 0 & 0 \\ (000) & y & 0 & P_6 & 0 \\ (000) & z & 0 & 0 & P_6 \end{array} \qquad \text{(A-6)}$$

$$\begin{array}{ll|ccc|} \frac{a}{2} & & (211)\ x & (211)\ y & (211)\ z \\ (000) & x & P_8 & P_9 & P_9 \\ (000) & y & P_9 & P_7 & P_{10} \\ (000) & z & P_9 & P_{10} & P_7 \end{array} \qquad \text{(A-7)}$$

$$\begin{array}{ccc|ccc|} & & \frac{a}{2} & (200) & (200) & (200) \\ & & & x & y & z \\ (000) & x & & P_{11} & P_{13} & 0 \\ (000) & y & & P_{13} & P_{11} & 0 \\ (000) & z & & 0 & 0 & P_{12} \end{array} \qquad \text{(A-8)}$$

The Green's function matrix connecting the defect to a fifth nearest neighbour shell atom is given in terms of

$$\begin{aligned} F_{14} = \; & 8(\sigma_x^j(\tilde{q})^2\cos(3\pi q_x)(\cos(\pi q_y)+\cos(\pi q_z)) \\ & +\sigma_y^j(\tilde{q})^2\cos(3\pi q_y)(\cos(\pi q_x)+\cos(\pi q_z)) \\ & +\sigma_z^j(\tilde{q})^2\cos(3\pi q_z)(\cos(\pi q_x)+\cos(\pi q_y))) \end{aligned}$$

$$\begin{aligned} F_{15} = \; & 8(\sigma_x^j(\tilde{q})^2\cos(\pi q_x)(\cos(3\pi q_y)+\cos(3\pi q_z)) \\ & +\sigma_y^j(\tilde{q})^2\cos(\pi q_y)(\cos(3\pi q_x)+\cos(3\pi q_z)) \\ & +\sigma_z^j(\tilde{q})^2\cos(\pi q_z)(\cos(3\pi q_x)+\cos(3\pi q_y))) \end{aligned}$$

$$\begin{aligned} F_{16} = \; & 8(\sigma_x^j(\tilde{q})^2(\cos(3\pi q_z)\cos(\pi q_y)+\cos(\pi q_z)\cos(3\pi q_y)) \\ & +\sigma_y^j(\tilde{q})^2(\cos(3\pi q_x)\cos(\pi q_z)+\cos(\pi q_x)\cos(3\pi q_z)) \\ & +\sigma_z^j(\tilde{q})^2(\cos(3\pi q_x)\cos(\pi q_y)+\cos(\pi q_x)\cos(3\pi q_y))) \end{aligned}$$

$$\begin{aligned} F_{17} = \; & -8(\sigma_x^j(\tilde{q})\sigma_y^j(\tilde{q})(\sin(3\pi q_x)\sin(\pi q_y)+\sin(\pi q_x)\sin(3\pi q_y)) \\ & +\sigma_x^j(\tilde{q})\sigma_z^j(\tilde{q})(\sin(3\pi q_x)\sin(\pi q_z)+\sin(\pi q_x)\sin(3\pi q_z)) \\ & +\sigma_y^j(\tilde{q})\sigma_z^j(\tilde{q})(\sin(3\pi q_y)\sin(\pi q_z)+\sin(\pi q_y)\sin(3\pi q_z))) \end{aligned}$$

by associating each P_i with ν^i and F_i for $i=14,\ldots,17$.

The Green's function matrix connecting a fifth nearest neighbour shell atom to the defect atom can thus be written as:

$$\begin{array}{cc|ccc|} & \frac{a}{2} & \begin{matrix}(310)\\ x\end{matrix} & \begin{matrix}(310)\\ y\end{matrix} & \begin{matrix}(310)\\ z\end{matrix} \\ (000) & x & P_{14} & P_{17} & 0 \\ (000) & y & P_{17} & P_{15} & 0 \\ (000) & z & 0 & 0 & P_{16} \end{array} \qquad \text{(A-9)}$$

APPENDIX II

THE REDUCTION MATRIX FOR THE FIRST NEAREST NEIGHBOUR DEFECT SPACE IN AN F.C.C. LATTICE

To obtain the reduction matrix for the first nearest neighbour defect space of an f.c.c. lattice, the character table for the O_h group must be used. This table can be obtained from any standard reference, such as Koster (1957). With this table and the character of the total representation of the group

$$\begin{array}{lcccccccccccl} & & E & 8C_3 & 3C_4^2 & 6C_2 & 6C_4 & I & 8S_6 & 3\sigma_h & 6\sigma_h & 6S_4 & \\ \chi(\underline{\underline{C}})_{f.c.c.} & = & 39 & 0 & -1 & -3 & 1 & 13 & 0 & 5 & 3 & -1 & \text{(A-10)} \end{array}$$

the total representation $\Gamma_{f.c.c.}$ is found to be composed of the following irreducible representations:

$$\Gamma_{f.c.c.} = A_{1g}+A_{2g}+2E_g+2F_{1g}+2F_{2g}+A_{2u}+E_u+4F_{1u}+2F_{2u} \quad \text{(A-11)}$$

It is seen from (A-11) that the largest block is a 4×4, and is associated with the F_{1u} irreducible representation.

Using this information, and the projection operators $\underline{\underline{P}}_{ij}^{(\sigma)}$, the eigenvectors $\Psi^{(\sigma_i)}$ are found to be, (A-12),(A-13):

	A_{1g}	A_{2g}	E_g^1	E_g^2	F_{1g}^1	F_{1g}^2	F_{1g}^3	F_{2g}^1	F_{2g}^2	F_{2g}^3	A_{2u}	E_u^1	E_u^2	F_{1u}^1	F_{1u}^2	F_{1u}^3	F_{2u}^1	F_{2u}^2	F_{2u}^3
x	0	0	0	0	0	0	0	0	0	0	0	0	0	d	0	0	0	0	0
0y	0	0	0	0	0	0	0	0	0	0	0	0	0	0	d	0	0	0	0
z	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	d	0	0	0
x	1	1	a-b	-(a+b)	0	0	-b	0	0	-b	0	0	0	a	-c	0	0	-a	b
1y	1	-1	a-b	a+b	0	0	b	0	0	-b	0	0	0	-b	b	0	0	b	-a
z	0	0	0	0	-b	-a	0	b	a	0	-1	-1	1	0	0	c	0	0	0
x	1	-1	-a	-a	a	0	0	a	0	0	0	0	0	a	0	-a	-a	a	0
2y	0	0	0	0	0	a	-a	0	a	-a	-1	-1	-1	0	a	0	0	0	0
z	1	1	b	b	-a	0	0	a	0	0	0	0	0	-b	0	b	b	-b	0
x	0	0	0	0	b	0	a	b	0	-a	-1	2	0	c	0	0	0	0	0
3y	1	1	-a	a	0	b	0	0	b	0	0	0	0	0	b	-a	a	0	a
z	1	-1	b	-b	0	-b	0	0	b	0	0	0	0	0	-c	b	-b	0	-b
x	1	1	a-b	-(a+b)	0	0	b	0	0	b	0	0	0	a	c	0	0	-a	-b
4y	-1	1	-(a-b)	-(a+b)	0	0	b	0	0	-b	0	0	0	b	b	0	0	-b	-a
z	0	0	0	0	-b	a	0	b	-a	0	1	1	-1	0	0	c	0	0	0
x	0	0	0	0	b	0	-a	b	0	a	1	-2	0	c	0	0	0	0	a
5y	-1	-1	a	-a	0	b	0	0	b	0	0	0	0	0	b	a	-a	0	0
z	1	-1	b	-b	0	b	0	0	-b	0	0	0	0	0	c	b	-b	0	b
x	-1	1	a	a	a	0	0	a	0	0	0	0	0	a	0	a	a	a	0
6y	0	0	0	0	0	a	a	0	a	a	1	1	1	0	a	0	0	0	0
z	1	1	b	b	a	0	0	-a	0	0	0	0	0	b	0	b	b	b	0
x	-1	-1	-(a-b)	a+b	0	0	b	0	0	b	0	0	0	a	-c	0	0	-a	b
7y	-1	1	-(a-b)	-(a+b)	0	0	-b	0	0	b	0	0	0	-b	b	0	0	b	-a
z	0	0	0	0	b	a	0	-b	-a	0	-1	-1	1	0	0	c	0	0	0
x	-1	1	a	a	-a	0	0	-a	0	0	0	0	0	a	0	-a	-a	a	0
8y	0	0	0	0	0	-a	a	0	-a	a	-1	-1	-1	0	a	0	0	0	0
z	-1	-1	-b	-b	a	0	0	-a	0	0	0	0	0	-b	0	b	b	-b	0
x	0	0	0	0	-b	0	-a	-b	0	-a	-1	2	0	c	0	0	0	0	0
9y	-1	-1	a	-a	0	-b	0	0	-b	0	0	0	0	0	b	-a	a	0	a
z	-1	1	-b	b	0	b	0	0	-b	0	0	0	0	0	-c	b	-b	0	-b
x	-1	-1	-(a-b)	a+b	0	0	-b	0	0	-b	0	0	0	a	c	0	0	-a	-b
10y	1	-1	a-b	a+b	0	0	-b	0	0	b	0	0	0	b	b	0	0	-b	-a
z	0	0	0	0	b	-a	0	-b	a	0	1	1	-1	0	0	c	0	0	0
x	0	0	0	0	-b	0	a	-b	0	-a	1	-2	0	c	0	0	0	0	a
11y	1	1	-a	a	0	-b	0	0	-b	0	0	0	0	0	b	a	-a	0	0
z	-1	1	-b	b	0	-b	0	0	b	0	0	0	0	0	c	b	-b	0	b
x	1	-1	-a	-a	-a	0	0	-a	0	0	0	0	0	a	0	a	a	a	0
12y	0	0	0	0	0	-a	-a	0	-a	-a	1	1	1	0	a	0	0	0	0
z	-1	-1	-b	-b	-a	0	0	a	0	0	0	0	0	b	0	b	b	b	0

(A-12)

The unnormalized eigenvectors $\Psi^{(\sigma i)}(\tilde{\ell}\ \alpha)$ for a substitution impurity in f.c.c. lattice possessing O_h symmetry

$a = 1/\sqrt{24}$, $b = 1/4$, $c = 1/\sqrt{48}$ $p = 1/\sqrt{12}$

$m = 1/\sqrt{8}$, $n = 1/\sqrt{728}$, $u = 1/\sqrt{28}$ $w = 1/\sqrt{13}$

W_1 =

		A_1	A_2	E^1	E^1	E^2	E^2	F_1^1	F_1^1	F_1^2	F_1^2	F_1^3	F_1^3	F_2^1	F_2^1	F_2^2	F_2^2	F_2^3	F_2^3
	x	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	y	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	z	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

(A-13_a)

W_2 =

		A_2	E^1	E^2	F_1^1	F_1^1	F_1^1	F_1^1	F_1^2	F_1^2	F_1^2	F_1^2	F_1^3	F_1^3	F_1^3	F_1^3	F_2^1	F_2^1	F_2^2	F_2^2	F_2^3	F_2^3
	x	0	0	0	w	-4u	16n	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	y	0	0	0	0	0	0	0	w	-4u	16n	0	0	0	0	0	0	0	0	0	0	0
	z	0	0	0	0	0	0	0	0	0	0	0	w	-4u	16n	0	0	0	0	0	0	0

(A-13_b)

$$
W_3 =
\begin{array}{|cc|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
 & & A_1 & A_2 & E^1 & E^1 & E^2 & E^2 & F_1^1 & F_1^1 & F_1^2 & F_1^2 & F_1^3 & F_1^3 & F_2^1 & F_2^1 & F_2^2 & F_2^2 & F_2^3 & F_2^3 \\
\hline
 & x & a & a & 0 & -2c & -2c & 0 & 0 & 0 & 0 & 0 & b & -b & 0 & 0 & 0 & 0 & -b & b \\
1 & y & a & -a & 0 & -2c & 2c & 0 & 0 & 0 & 0 & 0 & -b & b & 0 & 0 & 0 & 0 & -b & b \\
 & z & 0 & 0 & 0 & 0 & 0 & 0 & -b & -b & -b & -b & 0 & 0 & b & b & b & b & 0 & 0 \\
\hline
 & x & a & -a & -b & c & -c & -b & b & -b & 0 & 0 & 0 & 0 & b & -b & 0 & 0 & 0 & 0 \\
2 & y & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & b & -b & -b & 0 & 0 & b & b & -b & -b \\
 & z & a & a & b & c & c & -b & -b & b & 0 & 0 & 0 & 0 & b & -b & 0 & 0 & 0 & 0 \\
\hline
 & x & 0 & 0 & 0 & 0 & 0 & 0 & b & b & 0 & 0 & b & b & b & b & 0 & 0 & -b & -b \\
3 & y & a & a & -b & c & c & b & 0 & 0 & b & -b & 0 & 0 & 0 & 0 & b & -b & 0 & 0 \\
 & z & a & -a & b & c & -c & b & 0 & 0 & -b & b & 0 & 0 & 0 & 0 & b & -b & 0 & 0 \\
\hline
 & x & a & a & 0 & -2c & -2c & 0 & 0 & 0 & 0 & 0 & -b & b & 0 & 0 & 0 & 0 & b & -b \\
4 & y & -a & a & 0 & 2c & -2c & 0 & 0 & 0 & 0 & 0 & -b & b & 0 & 0 & 0 & 0 & -b & b \\
 & z & 0 & 0 & 0 & 0 & 0 & 0 & -b & -b & b & b & 0 & 0 & b & b & -b & -b & 0 & 0 \\
\hline
 & x & 0 & 0 & 0 & 0 & 0 & 0 & b & b & 0 & 0 & -b & -b & b & b & 0 & 0 & b & b \\
5 & y & -a & -a & b & -c & -c & -b & 0 & 0 & b & -b & 0 & 0 & 0 & 0 & b & -b & 0 & 0 \\
 & z & a & -a & b & c & -c & b & 0 & 0 & b & -b & 0 & 0 & 0 & 0 & -b & b & 0 & 0 \\
\hline
 & x & -a & a & b & -c & c & b & b & -b & 0 & 0 & 0 & 0 & b & -b & 0 & 0 & 0 & 0 \\
6 & y & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & b & b & b & 0 & 0 & b & b & b & b \\
 & z & a & a & b & c & c & -b & b & -b & 0 & 0 & 0 & 0 & -b & b & 0 & 0 & 0 & 0 \\
\hline
\end{array}
\tag{A-13$_c$}
$$

$$W_4 = \left[\begin{array}{c|ccccccccccccccccccccc}
 & A_2 & E^1 & E^2 & F_1^1 & F_1^1 & F_1^1 & F_1^1 & F_1^2 & F_1^2 & F_1^2 & F_1^2 & F_1^3 & F_1^3 & F_1^3 & F_1^3 & F_2^1 & F_2^1 & F_2^2 & F_2^2 & F_2^3 & F_2^3 \\
\hline
x & 0 & 0 & 0 & w & u & 3n & 0 & 0 & 0 & 0 & m & 0 & 0 & 0 & 0 & 0 & 0 & -b & -b & b & -b \\
1y & 0 & 0 & 0 & 0 & 0 & 0 & m & w & u & 3n & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & -b & -b & -b \\
z & -p & -a & m & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & w & -u & -10n & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
x & 0 & 0 & 0 & w & u & 3n & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & m & -b & b & b & b & 0 & 0 \\
2y & -p & -a & -m & 0 & 0 & 0 & 00 & w & -u & -10n & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
z & 0 & 0 & 0 & 0 & 0 & 0 & m & 0 & 0 & 0 & 0 & w & u & 3n & 0 & b & b & -b & b & 0 & 0 \\
\hline
x & -p & 2a & 0 & w & -u & -10n & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
3y & 0 & 0 & 0 & 0 & 0 & 0 & 0 & w & u & 3n & 0 & 0 & 0 & 0 & m & b & -b & 0 & 0 & b & b \\
z & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & m & w & u & 3n & 0 & -b & -b & 0 & 0 & -b & b \\
\hline
x & 0 & 0 & 0 & w & u & 3n & 0 & 0 & 0 & 0 & -m & 0 & 0 & 0 & 0 & 0 & 0 & -b & -b & -b & b \\
4y & 0 & 0 & 0 & 0 & 0 & 0 & -m & w & u & 3n & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -b & b & -b & -b \\
z & p & a & -m & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & w & -u & -10n & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
x & p & -2a & 0 & w & u & -10n & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
5y & 0 & 0 & 0 & 0 & 0 & 0 & 0 & w & u & 3n & 0 & 0 & 0 & 0 & -m & -b & b & 0 & 0 & b & b \\
z & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -m & w & u & 3n & 0 & -b & -b & 0 & 0 & b & -b \\
\hline
x & 0 & 0 & 0 & w & u & 3n & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -m & b & -b & b & b & 0 & 0 \\
6y & p & a & m & 0 & 0 & 0 & 0 & w & -u & -10n & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
z & 0 & 0 & 0 & 0 & 0 & 0 & -m & 0 & 0 & 0 & 0 & w & u & 3n & 0 & b & b & b & -b & 0 & 0
\end{array}\right]$$

$(A\text{-}13_d)$

$$M^{+} = \begin{array}{|c|c|} \hline W_1 & W_2 \\ \hline W_3 & W_4 \\ \hline -W_3 & W_4 \\ \hline \end{array} \qquad (A\text{-}13_e)$$

where the subscripts g and u denote the even and odd irreducible representations under inversion. As is seen in (A-12),

$$\Psi_g(\tilde{\ell}\ \alpha) = -\Psi_g(-\tilde{\ell}\ \alpha)$$

$$(A\text{-}14)$$

while

$$\Psi_u(\tilde{\ell}\ \alpha) = \Psi_u(-\tilde{\ell}\ \alpha)$$

Using (A-12), all the linearly independent normalized eigenvectors can be found and arranged into the matrix (A-13), which is equal to M^{+}.

This matrix M with the property

$$MM^{+} = I \qquad (A\text{-}15)$$

is the desired reducing matrix.

APPENDIX III

THE REDUCED FORM OF P_1 AND v^1 OF THE FIRST NEAREST NEIGHBOUR DEFECT SPACE IN AN F.C.C. LATTICE

By using (A-13) on matrices (A-4) and (A-27) as follows:

$$P^R = MP_1M^+ \tag{A-16}$$

$$v^R = Mv^1M^+ \tag{A-17}$$

the matrices P_1 and v^1 are block diagonalized. The various different block diagonal elements are:

$$P^R_{A1g} = 24a^2(P_1+2P_3-2P_4-P_5+P_6-2P_8-4P_9+2P_{10}-P_{11}-P_{13}) \qquad (A\text{-}18_a)$$

$$v^R_{A1g} = -24a^2(\alpha+\gamma) \qquad (A\text{-}18_b)$$

$$P^R_{A2g} = 24a^2(P_1-2P_3+2P_4-P_5+P_6+2P_8-4P_9-2P_{10}-P_{11}+P_{13}) \qquad (A\text{-}19_a)$$

$$v^R_{A2g} = 24a^2(\gamma-\alpha) \qquad (A\text{-}19_b)$$

$$P^R_{Eg} = \begin{bmatrix} -8b^2\begin{pmatrix}-2P_1-2P_3+2P_4+2P_5-2P_6\\+2P_8-4P_9-2P_{10}+2P_{11}-2P_{13}\end{pmatrix} & +24bc\begin{pmatrix}-2P_3-2P_4\\+2P_8+2P_{10}\end{pmatrix} \\ 24bc\begin{pmatrix}2P_8+2P_{10}\\-2P_3-2P_4\end{pmatrix} & 24c\begin{pmatrix}2P_1-2P_3+2P_4-2P_5+2P_6\\+2P_8+4P_9-2P_{10}-2P_{11}-2P_{13}\end{pmatrix} \end{bmatrix}$$

$$(A\text{-}20_a)$$

$$v^R_{Eg} = \begin{pmatrix} 16b^2(\alpha-\gamma) & 0 \\ 0 & -48c^2(\alpha+\gamma) \end{pmatrix} \qquad (A\text{-}20_b)$$

$$P^R_{F_{1g}} = \begin{bmatrix} 8b^2\left(\begin{array}{l} 2P_1+4P_2+2P_4+P_5 \\ -P_6-4P_7+4P_9-2P_{10} \\ -P_{11}-P_{12}+P_{13} \end{array}\right) & 8b^2\left(\begin{array}{l} 2P_4-P_5+P_6-2P_{10} \\ +P_{11}-P_{12}-P_{13} \end{array}\right) \\ 8b^2\left(\begin{array}{l} 2P_4-P_5+P_6-2P_{10} \\ +P_{11}-P_{12}-P_{13} \end{array}\right) & -8b^2\left(\begin{array}{l} -2P_1+4P_2-2P_4-P_5 \\ +P_6-4P_7+4P_9+2P_{10} \\ +P_{11}+P_{12}-P_{13} \end{array}\right) \end{bmatrix} \tag{A-21$_a$}$$

$$v^R_{F_{1g}} = \begin{pmatrix} 8b^2(\gamma-\alpha-\beta) & 8b^2(\alpha-\beta-\gamma) \\ 8b^2(\alpha-\beta-\gamma) & 8b^2(\gamma-\alpha-\beta) \end{pmatrix} \tag{A-21$_b$}$$

$$P^R_{F_{2g}} = \begin{bmatrix} 8b^2\left(\begin{array}{l} 2P_1+4P_2-2P_4+P_5 \\ -P_6-4P_7-4P_9+2P_{10} \\ -P_{11}-P_{12}-P_{13} \end{array}\right) & 8b^2\left(\begin{array}{l} -2P_4-P_5+P_6+2P_{10} \\ +P_{11}-P_{12}+P_{13} \end{array}\right) \\ 8b^2\left(\begin{array}{l} -2P_4-P_5+P_6+2P_{10} \\ +2P_{11}-P_{12}+P_{13} \end{array}\right) & -8b^2\left(\begin{array}{l} 2P_1-4P_2-2P_4+P_5 \\ -P_6+4P_7+4P_9+2P_{10} \\ -P_{11}-P_{12}-P_{13} \end{array}\right) \end{bmatrix} \tag{A-22$_a$}$$

$$v^R_{F_{2g}} = \begin{pmatrix} -8b^2(\alpha+\beta+\gamma) & 8b^2(\alpha-\beta+\gamma) \\ 8b^2(\alpha-\beta+\gamma) & -8b^2(\alpha+\beta+\gamma) \end{pmatrix} \tag{A-22$_b$}$$

$$P^R_{A_u} = -12p^2(-P_1+4P_4+2P_6+4P_{10}-P_{12}) \tag{A-23$_a$}$$

$$v^R_{A_u} = -12p^2\beta \tag{A-23$_b$}$$

$$P^R_{E_u} = 24a\ (P_1+2P_4-2P_6+2P_{10}+P_{12}) \tag{A-24$_a$}$$

$$v^R_{E_u} = -24a^2\beta \tag{A-24$_b$}$$

$$P^R_{F_{1u}} = \begin{bmatrix} w^2\left(\begin{array}{l}13P_1+48P_2\\ +24P_3+8P_5\\ +16P_6+32P_7\\ +16P_8+8P_{11}\\ +4P_{12}\end{array}\right) & 4uw\left(\begin{array}{l}-6P_2-P_3\\ +2P_5+4P_8\\ +2P_{11}-P_{12}\end{array}\right) & 8nw\left(\begin{array}{l}5P_2+9P_3\\ +3P_5-7P_6\\ -14P_7+6P_8\\ +3P_{11}-5P_{12}\end{array}\right) & 8mw\left(\begin{array}{l}P_4+4P_9\\ +P_{13}\end{array}\right) \\ & 4n^2\left(\begin{array}{l}7P_1-24P_2\\ +12P_3+2P_5\\ +4P_6-8P_7\\ +4P_8+2P_{11}\\ +P_{12}\end{array}\right) & 8nu\left(\begin{array}{l}-22P_2+18P_3\\ +3P_5+13P_6\\ -26P_7+6P_8\\ +3P_{11}+5P_{12}\end{array}\right) & 8mu(-4P_4+P_{13}) \\ & & 8n^2\left(\begin{array}{l}91P_1-24P_2\\ -142P_3+9P_5\\ +109P_6-120P_7\\ +18P_8+9P_{11}\\ +50P_{12}\end{array}\right) & 8mn\left(\begin{array}{l}16P_4-14P_9\\ +3P_{13}\end{array}\right) \\ & & & 8m^2\left(\begin{array}{l}P_1-2P_4\\ -P_5-P_6\\ -2P_{10}+P_{11}\end{array}\right) \end{bmatrix} \qquad (A\text{-}25_a)$$

$$v^R_{F_{1u}} = \begin{pmatrix} w^2\varepsilon\omega^2 & -4uw\varepsilon\omega^2 & 16nw\varepsilon\omega^2 & 0 \\ & u^2\left(\begin{array}{l}16\varepsilon\omega^2-200\alpha\\ -36\beta\end{array}\right) & un\left(\begin{array}{l}-64\varepsilon\omega^2+520\alpha\\ +312\beta\end{array}\right) & -40\gamma um \\ & & n^2\left(\begin{array}{l}256\varepsilon\omega^2-1352\alpha\\ -676\beta\end{array}\right) & 104\gamma nm \\ & & & -8m^2\alpha \end{pmatrix} \qquad (A\text{-}25_b)$$

where $P^R_{F_{1u}} = (P^R_{F_{1u}})^T$ and $v^R_{F_{1u}} = (v^R_{F_{1u}})^T$

$$P^R_{F_{2u}} = \begin{bmatrix} 8b^2\left(\begin{array}{l}2P_1-2P_3+2P_4-2P_8\\ +4P_9+2P_{10}+2P_{11}\\ -2P_{13}\end{array}\right) & 8b^2\left(\begin{array}{l}-2P_3-2P_4+2P_5\\ +2P_6-2P_8-2P_{10}\end{array}\right) \\ 8b^2\left(\begin{array}{l}-2P_3-2P_4+2P_5\\ +2P_6-2P_8-2P_{10}\end{array}\right) & -8b^2\left(\begin{array}{l}-2P_1+2P_3-2P_4\\ +2P_8+4P_9-2P_{10}\\ -2P_{11}-2P_{13}\end{array}\right) \end{bmatrix} \qquad (A\text{-}26_a)$$

$$v^R_{F_{2u}} = \begin{pmatrix} 16b^2(\gamma-\alpha) & 0 \\ 0 & -16b^2(\alpha+\gamma) \end{pmatrix} \qquad (A\text{-}26_b)$$

$$
\begin{array}{c|c|c|c|c|c|c|c|c|c|c|c|c|c}
 & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\
 & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z & x\;y\;z \\
\hline
0\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}w&0&0\\0&w&0\\0&0&w\end{matrix} & \begin{matrix}\alpha&\gamma&0\\\gamma&\alpha&0\\0&0&\beta\end{matrix} & \begin{matrix}\alpha&0&\gamma\\0&\beta&0\\\gamma&0&\alpha\end{matrix} & \begin{matrix}\beta&0&0\\0&\alpha&\gamma\\0&\gamma&\alpha\end{matrix} & \begin{matrix}\alpha&-\gamma&0\\-\gamma&\alpha&0\\0&0&\beta\end{matrix} & \begin{matrix}\beta&0&0\\0&\alpha&-\gamma\\0&-\gamma&\alpha\end{matrix} & \begin{matrix}\alpha&0&-\gamma\\0&\beta&0\\-\gamma&0&\alpha\end{matrix} & \begin{matrix}\alpha&\gamma&0\\\gamma&\alpha&0\\0&0&\beta\end{matrix} & \begin{matrix}\alpha&0&\gamma\\0&\beta&0\\\gamma&0&\alpha\end{matrix} & \begin{matrix}\beta&0&0\\0&\alpha&\gamma\\0&\gamma&\alpha\end{matrix} & \begin{matrix}\alpha&-\gamma&0\\-\gamma&\alpha&0\\0&0&\beta\end{matrix} & \begin{matrix}\beta&0&0\\0&\alpha&-\gamma\\0&-\gamma&\alpha\end{matrix} & \begin{matrix}\alpha&0&-\gamma\\0&\beta&0\\-\gamma&0&\alpha\end{matrix} \\
\hline
1\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\alpha&\gamma&0\\\gamma&\alpha&0\\0&0&\beta\end{matrix} & \begin{matrix}-\alpha&-\gamma&0\\-\gamma&-\alpha&0\\0&0&-\beta\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
2\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\alpha&0&\gamma\\0&\beta&0\\\gamma&0&\alpha\end{matrix} & 0 & \begin{matrix}-\alpha&0&-\gamma\\0&-\beta&0\\-\gamma&0&-\alpha\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
3\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\beta&0&0\\0&\alpha&\gamma\\0&\gamma&\alpha\end{matrix} & 0 & 0 & \begin{matrix}-\beta&0&0\\0&-\alpha&-\gamma\\0&-\gamma&-\alpha\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
4\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\alpha&-\gamma&0\\-\gamma&\alpha&0\\0&0&\beta\end{matrix} & 0 & 0 & 0 & \begin{matrix}-\alpha&\gamma&0\\\gamma&-\alpha&0\\0&0&-\beta\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
5\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\beta&0&0\\0&\alpha&-\gamma\\0&-\gamma&\alpha\end{matrix} & 0 & 0 & 0 & 0 & \begin{matrix}-\beta&0&0\\0&-\alpha&\gamma\\0&\gamma&-\alpha\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
6\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\alpha&0&-\gamma\\0&\beta&0\\-\gamma&0&\alpha\end{matrix} & 0 & 0 & 0 & 0 & 0 & \begin{matrix}-\alpha&0&\gamma\\0&-\beta&0\\\gamma&0&-\alpha\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
7\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\alpha&\gamma&0\\\gamma&\alpha&0\\0&0&\beta\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & \begin{matrix}-\alpha&-\gamma&0\\-\gamma&-\alpha&0\\0&0&-\beta\end{matrix} & 0 & 0 & 0 & 0 & 0 \\
\hline
8\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\alpha&0&\gamma\\0&\beta&0\\\gamma&0&\alpha\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \begin{matrix}-\alpha&0&-\gamma\\0&-\beta&0\\-\gamma&0&-\alpha\end{matrix} & 0 & 0 & 0 & 0 \\
\hline
9\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\beta&0&0\\0&\alpha&\gamma\\0&\gamma&\alpha\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \begin{matrix}-\beta&0&0\\0&-\alpha&-\gamma\\0&-\gamma&-\alpha\end{matrix} & 0 & 0 & 0 \\
\hline
10\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\alpha&-\gamma&0\\-\gamma&\alpha&0\\0&0&\beta\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \begin{matrix}-\alpha&\gamma&0\\\gamma&-\alpha&0\\0&0&-\beta\end{matrix} & 0 & 0 \\
\hline
11\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\beta&0&0\\0&\alpha&-\gamma\\0&-\gamma&\alpha\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \begin{matrix}-\beta&0&0\\0&-\alpha&\gamma\\0&\gamma&-\alpha\end{matrix} & 0 \\
\hline
12\;\begin{matrix}x\\y\\z\end{matrix} & \begin{matrix}\alpha&0&-\gamma\\0&\beta&0\\-\gamma&0&\alpha\end{matrix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \begin{matrix}-\alpha&0&\gamma\\0&-\beta&0\\\gamma&0&-\alpha\end{matrix} \\
\hline
\end{array}
\tag{A-27}
$$

$w=\varepsilon\omega^{2}-8\alpha-4\beta$, $\alpha=1XX$, $\gamma=1XY$, $\beta=1ZZ$

APPENDIX IV

SINGULARITIES

It is seen from equations (III-6) and (III-7) that the imaginary part of the Green's function Im $P_{\alpha\beta}(\tilde{\ell},\ell';\omega)$ is directly related to the weighted density of states $\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega)$. This weighted density of states is given by (III-7), i.e.,

$$\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega) = \frac{1}{(2\pi)^3}\,\frac{1}{n_A}\sum_j \int d^3k\,\sigma_\alpha^j(\tilde{k})\,\sigma_\beta^j(\tilde{k})\,e^{-i\tilde{k}.(\tilde{\ell}-\tilde{\ell}')}\,\delta(\omega_j(\tilde{k})-\omega) \tag{A-28}$$

Using the fact that

$$d^3k = dS_{\omega=\omega_j(\tilde{k})}\,dk_\perp = dS_{\omega=\omega_j(\tilde{k})}\,\frac{d\omega}{|\nabla_k\omega_j(\tilde{k})|} \tag{A-29}$$

equation (A-28) may be written as

$$\nu_{\alpha\beta}(\tilde{\ell}-\tilde{\ell}';\omega) = \frac{1}{(2\pi)^3}\,\frac{1}{n_A}\sum_j \int dS_{\omega=\omega_j(\tilde{k})}\,\frac{\sigma_\alpha(\tilde{k})\,\sigma_\beta(\tilde{k})\,e^{-i\tilde{k}.(\tilde{\ell}-\tilde{\ell}')}}{|\nabla_k\omega_j(k)|} \tag{A-30}$$

It is a well known fact that the critical points or singularities of the density of states is due to the term

$$|\nabla_k\omega_j(\tilde{k})| \tag{A-31}$$

and occurs at frequencies for which this denominator term vanishes. Since equation (A-30) for any weighted density of states has the same term affecting the denominator as the density of states, thus it too will have such singularities and at the same frequencies.

APPENDIX V

THE FACTOR 1/n FROM THE CONVOLUTION MODEL

The maximum amplitude of a Gaussian

$$\frac{\exp\left(-\dfrac{[\omega-c(s_o+s_1\omega_j(k))-\omega_j(k)]^2}{c^2[w_o+w_1\omega_j(k)]^2\ln 2}\right)}{\sqrt{\pi \ln 2}\; c(w\ +w\ \omega\ (k))} \qquad (A-32)$$

is

$$\frac{1}{\sqrt{\pi \ln 2}\; c(w_o+w_1\omega_j(k))} \qquad (A-33)$$

and so the frequency ω, at which the ratio of equations (A-32) and (A-33) is 1/n, can be found from

$$\frac{1}{n} = \exp\left(-\frac{[\omega-c(s_o+s_1\omega_j(k))-\omega_j(k)]^2}{c^2\ln 2[w_o+w_1\omega_j(k)]^2}\right)$$

That is to say,

$$\omega\ = c\sqrt{(\ln\ n)\ln(2)}\ (w_o+w_1\omega_j(k))+c(s_o+s_1\omega_j(k))+\omega_j(k) \qquad (A-35)$$

This factor 1/n is that point on the tail of the Gaussian which shifts in concentration, as does singularity B in the convolution model, i.e.,

$$\frac{d\omega}{dc} = A_{CM} \simeq \text{constant} = \sqrt{(\ln\ n)(\ln 2)}\ (w_o+w_1\omega_j(k))+(s_o+s_1\omega_j(k)) \qquad (A-36)$$

or

$$\frac{1}{n} = \exp\left\{-\frac{1}{\ln 2}\left(\frac{A_{CM}-s_0-s_1\omega_j(k)}{w_o+w_1\omega_j(k)}\right)^2\right\} \qquad \text{(A-37)}$$

Similarly, for a Lorentzian it can be shown that

$$\frac{1}{n} = \frac{(w_o+w_1\omega_j(k))^2}{(A_{CM}-s_o-s_1\omega_j(k))^2+(w_o+w_1\omega_j(k))^2} \qquad \text{(A-38)}$$

where A_{CM} in (A-38) must be determined, from the convolution model, using Lorentzians.

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