CALCULATION OF THE ENTROPY OF A COPPER

LATTICE CONTAINING RANDOM MASS DEFECTS

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ABSTRACT

Entropy of mixing for random mass defects is examined and equations for the phonon contribution are developed. The Green's function method used gives the entropy change due to the phonons at all temperatures, but for experimental comparison the high temperature region is used. There simple formulae obtain, but the mass defect is not sufficient to account for the observed entropy changes. This suggests that further work is necessary.

ACKNOWLEDGEMENTS B

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INTRODUCTION

The following report is set out in four sections. The first explores the mysteries of the entropy of mixing, which turns out to be the sum of many things

$$\Delta S_{MIX} = \Delta S_{CON} + \Delta S_{ph} + \Delta S_{VOL} + \Delta S_{EL} \quad .$$

This report deals only with the first two terms, the configuration entropy and the phonon entropy. It is also only a beginning and so the phonon entropy is treated as the result of a mass defect alone with no change in the force constants. The contribution due to a change in electronic configuration seems always to be argued away by pleading similarity to chemical species. The same will be done here.

The second section deals with the assumptions for a model of a crystal containing impurities and painstakingly derives formulae for the phonon entropy from basic principles (essentially Newton's force law, periodicity, energy conservation and Boltzmann's principle).

The third section tells the story of one student's battle with Fortran and the totally reduced Green's function that rose like a Pheonix from a generalized density of states. Armed with these functions the entropy

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due to a low concentration of single mass defects could be found by intensive Riemann summing over frequency bins.

The final section is a discussion of the results and a glimpse at some experimental data. The upshot of which is that for the copper-gold system, the mass change accounts for only one quarter of the observed entropy change.

For the readers delectation, some listings of the programs used in the thermodynamic calculations are included at the end.

CHAPTER I

ON ENTROPY CHANGES DUE TO IMPURITIES

If there are N atoms or molecules of a certain
sort, in equilibrium, on replacing M of these with
another sort, the new system will have different
equilibrium thermal properties even if chemical
reactions have not taken place. In particular, the
number of states (Ω) accessible to the system will change,
for a given set of external conditions (e.g., volume,
temperature). The entropy (S), properly a pure number,
is given by

$$S \equiv \ln\Omega \quad . \tag{1a}$$

For historic and philosophic reasons, it is usually given
in units of Energy/°K and defined by

$$S \equiv k\ln\Omega \quad . \tag{1b}$$

The units of k (Boltzmann's constant) stem from the
historic relation

$$dS = \frac{dQ}{T}$$

used to thermodynamically define entropy, and the
unshakeable conviction that temperature is what is read
from an ideal thermometer in °K[1].

Assuming that the molecules are tiny billiard
balls, and the impurities have a different color; then the
change in entropy will be purely geometric in origin. In
fact, for each state of the pure system, the introduction
of impurities will break it up into a multiplicity of
states arising from the physically different spatial
arrangements. If this multiplicity is Ω', then the total
number of states accessible to the impure system is

$$\Omega'\Omega$$

since for each state of the pure system, the impure system
can occupy any element in its range (Ω') of physically
different atomic configurations. The configurational
entropy change is defined by

$$S_{CON} \equiv \ell n(\Omega'\Omega) - \ell n(\Omega) = \ell n\Omega' \quad . \tag{2}$$

Relating Ω' to N and M is a simple matter of combinatorics.
We may consider N holes in space to be filled with (N-M)
red, and M blue balls. The N holes may be filled in N!
ways with N different colored balls. However, M of them
have the same color and any of these M may be switched

among themselves in M! ways; with no change in the physical consequences. So in the N! total, each physical state has been counted at least M! times too many. The same is true of the (N-M) red balls. Thus the multiplicity is

$$\Omega' = \frac{N!}{M!(N-M)!}$$

and (2) becomes

$$\Delta S_{CON} = \ln(N!) - \ln(M!) - \ln[(N-M)!] \tag{3}$$

on invoking Stirling's approximation

$$\ln(n!) \stackrel{\sim}{\sim} n\ln n - n$$

and for n large, (3) becomes

$$\Delta S_{CON} = N\ln N - M\ln M - (N-M)\ln(N-M) \quad . \tag{4}$$

Then setting $c \equiv \frac{M}{N}$, (4) can be written[2], after some algebra, as

$$\Delta S_{CON} = [-(1-c)\ln(1-c) - c\ln c]N \quad . \tag{5}$$

Picturing the differences between chemical species as purely one of quality and omitting precisely what might
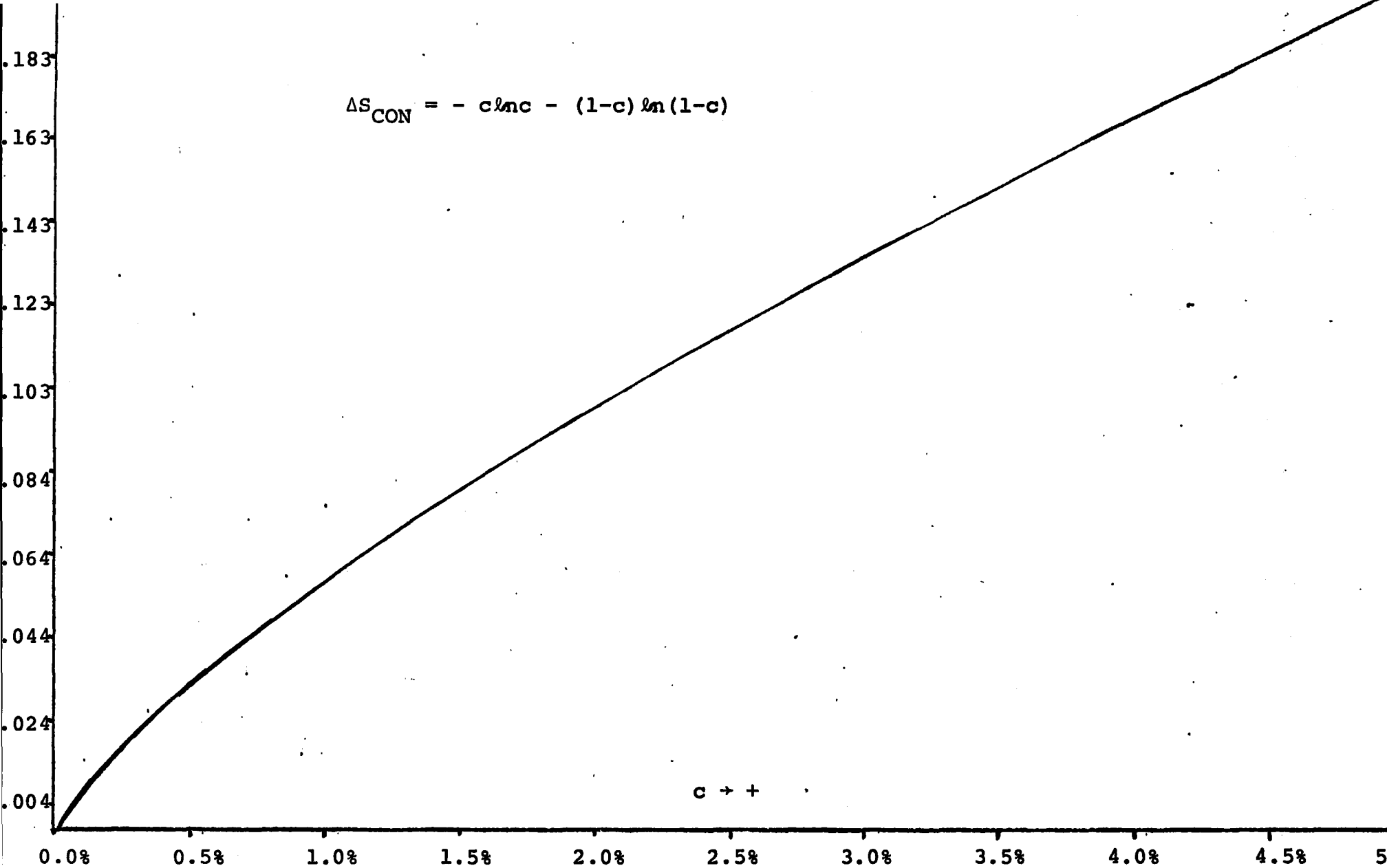
$$\Delta S_{CON} = - c \ln c - (1-c) \ln (1-c)$$

Fig. 1: Change in Configuration Entropy (ΔS_{CON}) vs. Defect Concentration (c)

be known – size, mass, and interaction; may seem

unphysical. But it is precisely the physical assumption

that the replacement atoms have the same degrees of freedom

though physically different from the host atoms, that lies

behind this geometric contribution to the entropy of

mixing. Since it is common to any simple solid, liquid[3], or

gas[4] mixture, it may be regarded as a "first order"

approximation.

When the entropy of mixing is actually measured,

the excess entropy is defined by

$$\Delta S_{EX} \equiv \Delta S_{MIX} - \Delta S_{CON} \quad . \tag{6}$$

This method of decomposition is suited to (and probably

motivated by) phenomenological model building. Provided

the entropy of mixing is experimentally well known, the

excess entropy can be honed down by expressing it in terms

of atomic parameters, which hopefully can be independently

measured. Thus, the concept of excess entropy appears as

a part of the scaffolding, to be eliminated on completion

of an adequate model.

CHAPTER II

THE MODEL

2.1 A Perfect Host Crystal With Impurity Atoms Placed Randomly On Lattice Sites

This ensures that host and impurity have the same spatial degrees of freedom and the configuration entropy can be applied as derived. Notice that if this assumption was not obeyed, then if the perfect host crystal had r atoms in each of the L unit cells ($r \cdot L = N$) and the M impurity atoms could sit on any of p non-lattice sites in a unit cell, then there would be (N-M+pL) holes to be filled with atoms and the spatial entropy would be

$$\Delta S = \ell n \left[\frac{(N-M+pL)!}{M!(N-M)!(pL-M)!} \right] \quad .$$

Clearly, if neutron or X-ray studies were not available, these sort of gimmicks would be some of the first things tried in order to eliminate the excess entropy. This assumption also removes odd-ball chemical effects such as long range superstructures or short range clustering of impurities. That the impurities can be treated as chemically inert and homogeneous (adequately annealed) must be confirmed independently.

2.2 The Lattice Will Obey the Simple Harmonic Approximation

Then the lattice will be effectively described by N point masses held together by Hookean springs[5]. The atoms will be distinguished only by differing masses and force constants. Some of the excess entropy can be explained by the local resonances; which are, in effect, new states accessible to the impure system but not to the pure one. Flynn[6] says that the excess entropy is not large when the impurity and host are similar chemically. Crudely speaking, changed force constants result from chemically dissimilar impurities, but dissimilar masses yield only dynamic differences. These dynamic differences although modified by force constant changes; are indeed significant for the entropy, provided the mass difference is adequate.

Most of the action in this report occurs under this assumption, so this is an appropriate place to set up its machinery. With respect to an arbitrary origin, the displacement of the αth component of the κth atom of the unit cell, in the ℓth unit cell may be written as

$$u_\alpha \begin{pmatrix} \ell \\ \kappa \end{pmatrix} \qquad \alpha \in (1, 2, 3)$$

$$\kappa \in (1, \ldots, r)$$

$$\ell \in (1, \ldots, L) \quad .$$

The Hamiltonian

$$H = T + V \tag{7}$$

has a Newtonian kinetic energy part

$$T = \frac{1}{2} \sum_{\ell,\kappa,\alpha} M_\alpha \binom{\ell}{\kappa} \dot{u}_\alpha^2 \binom{\ell}{\kappa} = \frac{1}{2} \sum_{\ell,\kappa,\alpha} P_\alpha^2 \binom{\ell}{\kappa} / M_\alpha \binom{\ell}{\kappa} \tag{8}$$

using $P_\alpha \binom{\ell}{\kappa} = M_\alpha \binom{\ell}{\kappa} \dot{u}_\alpha \binom{\ell}{\kappa}$, with $M_\alpha \binom{\ell}{\kappa}$ the mass point having displacement $u_\alpha \binom{\ell}{\kappa}$; and a potential V which is an instantaneous function of atomic positions. Expanding the potential in a Taylor's series about the equilbirium displacements ($u_0 \equiv 0$), gives

$$V = V_0 + \sum_{\ell,\kappa,\alpha} \left[\frac{\partial V}{\partial u_\alpha \binom{\ell}{\kappa}} \Big|_0 \right] u_\alpha \binom{\ell}{\kappa}$$

$$+ \frac{1}{2} \sum_{\substack{\ell,\alpha,\kappa \\ \ell',\alpha',\kappa'}} \left[\frac{\partial^2 V}{\partial u_\alpha \binom{\ell}{\kappa} \partial u_{\alpha'} \binom{\ell'}{\kappa'}} \Big|_0 \right] u_\alpha \binom{\ell}{\kappa} u_{\alpha'} \binom{\ell'}{\kappa'} + \ldots$$

The essence of the simple harmonic approximation is that the displacements are small, so that terms higher than the second order in this expansion are inconsequential. This makes the springs Hookean; as V_0 is an arbitrary static potential, and

$$- \frac{\partial V}{\partial u} = F_R(u)$$

is the restoring force at the displacement u and identically
zero at equilibrium, leaving

$$V = \frac{1}{2} \sum_{\substack{\ell,\kappa,\alpha \\ \ell',\kappa',\alpha'}} \Phi_{\alpha\alpha'}\left(\begin{smallmatrix}\ell\ell'\\\kappa\kappa'\end{smallmatrix}\right) u_\alpha\left(\begin{smallmatrix}\ell\\\kappa\end{smallmatrix}\right) u_{\alpha'}\left(\begin{smallmatrix}\ell'\\\kappa'\end{smallmatrix}\right) \tag{9}$$

with the force constant matrix defined by

$$\Phi_{\alpha\alpha'} \equiv \left.\frac{\partial^2 V}{\partial u_\alpha\left(\begin{smallmatrix}\ell\\\kappa\end{smallmatrix}\right) \partial u_{\alpha'}\left(\begin{smallmatrix}\ell'\\\kappa'\end{smallmatrix}\right)}\right|_0 \quad .$$

On combining Eqs. (7), (8), and (9), the Hamiltonian becomes

$$H = \frac{1}{2} \sum_{\ell,\kappa,\alpha} P_\alpha^2\left(\begin{smallmatrix}\ell\\\kappa\end{smallmatrix}\right)/M_\alpha\left(\begin{smallmatrix}\ell\\\kappa\end{smallmatrix}\right)$$

$$+ \frac{1}{2} \sum_{\substack{\ell,\kappa,\alpha \\ \ell',\kappa',\alpha'}} \Phi_{\alpha\alpha'}\left(\begin{smallmatrix}\ell\ell'\\\kappa\kappa'\end{smallmatrix}\right) u_\alpha\left(\begin{smallmatrix}\ell\\\kappa\end{smallmatrix}\right) u_{\alpha'}\left(\begin{smallmatrix}\ell'\\\kappa'\end{smallmatrix}\right) \tag{10}$$

and Hamilton's equations are

$$\dot{P}_\alpha\left(\begin{smallmatrix}\ell\\\kappa\end{smallmatrix}\right) = - \sum_{\ell',\kappa',\alpha'} \Phi_{\alpha\alpha'}\left(\begin{smallmatrix}\ell\ell'\\\kappa\kappa'\end{smallmatrix}\right) u_{\alpha'}\left(\begin{smallmatrix}\ell'\\\kappa'\end{smallmatrix}\right)$$

or

$$M_\alpha\left(\begin{smallmatrix}\ell\\\kappa\end{smallmatrix}\right)\ddot{u}_\alpha\left(\begin{smallmatrix}\ell\\\kappa\end{smallmatrix}\right) = - \sum_{\ell',\kappa',\alpha'} \Phi_{\alpha\alpha'}\left(\begin{smallmatrix}\ell\ell'\\\kappa\kappa'\end{smallmatrix}\right) u_{\alpha'}\left(\begin{smallmatrix}\ell'\\\kappa'\end{smallmatrix}\right) \quad . \tag{11}$$

Equations (11) are indeed of the form required by Hookes
law

$$F = kx \quad .$$

Equation (11) may be rewritten by Fourier transforming the position operators

$$u_\alpha(^\ell_\kappa;t) = \int_{-\infty}^{+\infty} e^{-i\omega t} u_\alpha(^\ell_\kappa;\omega)\,d\omega$$

to give

$$M_\alpha(^\ell_\kappa)\frac{d^2}{dt^2}\int_{-\infty}^{+\infty} e^{-i\omega t} u_\alpha(^\ell_\kappa;\omega)\,d\omega = -\sum_{\ell',\kappa',\alpha'}\Phi_{\alpha\alpha'}(^{\ell\ell'}_{\kappa\kappa'})$$
$$\times \int_{-\infty}^{+\infty} e^{-i\omega t} u_{\alpha'}(^{\ell'}_{\kappa'};\omega)\,d\omega$$

which simplifies to

$$M_\alpha(^\ell_\kappa)\omega^2 u_\alpha(^\ell_\kappa;\omega) = \sum_{\ell',\kappa',\alpha'}\Phi_{\alpha\alpha'}(^{\ell\ell'}_{\kappa\kappa'}) u_{\alpha'}(^{\ell'}_{\kappa'};\omega)$$

or

$$\sum_{\ell',\kappa',\alpha'}[\omega^2 M_\alpha^{\frac{1}{2}}(^\ell_\kappa) M_{\alpha'}^{\frac{1}{2}}(^{\ell'}_{\kappa'})\delta_{\alpha\alpha'}(^{\ell\ell'}_{\kappa\kappa'})$$
$$- \Phi_{\alpha\alpha'}(^{\ell\ell'}_{\kappa\kappa'})] u_{\alpha'}(^{\ell'}_{\kappa'};\omega) = 0 \quad . \tag{12}$$

To actually calculate the phonon entropy one must know not only that the phonons are a boson gas, but also the difference in the temperature independent density of phonon states between the pure and impure cases. To obtain the latter quantity the full sophistication of the Green's

function method of Elliot and Taylor[7] is not required. In fact a neat derivation due to Taylor[8] uses the resolvent

$$G^{-1}_{\alpha\alpha'}\left(^{\ell\ell'}_{\kappa\kappa'};\omega\right) \equiv M^{\frac{1}{2}}_{\alpha}\left(^{\ell}_{\kappa}\right)M^{\frac{1}{2}}_{\alpha'}\left(^{\ell'}_{\kappa'}\right)\delta_{\alpha\alpha'}\left(^{\ell\ell'}_{\kappa\kappa'}\right)\omega^2 - \Phi_{\alpha\alpha'}\left(^{\ell\ell'}_{\kappa\kappa'}\right)$$

(13)

for (12). On shifting around the masses, Eq. (13) becomes

$$M^{-\frac{1}{2}}_{\alpha}\left(^{\ell}_{\kappa}\right)G^{-1}_{\alpha\alpha'}\left(^{\ell\ell'}_{\kappa\kappa'};\omega\right)M^{-\frac{1}{2}}_{\alpha'}\left(^{\ell'}_{\kappa'}\right) = \delta_{\alpha\alpha'}\left(^{\ell\ell'}_{\kappa\kappa'}\right)\omega^2$$

$$- M^{-\frac{1}{2}}_{\alpha}\left(^{\ell}_{\kappa}\right)\Phi_{\alpha\alpha'}\left(^{\ell\ell'}_{\kappa\kappa'}\right)M^{-\frac{1}{2}}_{\alpha'}\left(^{\ell'}_{\kappa'}\right) \quad .$$

(14)

Inverting Eq. (14) gives

$$M^{\frac{1}{2}}_{\alpha}\left(^{\ell}_{\kappa}\right)G_{\alpha\alpha'}\left(^{\ell\ell'}_{\kappa\kappa'};\omega\right)M^{\frac{1}{2}}_{\alpha'}\left(^{\ell'}_{\kappa'}\right) = [\delta_{\alpha\alpha'}\left(^{\ell\ell'}_{\kappa\kappa'}\right)\omega^2$$

$$- M^{-\frac{1}{2}}_{\alpha}\left(^{\ell}_{\kappa}\right)\Phi_{\alpha\alpha'}\left(^{\ell\ell'}_{\kappa\kappa'}\right)M^{-\frac{1}{2}}_{\alpha'}\left(^{\ell'}_{\kappa'}\right)]^{-1} \quad .$$

(15)

Note that the second term on the right hand side of Eq. (15) is the dynamical matrix and its eigenvalues are precisely the squares of the frequencies allowed by (12). Taking the trace of both sides of (15) then yields

$$\sum_{\ell,\kappa,\alpha} M^{\frac{1}{2}}_{\alpha}\left(^{\ell}_{\kappa}\right)G_{\alpha\alpha}\left(^{\ell\ell}_{\kappa\kappa};\omega\right)M^{\frac{1}{2}}_{\alpha}\left(^{\ell}_{\kappa}\right)$$

$$= \sum_{\ell,\kappa,\alpha} [\delta_{\alpha\alpha}\left(^{\ell\ell}_{\kappa\kappa}\right)\omega^2 - M^{\frac{1}{2}}_{\alpha}\left(^{\ell}_{\kappa}\right)\Phi_{\alpha\alpha}\left(^{\ell\ell}_{\kappa\kappa}\right)M^{-\frac{1}{2}}_{\alpha}\left(^{\ell}_{\kappa}\right)]^{-1} \quad . \quad (16)$$

Since the trace of a symmetric matrix is the sum of its eigenvalues, Eq. (16) simplifies to

$$\sum_{\ell,\kappa,\alpha} M_\alpha(^\ell_\kappa) G_{\alpha\alpha}(^{\ell\ell}_{\kappa\kappa};\omega) = \sum_S [\omega^2 - \omega_S^2]^{-1} \tag{17}$$

where ω_S is one of the 3N angular frequencies of the lattice vibrations permitted by Eq. (12). Allowing ω to wander slightly into the complex plane, the right hand side of Eq. (17) may be written as

$$\sum_S \frac{1}{\omega^2 - \omega_S^2 + i\varepsilon}$$

with ω, ω_S still real which becomes

$$\sum_S \frac{\omega^2 - \omega_S^2 - i\varepsilon}{(\omega^2 - \omega_S^2)^2 + \varepsilon^2}$$

on rationalizing the denominator. But

$$\lim_{\varepsilon\to 0} \left(- \text{Im} \sum_S \left[\frac{\omega^2 - \omega_S^2 - i\varepsilon}{(\omega^2 - \omega_S^2)^2 + \varepsilon^2}\right]\right)$$

$$= \lim_{\varepsilon\to 0} \left(\sum_S \frac{\varepsilon}{(\omega^2 - \omega_S^2)^2 + \varepsilon^2}\right)$$

is within a normalizing constant of the arc tan representation of Dirac's delta function

$$\lim_{\varepsilon\to 0} \frac{1}{\pi} \left[\frac{\varepsilon}{(x-x_0)^2 + \varepsilon^2}\right] = \delta(x-x_0) \quad .$$

Thus

$$\text{Im} \sum_S [\omega^2 - \omega_S^2]^{-1} = -\pi \sum_S \delta(\omega^2 - \omega_S^2)$$

and finally

$$\text{Im} \sum_S [\omega^2 - \omega_S^2]^{-1} = -\frac{\pi}{2\omega} \sum_S \delta(\omega - \omega_S) \qquad (18)$$

so that in view of Eq. (18), taking imaginary parts of Eq. (17) gives

$$\text{Im} \sum_{\ell, \kappa, \alpha} M_\alpha \binom{\ell}{\kappa} G_{\alpha\alpha} \binom{\ell \ell}{\kappa \kappa}; \omega) = -\frac{\pi}{2\omega} \sum_S \delta(\omega - \omega_S) \quad . \qquad (19)$$

The right hand side of (19) is virtually the required density of states, $g(\omega)$. Now $3Ng(\omega)d\omega$ will count the number of permitted frequencies in a small neighbourhood, $d\omega$, about the frequency ω; and being a distribution function will obey the normalization condition

$$\int_0^\infty g(\omega)d\omega = 1 \quad .$$

But

$$\int_0^\omega \sum_S \delta(\omega - \omega_S)d\omega = N(\omega) \qquad (20)$$

is the number of permitted frequencies between zero and ω. Considering that there are 3N total frequencies between zero and infinity, $g(\omega)d\omega$ may be written as

$$g(\omega)d\omega = \frac{1}{3N} (N(\omega+d\omega) - N(\omega)) \quad .$$

Then treating $d\omega$ as an infinitesimal

$$g(\omega) = \frac{1}{3N} (\frac{N(\omega+d\omega) - N(\omega)}{d\omega}) \quad . \tag{21}$$

Taking the limit, Eq. (21) becomes

$$g(\omega) = \frac{1}{3N} \frac{dN(\omega)}{d\omega} \quad .$$

and substituting from Eq. (20)

$$\sum_S \delta(\omega - \omega_S) = 3Ng(\omega) \tag{22}$$

so Eq. (19) becomes

$$\text{Im} \sum_{\ell,\kappa,\alpha} M_\alpha (^\ell_\kappa) G_{\alpha\alpha} (^{\ell\ell}_{\kappa\kappa};\omega) = - \frac{\pi}{2\omega} 3Ng(\omega) \quad . \tag{23}$$

Apparently the rather "intuitive" way of handling distribution functions that led to Eq. (23) can be justified by practitioners of Lebesgue theory and classical analysis.

The stage is now set to derive the phonon entropy.
Now a phonon can have any of the 3N permitted frequencies
and its energy will be

$$\epsilon_S = \hbar\omega_S \; .$$

(24)

Although the subscript 'S' labels all the distinct phonon
states (3N normal modes), some of these states will have
the same energy (e.g., at least 48 for a cubic crystal).
To derive the entropy from Eq. (24) using energy
conservation and Boltzmann's principle, requires attention
to this detail. Essentially it is a choice between the
expressions

$$E = \sum_S n_S \epsilon_S$$

(25a)

or

$$E = \sum_i n_i \epsilon_i$$

(25b)

giving the total energy E of the phonon gas. In (25a) the
sum is over distinct phonon states labelled by 'S' and in
(25b) the sum is over distinct energy states labelled by 'i'.
Now n_S is the number of phonons in state 'S' and n_i is the
number of phonons in the ith energy level. Since we are
after the result that the entropy is an additive function

of the normal mode frequencies, it would appear that (25a) is the most natural way to write the total energy. But Boltzmann's principle demands (25b) and the trick is to keep the 'i' and 'S' straight.

Suppose that the crystal is weakly coupled to the environment, so that even though the Hamiltonian (10) will not let the crystal reach equilibrium, it does so by appropriately creating and destroying phonons. Once it has reached equilibrium, the coupling will be turned off and the total energy E treated like a constant. Assymptotic formulae for n_S or n_i can then be found: since they must maximize the number of states accessible to the system at equilibrium, subject to the constraint of constant total energy. How does one calculate the number of accessible states? On choosing (25a) one sees that there is only one way to put n_S or any other number of phonons into the state 'S'. In fact knowing the coefficients n_S completely specifies the state of the phonon gas. Thus knowing the decomposition (25a), one would know the state of a single crystal's phonons and not the possible states that the crystal's phonons could have. Since Boltzmann's principle requires maximizing the possible states, one must resort to (25b) as only then is there any freedom in stuffing the crystal with phonons. The freedom arises since more than one distinct state can have the same energy, and if n_i

phonons go into the ith energy level they can do so in many ways depending on how they are shared out among the distinct states belonging to the level.

If the number of ways of parcelling out the energy at each level can be found, then the problem is solved. Since what happens at one energy level is independent of what happens at another, the total number of possibilities for the crystal is simply the product of the number of possibilities at each level. So what can happen in the ith energy level?

Suppose that there are g_i distinct phonon states having the energy (or at least extremely close to g_i). Notice that

$$\sum_i g_i = 3N \quad . \tag{26}$$

Again it is a matter of combinatorics. Rephrasing the problem: "How many ways can n_i balls be placed in g_i boxes, with certain restraints?" It is the restraints that make the problem non-trivial. Firstly the n_i balls are indistinguishable; in that one can decompose a big ripple in the lattice into a whole bunch of linearly adding little ones (normal modes). The only thing that is physically significant is the big ripple and not how the little ripples (excited normal modes) are labelled or added. Secondly the boxes which are the labels for the normal modes are "indistinguishable" since the labelling is quite arbitrary.

Thus both balls and boxes are to be considered interchangeable among themselves. To actually find the number of possible arrangements, imagine all the balls and boxes lying in a heap of $(n_i + g_i)$ objects. The idea is to arrange the objects arbitrarily, but so that every ball will have a single box associated with it. Then each ball can be placed in that box. To insure that there is at least one box for every ball; remove one box from the pile, leaving $(n_i + g_i - 1)$ objects in the pile. If a row of the remaining $(n_i + g_i - 1)$ objects is then made to the right of this box,

initial box $\longleftarrow$ $n_i + g_i - 1$ objects $\longrightarrow$
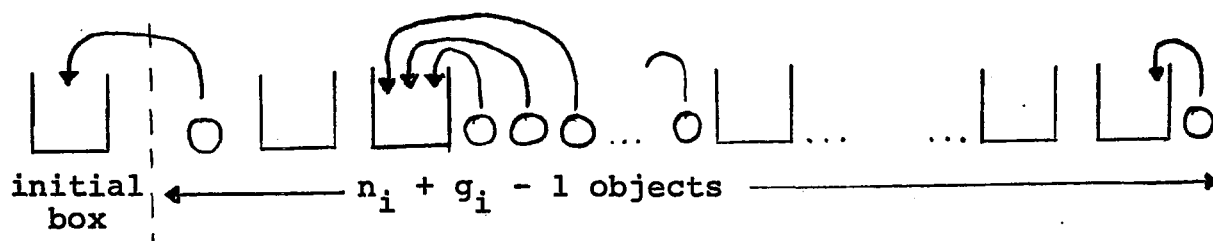
then there is a single box which is left most to every ball. Clearly, every possible way of putting the balls in boxes will be generated in the

$$(n_i + g_i - 1)!$$

possible ways of picking labelled objects from the heap to build the row beside the initial box. However, the n_i balls may be labelled in $n_i!$ possible ways and the $g_i - 1$ boxes may be labelled in $(g_i - 1)!$ ways. Thus the total number of ways n_i balls can be placed in g_i boxes while allowing interchanges

of balls and boxes respectively is

$$\frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \quad .$$

Returning to the interpretation of n_i phonons and g_i phonon states at or near energy ε_i the number of states accessible to these n_i phonons is then

$$\Omega_i = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \quad .$$

Since

$$\sum_i g_i = 3N \tag{26}$$

and the asymptotic formulae occur at $N \to \infty$, it is reasonable to assume that as $N \to \infty$, the g_i at or near ε_i become quite large and the -1 may be omitted giving

$$\Omega_i = \frac{(n_i + g_i)!}{n_i!g_i!} \quad . \tag{27}$$

Then the total number of states accessible to the phonon gas is

$$\Omega_{ph} = \prod_i \Omega_i \quad . \tag{28}$$

Using Eqs. (1a), (26), and (27), the phonon entropy is

$$S_{ph} = \sum_i \ln\left[\frac{(n_i + g_i)!}{n_i! g_i!}\right]$$

and with the aid of Stirling's approximation

$$S_{ph} = \sum_i [(n_i + g_i)\ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i] \quad .$$
(29)

At this point the phonon entropy is known as a function of the thermodynamic unknowns, n_i. The g_i are fixed and in principle known from the equation of motion (12). Boltzmann's principle now comes to the rescue and enables the n_i to be solved in terms of the g_i. Then with this expression for the n_i one can return to (29) and give the entropy explicitly as an additive function of the normal modes. Since maximizing the number of states accessible to the system is equivalent to maximizing its entropy, we have from (29)

$$dS_{ph} = 0 = \sum_i dn_i(\ln(n_i + g_i) - \ln n_i) \quad .$$
(30)

Equation (30) cannot yet be solved as the restriction (25) of constant total energy has not been used. Differentiating (25b) gives

$$dE = 0 = \sum_i dn_i \epsilon_i$$
(31)

since the energy is a constant and the ϵ_i are fixed by the equations of motion (12). Perspicatiously picking $-\frac{1}{T}$ as

a Lagrange multiplier for Eq. (31) gives

$$dS_{ph} - \frac{1}{T} dE = 0 \quad . \tag{32}$$

This T has the dimensions of energy and turns out to have all the properties required of a temperature. On substituting from Eqs. (30) and (31), Eq. (32) becomes

$$\sum_i dn_i (\ln(n_i + g_i) - \ln n_i - \frac{1}{T} \varepsilon_i) = 0 \quad . \tag{33}$$

The only way the sum can be zero is for each of the coefficients of dn_i to be identically zero. This gives

$$\ln(n_i + g_i) - \ln n_i - \frac{1}{T} \varepsilon_i = 0 \tag{34}$$

which can now be solved for n_i

$$n_i = g_i [e^{\varepsilon_i/T} - 1]^{-1} \quad . \tag{35}$$

Returning to Eq. (29) and armed with Eq. (35), the phonon entropy becomes almost accessible

$$S_{ph} = \sum_i g_i [(e^{\varepsilon_i/T} - 1]^{-1} + 1) \ln(g_i([e^{\varepsilon_i/T} - 1]^{-1} + 1))$$

$$- g_i [e^{\varepsilon_i/T} - 1]^{-1} \ln(g_i[e^{\varepsilon_i/T} - 1]^{-1}) - g_i \ln g_i \tag{36}$$

or

$$S_{ph} = \sum_i g_i [([e^{\varepsilon_i/T} - 1]^{-1} + 1) \ln([e^{\varepsilon_i/T} - 1]^{-1} + 1)$$

$$- [e^{\varepsilon_i/T} - 1]^{-1} \ln[e^{\varepsilon_i/T} - 1]^{-1}]$$

$$+ \sum_i g_i \ln g_i [(e^{\varepsilon_i/T} - 1)^{-1} + 1 - (e^{\varepsilon_i/T} - 1)^{-1} - 1] \tag{37}$$

and the second sum in (37) is identically zero. The structure of each term in the first sum of (37) is the number of phonon states at or near energy ε_i multiplied by a function involving only this energy. This fact and Eq. (24) enables (37) to be rewritten as

$$S_{ph} = \sum_S ([e^{\hbar\omega_S/T} - 1]^{-1} + 1) \ln([e^{\hbar\omega_S/T} - 1]^{-1} + 1)$$

$$- [e^{\hbar\omega_S/T} - 1]^{-1} \ln[e^{\hbar\omega_S/T} - 1]^{-1} . \tag{39}$$

Since the phonon entropy is thus an additive function of the normal mode frequencies, the hard won sum over S in Eq. (39) can be replaced by the integral over the density of states according to

$$\sum_S \rightarrow 3N \int g(\omega) d\omega .$$

Using this prescription and further simplifying, Eq. (39) becomes

$$S_{ph} = 3N \int (\frac{e^{\hbar\omega/T}}{e^{\hbar\omega/T} - 1} \ln \frac{e^{\hbar\omega/T}}{e^{\hbar\omega/T} - 1}$$

$$- \frac{1}{e^{\hbar\omega/T} - 1} \ln \frac{1}{e^{\hbar\omega/T} - 1}) g(\omega) d\omega \quad . \tag{40}$$

Unfortunately (40) is algebraically distant from formulae given in the literature[11]. To retrieve Maradudin's formula, Eq. (40) is rearranged to give

$$S_{ph} = 3N \int [\frac{\hbar\omega}{T} (\frac{e^{\hbar\omega/T}}{e^{\hbar\omega/T} - 1}) - \ln(e^{\hbar\omega/T} - 1)] g(\omega) d\omega \quad . \tag{41}$$

The first term in the square brackets can be rewritten as

$$\frac{\hbar\omega}{2T} [\frac{e^{\hbar\omega/T} + 1 + e^{\hbar\omega/T} - 1}{e^{\hbar\omega/T} - 1}]$$

which breaks into two terms

$$\frac{\hbar\omega}{2T} (\frac{e^{\hbar\omega/T} + 1}{e^{\hbar\omega/T} - 1}) + \frac{\hbar\omega}{2T} \quad . \tag{42}$$

Taking the second term of (42) inside the logarithm in Eq. (41) and fiddling with the definitions of hyperbolic trigonometric functions, results in Maradudin's expression

$$S_{ph} = 3N \int g(\omega) d\omega [\frac{\hbar\omega}{2T} \coth \frac{\hbar\omega}{2T} - \ln(2\sinh \frac{\hbar\omega}{2T})] \quad . \tag{43}$$

Finally, the change in phonon entropy

$$\Delta S_{ph} = S'_{ph} - S_{ph}$$

can be written as

$$\Delta S_{ph} = 3N \int \Delta g(\omega) [\frac{\hbar\omega}{2T} \coth \frac{\hbar\omega}{2T} - \ell n(2\sinh \frac{\hbar\omega}{2T})]d\omega \quad (44)$$

where

$$\Delta g = g'(\omega) - g(\omega) \quad (45)$$

with the primes referring to the impure system. Harking back to Eq. (23), it then becomes possible to write Eq. (45) as

$$\Delta g(\omega) = \frac{2\omega}{3\pi N} \text{Im} \sum_{\ell,\kappa,\alpha} [mP_{\alpha\alpha}(^{\ell\ell}_{\kappa\kappa};\omega) - M_\alpha(^{\ell}_{\kappa}) G_{\alpha\alpha}(^{\ell\ell}_{\kappa\kappa};\omega)] \quad (46)$$

with P as the perfect crystal Green's function and m, the mass of the host atom.

2.3 The Host Will Be Copper and the Impurities Will Be At a Sufficiently Low Concentration

The immediate consequence of the face centered cubic host is the disappearance of the K's in all equations. The real reason for picking copper is the accessibility of pure copper Green's functions from the work of Taylor, Hampson, and Bruno. "Sufficiently low concentration" translates into less than a few percent. The idea is that the defects should in the overwhelming number of cases be widely enough separated so that they do not affect one another. Since an f.c.c. crystal has twelve nearest neighbours, already 8% impurity will have at the very best only one host atom separating the defects. From Hampson's work[11], it appears as though the affect of the impurity is mostly felt on first neighbours and is insignificant beyond third. Thus definitely less than 2% should be sufficiently low considering that 42 atoms are inside the third nearest neighbour shell. In this way there are M single defects in the crystal. Then for a single defect at the origin, Eq. (46) becomes

$$\Delta g_1(\omega) = \frac{2\omega}{3\pi N} \text{ Im } \sum_{\alpha} (\sum_{\ell} mP_{\alpha\alpha}(\ell\ell;\omega) - m'G_{\alpha\alpha}(00;\omega)$$

$$- \sum_{\ell\neq 0} mG_{\alpha\alpha}(\ell\ell;\omega)) \qquad (47)$$

with m' as the mass of the defect atom. Introducing

$$\varepsilon \equiv 1 - m'/m \tag{48}$$

enables Eq. (47) to be rewritten as

$$g_1(\omega) = \frac{2\omega m}{3\pi N} \text{ Im} \sum_\alpha (\sum_\ell P_{\alpha\alpha}(\ell\ell;\omega) + (\varepsilon-1)G_{\alpha\alpha}(00;\omega)$$

$$- \sum_{\ell\neq 0} G_{\alpha\alpha}(\ell\ell;\omega))$$

or

$$\Delta g_1(\omega) = \frac{2\omega m}{3\pi N} \text{ Im}\{ \sum_{\ell\alpha} [P_{\alpha\alpha}(\ell\ell;\omega) - G_{\alpha\alpha}(\ell\ell;\omega)]$$

$$+ \varepsilon G_{\alpha\alpha}(00;\omega)\} \quad . \tag{49}$$

Since the defects do not act in concert, it is reasonable to assume, at least to first order in the concentration, that for M defects

$$\Delta g(\omega) \underset{\sim}{\sim} M\Delta g_1(\omega)$$

or

$$\Delta g(\omega) = \frac{2\omega mc}{3\pi} \text{ Im}\{ \sum_{\ell\alpha} [P_{\alpha\alpha}(\ell\ell;\omega) - G_{\alpha\alpha}(\ell\ell;\omega)]$$

$$+ \varepsilon G_{\alpha\alpha}(00;\omega)\} \quad . \tag{50}$$

Finally, the phonon entropy can be calculated, using Eq. (50) in Eq. (44), provided the single defect Green's functions are known in terms of the perfect crystal Green's functions and the perfect crystal Green's functions are themselves known.

2.4 The Influence of the Defect Shall Be Considered Insignificant Beyond Its Twelve Nearest Neighbours

This assumption helps in the relating of the defect and perfect Green's functions; in that, the force constant changes can be handled with a 39×39 matrix, instead of a 129×129 matrix necessary for effects extending to the third nearest neighbour. The Dyson equation relating the two functions will now be developed. Interpreting the definition (13) for the defect resolvent and postmultiplying it by G gives

$$\sum_{\ell,\alpha} G_{\alpha\alpha'}^{-1}(\ell\ell';\omega) G_{\alpha'\alpha''}(\ell'\ell'';\omega) = \delta_{\alpha\alpha''}(\ell\ell') \quad ,$$

i.e.,

$$\delta_{\alpha'\alpha''}(\ell\ell'') = \sum_{\alpha'\ell'} [\omega^2 M_\alpha^{\frac{1}{2}}(\ell) M_{\alpha'}^{\frac{1}{2}}(\ell') \delta_{\alpha\alpha'}(\ell\ell') G_{\alpha'\alpha''}(\ell'\ell'';\omega)$$

$$- \Phi_{\alpha\alpha'}'(\ell\ell') G_{\alpha'\alpha''}(\ell'\ell'';\omega)] \quad . \tag{51}$$

Having the mass defect at the origin "simplifies" Eq. (51) to

$$\delta_{\alpha\alpha''}(\ell\ell'') = \sum_{\alpha'\ell'} [\omega^2 m \delta_{\alpha\alpha'}(\ell\ell') G_{\alpha'\alpha''}(\ell'\ell'';\omega)$$

$$- \omega^2 \epsilon m \delta(0\ell) \delta_{\alpha\alpha'}(\ell\ell') G_{\alpha'\alpha''}(\ell'\ell'';\omega)$$

$$- \Phi_{\alpha\alpha'}'(\ell\ell') G_{\alpha'\alpha''}(\ell'\ell'';\omega)] \tag{52}$$

on using the definition of ε, (48). Invoking assumption of 2.4 and defining

$$\Delta_{\alpha\alpha'}(\ell\ell') \equiv \Phi'_{\alpha\alpha'}(\ell\ell') - \Phi_{\alpha\alpha'}(\ell\ell') \tag{53}$$

gives the force constant change Δ whose only potential non-zero values occur at ℓ and ℓ' values ranging from zero to twelve. Applying this definition to Eq. (52) gives

$$\delta_{\alpha\alpha''}(\ell\ell'') = \sum_{\ell'\alpha'} [\omega^2 m \delta_{\alpha\alpha'}(\ell\ell') - \Phi_{\alpha\alpha'}(\ell\ell')]$$

$$\times G_{\alpha'\alpha''}(\ell'\ell'';\omega) - \sum_{\ell'\alpha'} [\omega^2 \varepsilon m \delta(0\ell)$$

$$\times \delta_{\alpha\alpha'}(\ell\ell') + \Delta_{\alpha\alpha'}(\ell\ell')]G_{\alpha'\alpha''}(\ell'\ell'';\omega) \quad . \tag{54}$$

Comparing the first coefficient of G in Eq. (54) with the definition (13), shows that it is the perfect crystal resolvent. Then by defining

$$V_{\alpha\alpha'}(\ell\ell';) \equiv \omega^2 \varepsilon m \delta(0\ell)\delta_{\alpha\alpha'}(\ell\ell') + \Delta_{\alpha\alpha'}(\ell\ell') \quad , \tag{55}$$

Eq. (54) is seen to be

$$\delta_{\alpha\alpha''}(\ell\ell'') = \sum_{\ell'\alpha'} P^{-1}_{\alpha\alpha'}(\ell\ell';\omega)G_{\alpha'\alpha''}(\ell'\ell'';\omega)$$

$$- \sum_{\ell'\alpha'} V_{\alpha\alpha'}(\ell\ell';\omega)G_{\alpha'\alpha''}(\ell'\ell'';\omega) \quad .$$

Now premultiplying by the perfect crystal Green's function
and chasing indices finally gives the Dyson equation

$$P_{\alpha\alpha'}(\ell\ell';\omega) = G_{\alpha\alpha'}(\ell\ell';\omega) - \sum_{\substack{\ell''\alpha'' \\ \ell'''\alpha'''}} P_{\alpha\alpha''}(\ell\ell'';\omega)$$

$$\times V_{\alpha''\alpha'''}(\ell''\ell''';\omega) G_{\alpha'''\alpha'}(\ell'''\ell';\omega) \quad . \qquad (56)$$

CHAPTER III

CALCULATIONS

3.1 Perfect Crystal Green's Function

The first item on the list is a set of perfect crystal Green's functions. This calculation has been described in great detail by Bruno[12]. The real and imaginary parts are given by

$$\text{Re } P_{\alpha\alpha'}(\ell\ell';\omega) = \int_0^{\omega_{MAX}} \frac{\nu_{\alpha\alpha'}(\ell\ell';\omega')d\omega'}{\omega^2 - \omega'^2} \tag{57}$$

$$\text{Im } P_{\alpha\alpha'}(\ell\ell';\omega) = -\frac{\pi}{2\omega}\nu_{\alpha\alpha'}(\ell\ell';\omega) \tag{58}$$

where the integral in (57) is taken as the principal value integral. The generalized density of states

$$\nu_{\alpha\alpha'}(\ell\ell';\omega) = \frac{V}{2\pi^3} \sum_j \int \delta_\alpha^{*j}(\vec{k})\delta_{\alpha'}^j(\vec{k})e^{-ik(\ell-\ell')}$$

$$\times \text{S}(\omega_j(\vec{k}) - \omega)d^3\vec{k} \tag{59}$$

is related to the density of states (23) by

$$\sum_{\ell,\alpha} \nu_{\alpha\alpha}(\ell\ell;\omega) = \frac{3N}{m} g(\omega) \quad .. \tag{60}$$

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Using the symmetry properties of the crystal, it turns out
that there are only thirteen independent ν's for a nearest
neighbour defect space[12]. A set of data belonging to
Hampson turned out to contain the real part of the Green's
function and the generalized density of states. The
maximum phonon frequency in copper is 7.44 Teraherz and so
a frequency window of zero to eight Teraherz, chopped into
100 bins was used for Riemann summing on a reduced frequency

$$X = \omega/\omega_{MAX} \quad .$$

The data used frequency instead of angular frequency
(= 2π frequency) and care had to be taken in keeping track
of stray factors of 2π. Further the data Green's functions
were "mass reduced"

$$P_{\alpha\alpha'}(\ell\ell';\omega) = mP_{\alpha\alpha'}(\ell\ell';\ddot{\omega}) \quad .$$

So a set of Green's functions p_1 were punched up, related
to Hampson's real and imaginary items, H, by

$$\text{Im } p_1(\ell\ell';X) = -\frac{\pi}{2X} \left(\frac{\text{Im } H(\ell\ell';X)}{\int_0^1 \text{Im } H(\ell\ell;X)\,dX} \right)$$

$$\text{Re } p_1(\ell\ell';X) = 64\text{Re } H(\ell\ell';X) \quad .$$

The factor 64 arose from the denominator of the right hand side of (57). A mass reduced density of states, V, was punched out as well

$$V(\ell\ell';X) = -\frac{2X}{\pi} \text{ Im } p_1(\ell\ell';X) \tag{61}$$

To make sure Re p_1 was indeed what it should be, two more Green's functions were calculated; p_2, p_3. All three have the same imaginary part, but Re p_2 and Re p_3 are calculated from

$$\fint_0^1 \frac{V(\ell\ell';X')dX'}{X^2 - X'^2} = \text{Re } p(\ell\ell';X) \tag{62}$$

differently, Re p_2 was calculated by assuming that $V(\ell\ell';X)$ would not change much from bin to bin, so the left side of (62) can be decomposed to

$$\text{Re } p_2(\ell\ell';X) = \sum_{L=1}^{100} V(\ell\ell';X_L) \fint_{X_L}^{X_{L+1}} \frac{dX'}{X^2 - X'^2} \, . \tag{63}$$

Noting that

$$\frac{1}{X^2 - X'^2} = -\frac{1}{2X}\left(\frac{1}{X'-X} - \frac{1}{X'-X}\right)$$

allows (63) to be written as

$$\text{Re } p_2(\ell\ell';X) = \sum_{L=1}^{100} \frac{V(\ell\ell';X_L)}{2X} \fint_{X_L}^{X_{L+1}} [\frac{1}{X'+X} - \frac{1}{X'-X}]dX'$$

or

$$\text{Re } p_2(\ell\ell';X) = \sum_{L=1}^{100} \frac{V(\ell\ell';X_L)}{2X} [\ell n(\frac{X_{L+1}+X}{X_L+X})$$

$$- \ell n(\frac{X_{L+1}-X}{X_L-X})]$$

or

$$\text{Re } p_2(\ell\ell';X) = \sum_{L=1}^{100} \frac{V(\ell\ell';X_L)}{2X} \ell n(\frac{(X_{L+1}+X)(X_L-X)}{(X_L+X)(X_{K+1}-X)}) \quad (64)$$

which is well defined as long as the X bins are slightly shifted from the X_i bins. Re $p_3(\ell\ell';X)$ was found using

$$\text{Re } p_3(\ell\ell';X) = \fint_0^1 \frac{V(\ell\ell';X') - V(\ell\ell';X)}{X^2 - X'^2} dX'$$

$$+ V(\ell\ell';X) \fint_0^1 \frac{dX'}{X^2 - X'^2} \quad . \quad (65)$$

In evaluating the Riemann sum for the first integral one simply omits the term that has the X bin equal to the X' bin. The second integral is simply that in (63) between different limits and it reduces to

$$\fint_0^1 \frac{dX'}{X^2 - X'^2} = \frac{1}{2X} \ell n\left|\frac{1+X}{1-X}\right| \quad .$$

A staggered bin prevents X = 1, 0. The differences between the real parts of p_2 and p_3 appeared systematic and greatest where the slope of V was greatest. It was the assumption that the slope differed little from bin to bin that led from (62) to (63). Although the discrepancies were not more than a few percent, the thermodynamic quantities were quite insensitive to them. A glance at the differences of p_1 and p_2 showed how p_1 was calculated, since it was read in to only 8 significant figures.
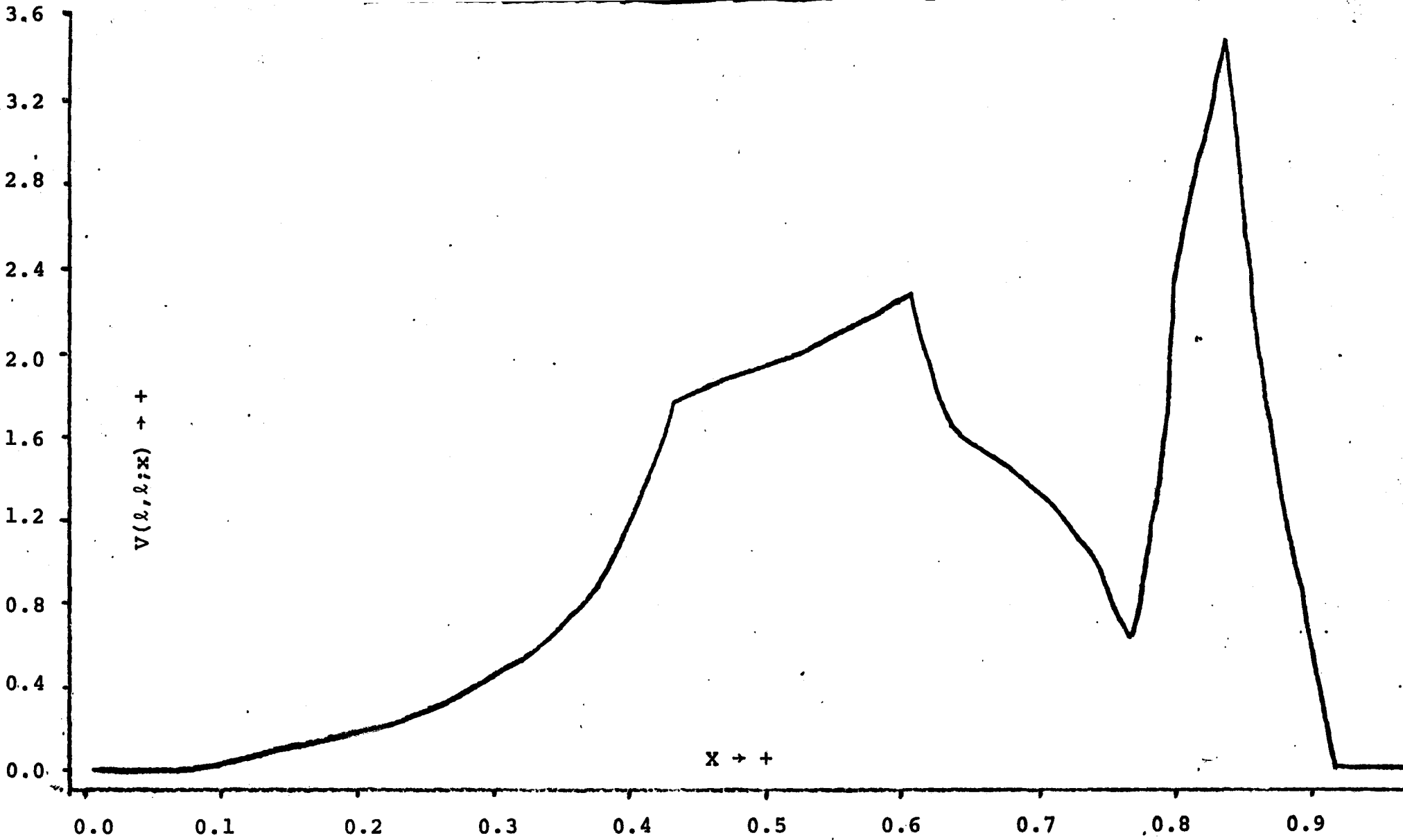
Fig. 2: Normalized Density of States ($V(\ell,\ell;x)$) vs. Reduced Frequency
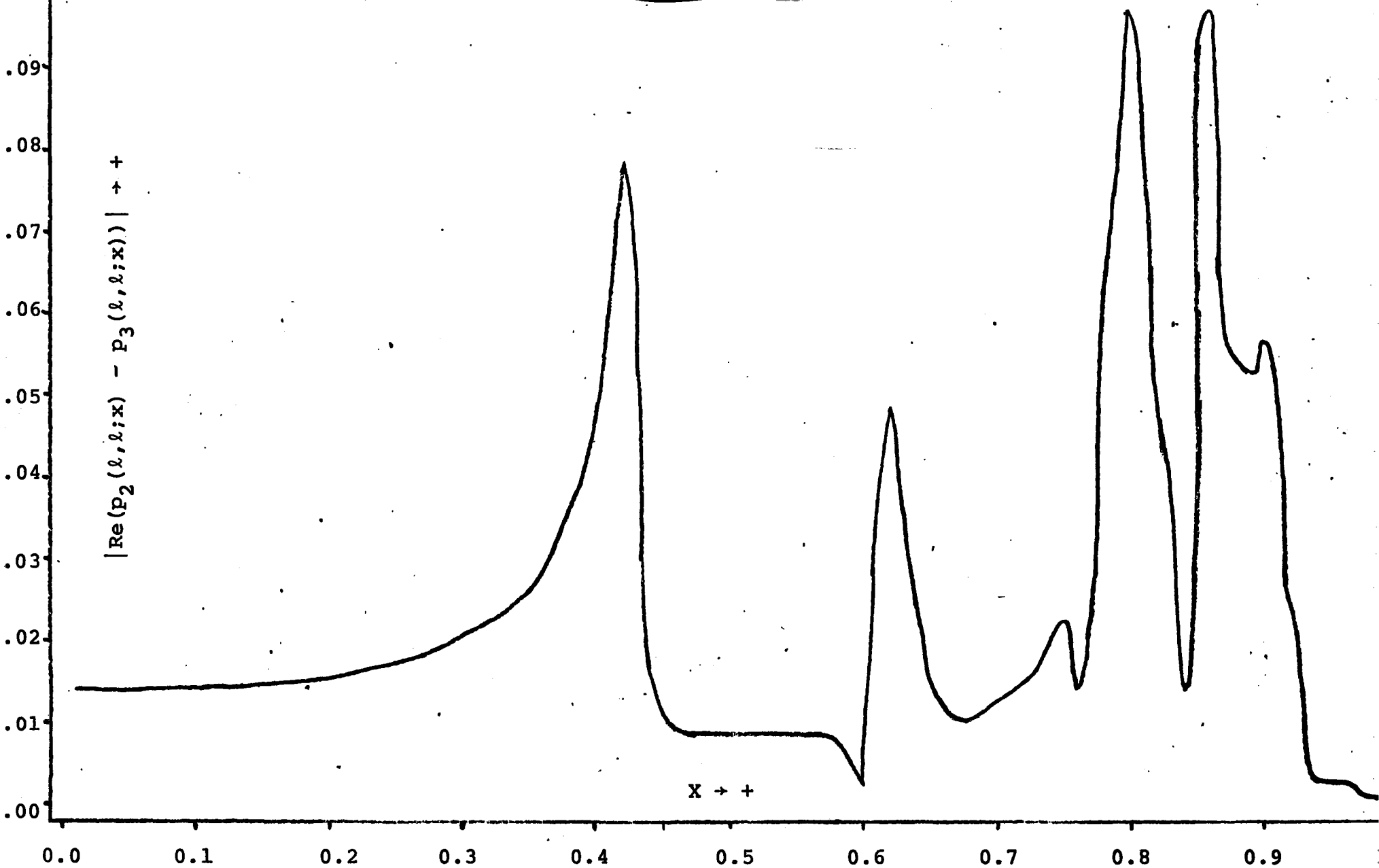
$$(X = \omega/\omega_{MAX})$$

Fig. 3: Absolute Difference Between Real Parts of the p_2, p_3 Green's Function ($|Re(p_2(\ell, \ell; x) - p_3(\ell, \ell; x))|$) vs. Reduced Frequency (X)
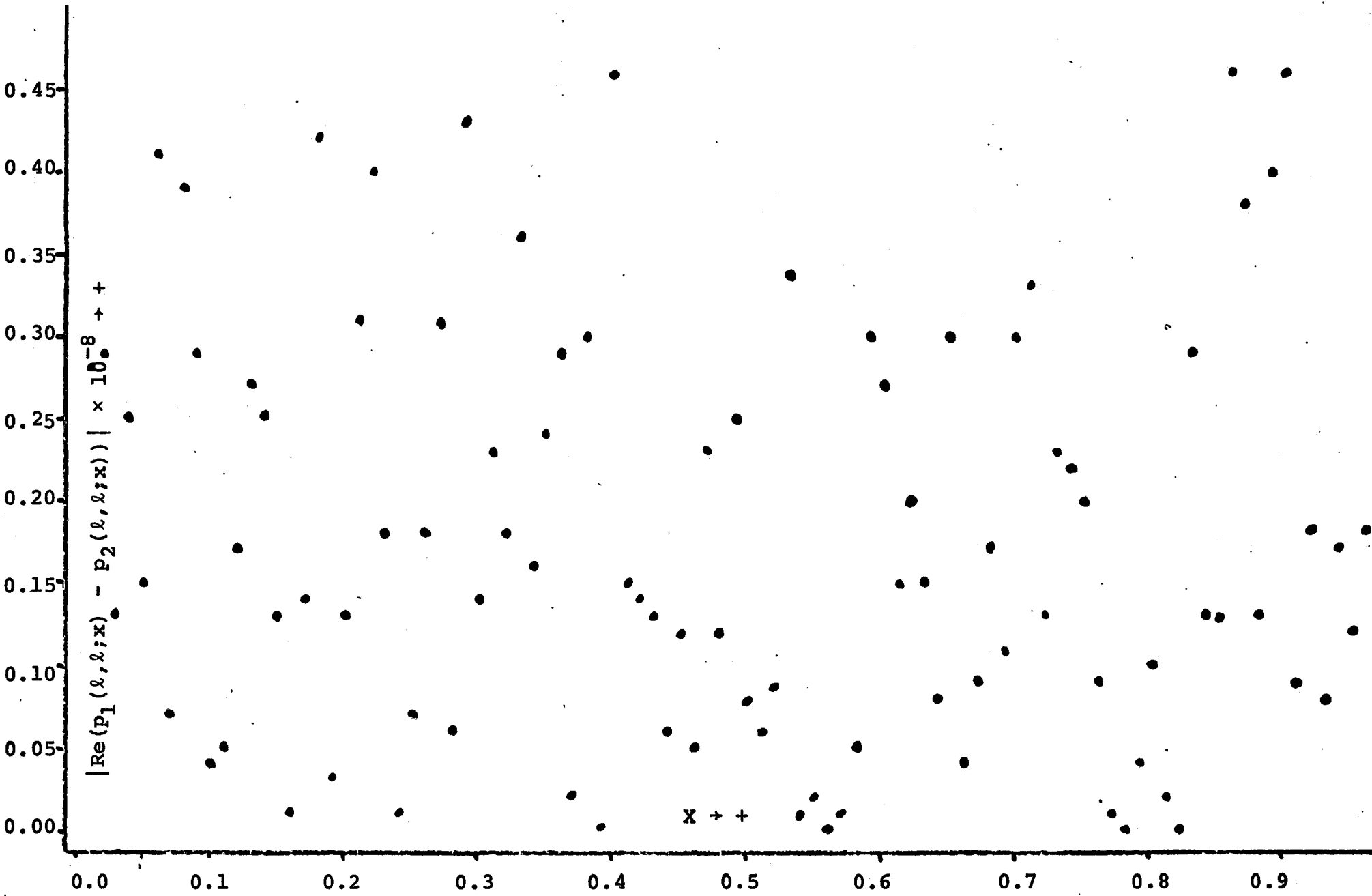
Fig. 4: Absolute Difference Between Real Parts of the p_1, p_2 Green's Functions ($|\text{Re}p_1(\ell,\ell;x) - \text{Re}p_2(\ell,\ell;x)|$) vs. Reduced Frequency (X)

3.2 Phonon Entropy For Mass Defect Only

This problem has more than just pedagogical merit. The force constants appear to change by not more than 50% , while the mass change for gold in copper is about 300%. The possibility of defining effective mass changes also emerges.

With no force constant changes, V in (55) becomes a constant diagonal matrix and the Dyson equation (56) for the single mass defect at the origin is

$$P_{\alpha\alpha'}(\ell\ell';\omega) = G_{\alpha\alpha'}(\ell\ell';\omega) - \sum_{\substack{\ell''\alpha'' \\ \ell'''\alpha'''}} P_{\alpha\alpha''}(\ell\ell'';\omega)$$

$$\times \omega^2 \varepsilon m \delta(0\ell'') \delta_{\alpha''\alpha'''}(\ell''\ell''') G_{\alpha'''\alpha'}(\ell'''\ell';\omega)$$

and

$$P_{\alpha\alpha'}(\ell\ell';\omega) = G_{\alpha\alpha'}(\ell\ell';\omega) - \sum_{\alpha''} P_{\alpha\alpha''}(\ell0;\omega) \omega^2 \varepsilon m$$

$$\times G_{\alpha''\alpha'}(0\ell';\omega) \quad . \tag{66}$$

Premultiplying through by $\delta_{\alpha''\alpha}(0\ell)$ gives

$$P_{\alpha''\alpha'}(0\ell';\omega) = G_{\alpha''\alpha'}(0\ell';\omega)$$

$$- P_{\alpha''\alpha''}(00;\omega) \omega^2 \varepsilon m G_{\alpha''\alpha'}(0\ell';\omega) \tag{67}$$

because the crystal is cubic, the three-fold and four-fold axes conspire to give

$$P_{\alpha\alpha''}(\ell\ell;\omega) = P(0;\omega)\delta_{\alpha\alpha''}(\ell 0) \qquad (68)$$

where $P(0;\omega)$ is a scalar function of ω. So (67) becomes

$$P_{\alpha''\alpha'}(0\ell';\omega) = [1 - \omega^2\varepsilon m P(0;\omega)]$$

$$\times \delta_{\alpha\alpha''}(\ell 0)G_{\alpha''\alpha'}(0\ell';\omega) \quad .$$

The Kronecker δ does nothing and the quantity in the square brackets is a scalar, so exactly

$$G_{\alpha''\alpha'}(0\ell;\omega) = \frac{P_{\alpha''\alpha'}(0\ell;\omega)}{1 - \omega^2\varepsilon m P(0;\omega)}$$

and (66) can be rewritten

$$G_{\alpha\alpha'}(\ell\ell';\omega) = P_{\alpha\alpha'}(\ell\ell';\omega) + \sum_{\alpha''} P_{\alpha\alpha''}(\ell 0;\omega)$$

$$\times \frac{\omega^2\varepsilon m}{1 - \omega^2\varepsilon m P(0;\omega)} P_{\alpha''\alpha'}(0\ell;\omega) \qquad (69)$$

which is clearly an exact solution. Substituting (69) into (50) gives the density of states to first order in concentration, completely in terms of the pure crystal Green's function

$$\Delta g(\omega) = \frac{2\omega mc}{3\pi} \text{ Im } [\sum_{\substack{\ell\alpha \\ \alpha'}} [- P_{\alpha\alpha'}(\ell 0;\omega) \frac{\omega^2 \epsilon m}{1 - \omega^2 \epsilon m P(0;\omega)}$$

$$\times P_{\alpha'\alpha}(0\ell;\omega)] + \epsilon \sum_{\alpha} (P_{\alpha\alpha}(00;\omega)$$

$$+ \sum_{\alpha'} P_{\alpha\alpha'}(00;\omega) \frac{\omega^2 \epsilon m}{1 - \omega^2 \epsilon m P(0;\omega)} P_{\alpha'\alpha}(00;\omega)] \quad .$$

$$(70)$$

Passing to reduced coordinates

$$\omega \rightarrow X \quad ;$$

$$mP \rightarrow p$$

and using (68), Eq. (70) becomes

$$\Delta g(X) = \frac{2Xc\epsilon}{3\pi} \text{ Im } \sum_{\ell\alpha} (- \frac{X^2}{1 - X^2 \epsilon p(0;X)} \sum_{\alpha'} P_{\alpha\alpha'}(\ell 0;X)$$

$$\times P_{\alpha'\alpha}(0\ell;X) + \frac{3p(0:X)}{1 - X^2 \epsilon p(0;X)}$$

$$\times [1 - X^2 \epsilon p(0;X) + X^2 \epsilon p(0;X)]$$

or

$$\Delta g(X) = \frac{2Xc\epsilon}{3\pi} \text{ Im } \sum_{\ell\alpha} (\frac{3p(0;X) - X^2 \sum_{\alpha'} P_{\alpha\alpha'}(\ell 0;X) p_{\alpha'\alpha}(0\ell;X)}{1 - X^2 \epsilon p(0;X)})$$

or

$$\Delta g(X) = \frac{2Xc\varepsilon}{3\pi} \text{ Im } [\frac{3p(0;X) - X^2 \underset{\underset{\alpha'}{\ell\alpha}}{\Sigma} p_{\alpha\alpha'}(\ell 0;X)p_{\alpha'\alpha}(0\ell;X)}{1 - X^2 \varepsilon p(0;X)}] \quad .$$

(71)

Now provided the enormous sum on $\ell\alpha$ in (71) could be eliminated, (71) would be fine for actual calculations. The fact

$$\underset{\ell\alpha}{\Sigma} p_{\alpha\alpha'}(\ell 0;X)p_{\alpha'\alpha}(0\ell;X) = - \frac{d}{dX^2} p_{\alpha\alpha}(00)$$

(72)

comes to the rescue. It can be established by returning to the definitions of the Green's function at the beginning of this section, (58) and (59). If the ω is allowed to sneak into the complex plane, the Green's function can be written as a single integral. Changing the integral back to a sum on the modes and substituting into the left side of (72); gives, on collapsing the polarization vectors, exactly the right hand side of (72). Now (71) becomes

$$\Delta g(X) = \frac{2Xc\varepsilon}{\pi} [\frac{p(0;X) + \frac{X}{2} \frac{d}{dX} p(0;X)}{1 - X^2 \varepsilon p(0;X)}] \quad .$$

(73)

Derivative subroutines can be avoided with a method published by Hartmann et al.[13]. Introducing

$$\theta(X) \equiv \text{Im } \ell n(1 - \varepsilon X^2 p(0;X))$$

(74)

and taking its X derivative gives

$$\frac{d\theta(X)}{dX} = Im[\frac{1}{1 - \epsilon X^2 p(0;X)} (- 2\epsilon X p(0;X) - \epsilon X^2 \frac{d}{dX} p(0;X))]$$

or

$$\frac{d\theta(X)}{dX} = - 2\epsilon X \; Im[\frac{p(0'X) + \frac{X}{2} \frac{d}{dX} p(0;X)}{1 - \epsilon X^2 p(0;X)}] \quad , \tag{75}$$

which gives a neat expression for Δg on combining (73) and (75)

$$\Delta g(X) = - \frac{c}{\pi} \frac{d\theta(X)}{dX}$$

or

$$\Delta g(X) dX = - \frac{c}{\pi} d\theta(X) \quad . \tag{76}$$

Now rewriting (44) as

$$\Delta S_{ph} = 3N \int_0^1 \Delta g(X) dX [BX \coth(BX) - \ln(2 \sinh(BX))] \tag{77}$$

with

$$B \equiv \hbar\omega_{MAX}/2T \quad . \tag{78}$$

Using (76), (77) can be integrated by parts to give

$$\Delta S_{ph} = - \frac{3Nc}{\pi} [(BX \coth BX - \ln(2 \sinh BX)) \theta(X) \Big|_0^1$$

$$- \int_0^1 \theta(X) \frac{d}{dX} [BX \coth BX - \ln 2 \sinh BX] dX \quad .$$

$$(79)$$

The integrated term on the right disappears because $\theta(X)$ is zero at these limits as can be seen from (76); regardless of the horrors that occur in the hyperbolic functions at these limits. Using the well known facts

$$\frac{d}{dX} \coth BX = - B \operatorname{csch}^2 BX \qquad (80)$$

$$\frac{d}{dX} \sinh BX = B \cosh BX \quad . \qquad (81)$$

Equation (79) becomes

$$\Delta S_{ph} = \frac{3Nc}{\pi} \int_0^1 \theta(X) [(- B^2 X \operatorname{csch}^2 BX + B \coth BX)$$

$$- (\frac{1}{2 \sinh BX} 2B \cosh BX)] dX$$

or

$$\Delta S_{ph} = - \frac{3NBc}{\pi} \int_0^1 \theta(X) BX \operatorname{csch}^2(BX) dX \qquad (82)$$

using

$$\coth = + \frac{\cosh}{\sinh} \quad .$$

Finally by using (74), (78), (82), and the zero-zero Green's function $p(0;X)$; the phonon entropy can be calculated for mass defect only.

$$\theta(X) \equiv \text{Im } \ln[1 - \epsilon X^2 p(0;X)] \qquad (74)$$

$$B \equiv \hbar\omega_{\text{MAX}}/2T \qquad (78)$$

$$\Delta S_{\text{ph}} = - \frac{3cNB^2}{\pi} \int_0^1 X\theta(X)\,\text{csch}^2(BX)\,dX \quad . \qquad (82)$$

Since Hartmann et al. only considered specific heat (C_v) and for an Al-Ag, host-defect system, it was decided to check the computation by running the Al-Ag masses with the copper Green's functions in a heat capacity calculation and looking for good agreement, since the density of states are similar and both are f.c.c. Since the constant volume heat capacity is defined by

$$C_v \equiv \left. \frac{d\!\!\!/Q}{dT} \right|_V$$

where $d\!\!\!/Q$ is a small change in heat and from the relation

$$dS = \frac{d\!\!\!/Q}{T} \quad ,$$

we have

$$C_v = T \frac{dS}{dT}\bigg|_V \quad . \tag{83}$$

Further from (78), we can write

$$\frac{1}{B} dB = - \frac{1}{T} dT \quad .$$

Then (83) becomes

$$C_v = - B \frac{dS}{dB}\bigg|_V \quad . \tag{84}$$

So from (82) and (84), one finds

$$C_v = \frac{3cNB}{\pi} \left[2B \int_0^1 X\theta(X) \operatorname{csch}^2(BX) dX \right.$$

$$\left. + B^2 \int_0^1 X\theta(X) 2\operatorname{csch}(BX) \frac{d[\operatorname{csch}(BX)]}{dB} dX\right] \quad .$$

Using the relation

$$\frac{d}{dy} \operatorname{csch}(u) = - \operatorname{csch}(u)\operatorname{coth}(u) \frac{du}{dy}$$

the heat capacity is

$$C_v = \frac{3cN}{\pi} \left[2B^2 \int_0^1 X\theta(X) \operatorname{csch}^2(BX) [1 - BX\operatorname{coth}(BX)] dX\right.$$

or

$$C_v = \frac{6cNB^2}{\pi} \int_0^1 X\theta(X) \operatorname{csch}^2(BX)[1 - BX\coth(BX)]dX \quad . \quad (85)$$

Equation (85) is equivalent to Hartmann's formula.

In the "natural" units employed here the heat capacity is dimensionless. To reproduce the results of Hartmann et al., temperature must be in °K. Now the entropy is in units of Boltzmann's constant and from (83) so is heat capacity. On writing the number of atoms N as

$$N = nN_A \quad\quad (86)$$

where n, N_A are the number of moles and Avogadro's number respectively, N in (85) can be replaced by n and the heat capacity has the units of the gas constant

$$R = N_A k = 8.31434 \times 10^3 \text{ millijoule/mole-°K} \quad . \quad (87)$$

Since the specific heat is the heat capacity per mole and using (85), (86), and (87), the specific heat at constant volume is

$$C_v = \frac{C_v}{n} = \frac{6cB^2}{\pi} [\int_0^1 X\theta(X) \operatorname{csch}^2(BX)[1 - BX\coth(BX)]dX]$$

$$\times 8.31434 \times 10^3 \text{ millijoules/mole·°K} \quad . \quad (88)$$

With this equation half the battle for Hartmann's specific
heats is over. The remainder amounts to using the copper
Green's functions correctly. From (58), (60), and (68), we
have

$$m \text{ImP}(0;\omega) = - \frac{\pi}{2\omega} g(\omega) \quad . \tag{89}$$

Changing the variables on the right hand side by

$$X = \frac{\omega}{\omega_m} \tag{90}$$

gives

$$m \text{ImP}(0;\omega) = \frac{1}{\omega_m^2} \left(- \frac{\pi}{2X} g(X) \right) \quad . \tag{91a}$$

The same will hold for aluminium with $X = \omega'/\omega_m'$

$$m' \text{ImP}'(0;\omega) = \frac{1}{\omega_m'^2} \left(- \frac{\pi}{2X} g'(X) \right) \quad . \tag{91b}$$

But if the "reduced coordinate" density of states, $g(X)$, is
assumed the same for both metals, then

$$m \omega_m^2 \text{ImP}(0;\omega) = - \frac{\pi}{2X} g(X) = m' \omega_m'^2 \text{ImP}'(0;\omega) \quad . \tag{92}$$

With a reduced coordinate Green's function

$$\text{ImP}(0;X) \equiv - \frac{\pi}{2X} \, g(X)$$

(92) becomes

$$\text{mImP}(0;X) = \text{m'ImP'}(0;X)$$

and in mass reduced Green's functions

$$\text{Imp}(0;X) = \text{Imp'}(0;X) \quad . \tag{93}$$

Thus provided that the maximum frequencies are changed, as required by the thermodynamic part of the calculation, the totally reduced copper Green's functions can be used unchanged in (74).
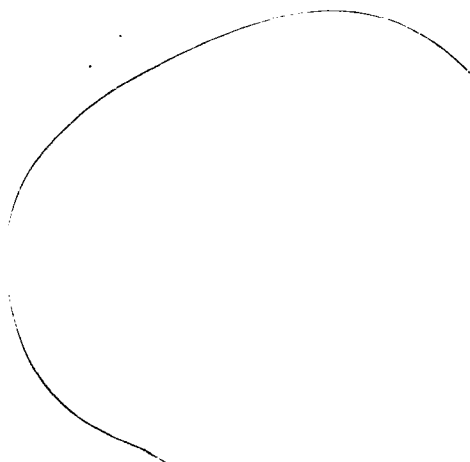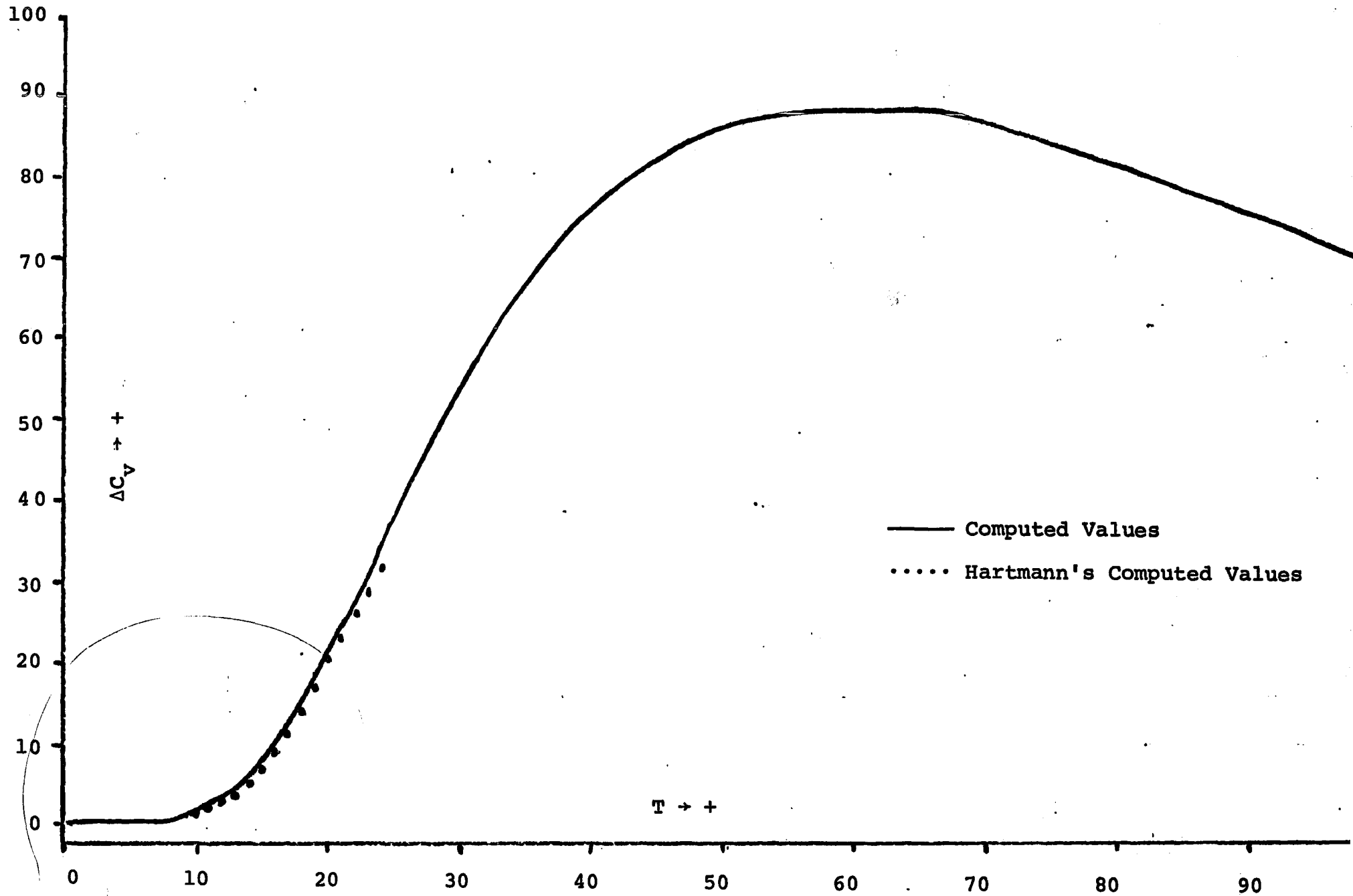
Fig. 5: Change in Heat Capacity (ΔC_v) in millijoules per mole -°K vs. Temperature (T) in °K

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CHAPTER IV

DISCUSSION

When the comparison with Hartmann's heat capacity was finally achieved (see Fig. 5), the difference was less than 10%. This discrepancy was systematic with Hartmann's values always being lower. A 5% increase in the maximum frequency of aluminium would have brought about an agreement well within the errors set by the visual estimate of Hartmann's data.

Probably the most venerated paper on this topic was written in 1955 by Huntingdon, Shirn, and Wajda[14]. Their main result was

$$\Delta S_{ph} = \sum_{S} \ln(\omega_S/\omega_S') \qquad (94)$$

for temperatures well above the Debye temperature of the solvent, and ω_S was the eigenfrequency before the addition of the impurity and ω_S' its value after. The remarkable thing about (94) is its temperature independence. The Debye temperature of copper according to Kittel[15] is 343°K and according to Fig. 6, the phonon entropy has already begun to level out by 350°K. Since the mass defect will probably account for only some of the phonon entropy change (the rest being due to the effect of the force constant

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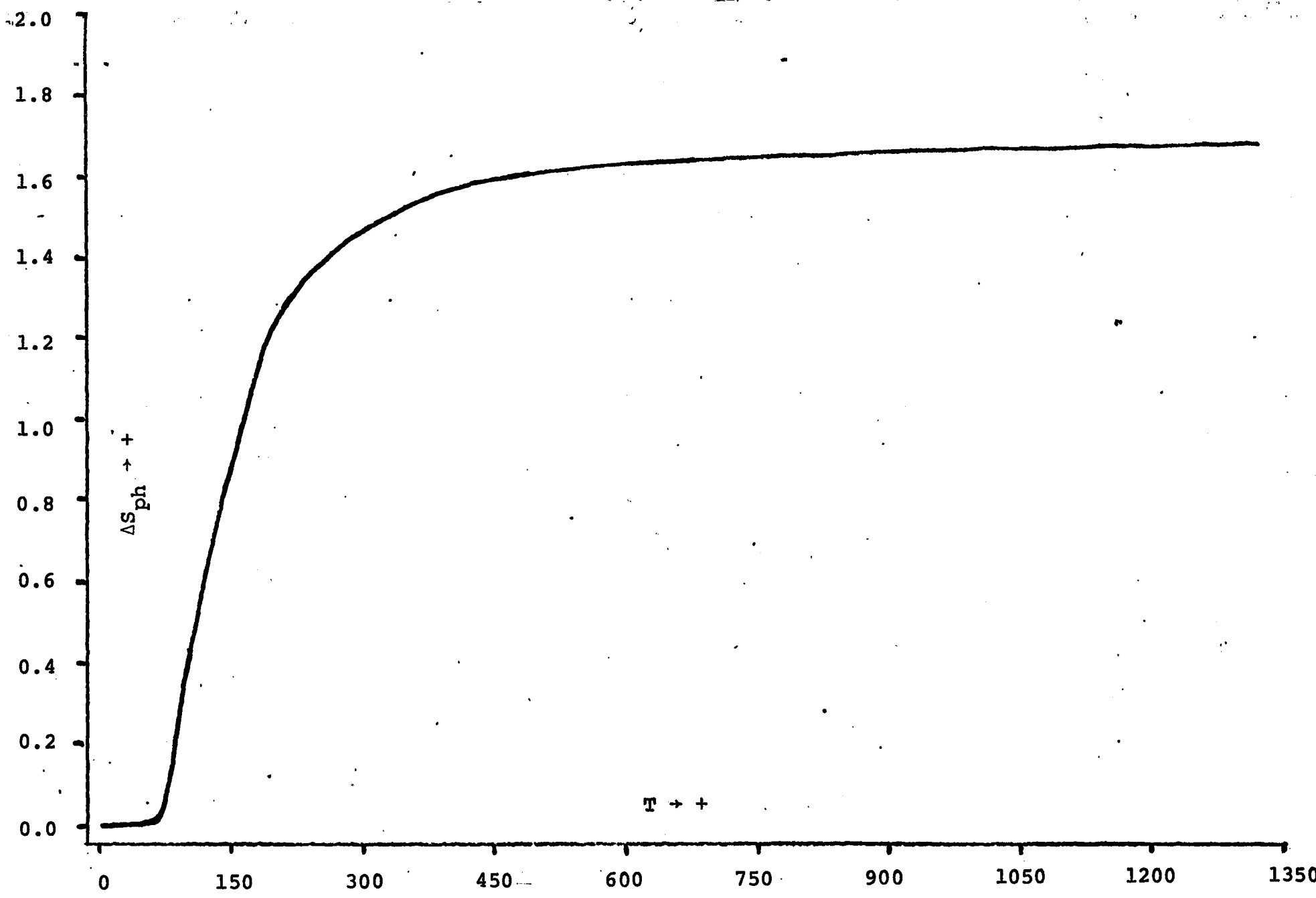
Fig. 6: Phonon Entropy (ΔS_{ph}) per defect atom vs. Temperature (T) in °K

change), it is surprising that the mass defect phonon entropy is already close to temperature independence at the Debye temperature.

To derive (94) is not hard. Starting from (39)

$$S_{ph} = \sum_{S} \{([e^{\hbar\omega_S/T} - 1]^{-1} + 1) \ln([e^{\hbar\omega_S/T} - 1]^{-1} + 1)$$

$$- [e^{\hbar\omega_S/T} - 1]^{-1} \ln[e^{\hbar\omega_S/T} - 1]^{-1}\} \quad . \qquad (39)$$

For high temperature, $T \gg \hbar\omega_{MAX}$, the exponent is less than one and the expansion

$$e^{\hbar\omega/T} = 1 + \hbar\omega/T + \ldots$$

may be taken to first order. Equation (39) then becomes

$$S_{ph} = \sum_{S} [(\frac{T}{\hbar\omega_S} + 1) \ln(\frac{T}{\hbar\omega_S} + 1) - \frac{T}{\hbar\omega_S} \ln(\frac{T}{\hbar\omega_S})] \quad . \qquad (95)$$

Since $T/\hbar\omega_S \gg 1$ and the logarithm is a very slowly varying function

$$\ln(\frac{T}{\hbar\omega_S} + 1) \underset{\sim}{\sim} \ln(\frac{T}{\hbar\omega_S}) \qquad (96)$$

is more accurate than

$$\frac{T}{\hbar\omega_S} + 1 \underset{\sim}{\sim} \frac{T}{\hbar\omega_S} \quad .$$

Using (96) in (95) and simplifying gives

$$S_{ph} \underset{\sim}{\sim} \sum_{S} \ell n \left(\frac{T}{\hbar \omega_S} \right) \quad . \tag{97}$$

Then the entropy difference

$$\Delta S_{ph} = S'_{ph} - S_{ph}$$

where the primes refer to the impure system, is given by

$$S_{ph} = \sum_{S'} \ell n \left(\frac{T}{\hbar \omega_{S'}} \right) - \sum_{S} \ell n \left(\frac{T}{\hbar \omega_S} \right) \quad . \tag{98}$$

Since there are still 3N modes in the impure system, then S and S' are the same index so that (98) becomes

$$\Delta S_{ph} = \sum_{S} \ell n \left(\frac{\omega_S}{\omega'_S} \right) \quad . \tag{94}$$

As with many simple equations, (94) is difficult to use. It is useless unless one knows the dependence of ω'_S on ω_S and the mass and force constant changes. Several ingenious models have been given[14,16], but the method commenced in this report is capable of giving reliable calculations of thermal properties valid at all temperatures for low concentrations of defects.

$$\Delta S_{ph} = - \frac{3B^2}{\pi} \int_0^1 x\theta(x) \operatorname{csch}^2(BX) dx$$

with $\theta(x) = \operatorname{Im}(\ln[1 - (1-M)x^2 p(0;x)])$

$$B = h\omega_{MAX}/2T$$

$$\Delta S_{ph} = \frac{3}{2} \ln(M)$$
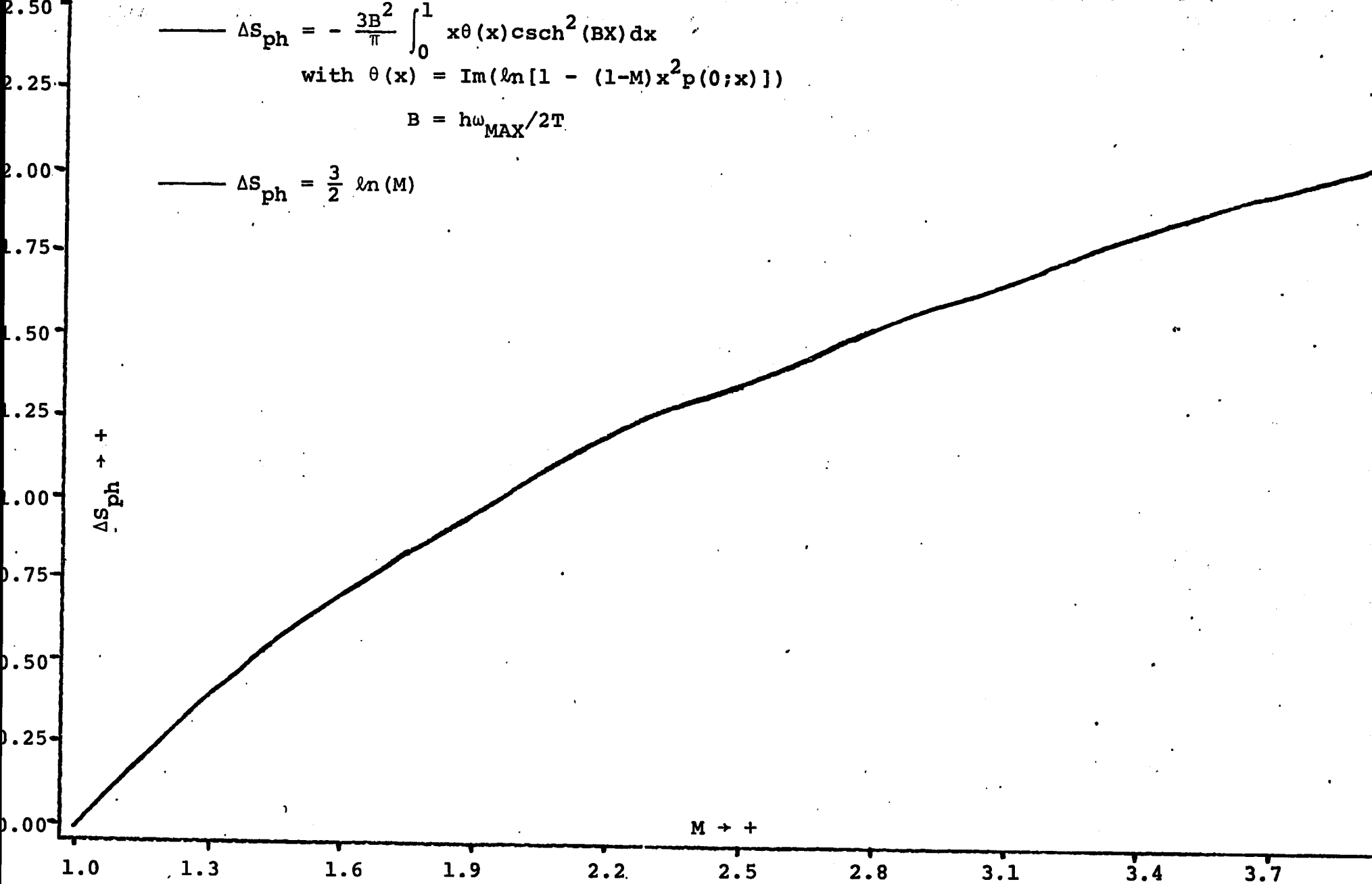
Fig. 7: Phonon Entropy (ΔS_{ph}) per defect atom at 1200°K vs. Mass
Ratio (M = mass of defect/mass of copper)

The solution to (94) is especially simple for a mass defect only. For two springs with force constants k, connected to masses m, m' the ratio of the frequencies is

$$\frac{\omega}{\omega'} = \sqrt{\frac{m'}{m}} \quad . \tag{99}$$

If the entire lattice were suddenly made heavier, then each of the 3N modes would change according to (99), and (94) would become

$$\Delta S_{ph} = \frac{3}{2} N \ell n \frac{m'}{m} \quad . \tag{100}$$

Then just changing a small concentration, c, to a greater mass m' would give

$$\Delta S_{ph} = \frac{3}{2} cN \ell n \left(\frac{m'}{m}\right) \quad . \tag{101}$$

Figure 7 shows a comparison of ΔS_{ph} given by (100) and that given by (74), (78), and (82) at a 1% concentration and at 1200°K. From the agreements in Figs. 5 and 7, it would appear that the calculations presented so far are correct.

According to Fig. 6 the mass defect phonon entropy goes to its maximum in the high temperature limit so it would be near to this limit that the phonon entropy might not be swamped by the configurational entropy. To get a feeling for the relative sizes, Fig. 8 was prepared. The
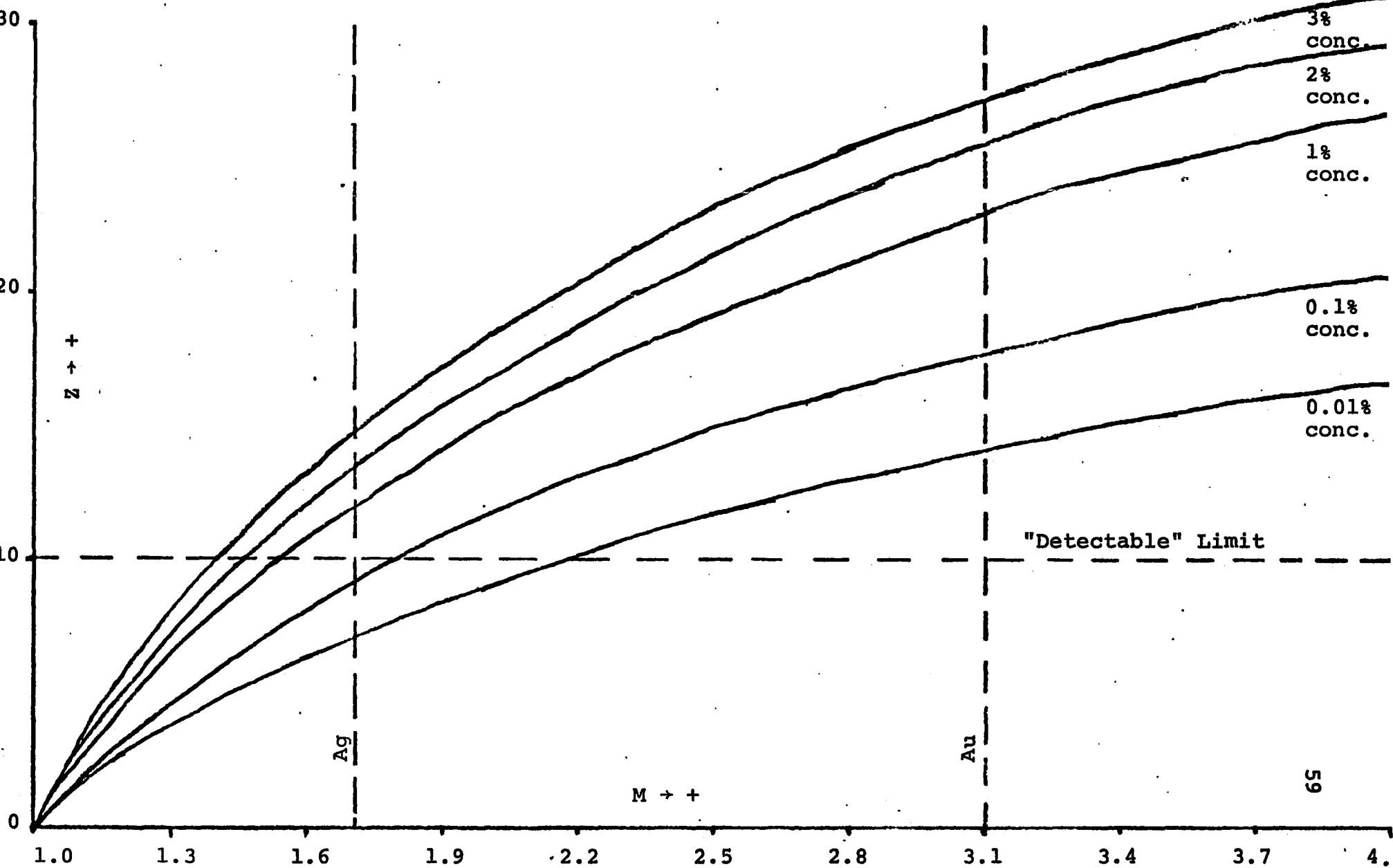
Fig. 8: Phonon Entropy as a percent of Phonon and Configurational Engropy (Z) at

curves correspond to different concentrations and are labelled by these concentrations and the configurational entropy per defect atom. Although the mass defect phonon entropy is linear in the concentration, the configurational entropy is not: hence the separation in the curves. Considering that the entropy can be measured to about three significant figures, the horizontal 10% line has been drawn to indicate where the mass defect entropy ought to make its appearance. Thus, assuming that the entropy is made up only from configurational and mass defect contributions, a 3% concentration of defects with a mass of 1.5 times that of copper would have a visible phonon effect, but for a 0.01% concentration the mass of the impurity would have to have a mass of at least 2.20 times that of copper. The vertical lines are the mass parameters corresponding to silver and gold.

A paper by McLellan and Shuttleworth[16], found by Dr. Taylor towards the end of this project, claims to experimentally determine the vibrational entropy of mixing gold in copper. Either the value they obtain or its equivalent appears several times in the paper as several different numbers. Assuming that the misprints disagree, the value they report is about 7.0 ± 0.20 per defect atom. This is a far cry from the value 1.68 per defect atom calculated here. The same is true for silver. Their reported value of 4.71 per defect atom compares badly with

the calculated value of 0.782 per defect atom. The
puzzling thing, however, is that an inclusion of force
constant changes of some 30% must send the calculated
entropies rocketing up by a factor ∿4 to the observed
values. This is because McLellan and Shuttleworth's
calculation of the effect of just the mass defect is
1.70 (cf. 1.68) and 0.79 (cf. 0.782) per atom of gold and
silver respectively, and their elastic model calculation
comes to within 50% of their observed values. It should
be noted that their reported values per defect atom for
gold impurities at 0.5% and 2.5% concentration were not
the same. Since the vibrational entropy is no longer
linear in the concentration at 2.5% this suggests that the
envisaged theory containing force constant changes as well
as mass defects, will only be good at very low concentrations.

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LISTINGS

```
              PROGRAMMETST (INPUT,OUTPUT,TAPE5=INPUT)
       C
       C
       C      THIS PROGRAMME TAKES COPPER GREENS FUNCTIONS, RESCALES THE FREQUENCY TO
 5     C      THAT OF ALUMINUM AND CALCULATES THE CHANGE IN HEAT CAPACITY DUE TO A CONC.
       C      OF SILVER ATOMS IN AN ALUMINUM HOST. THE METHOD IS FROM W. M. HARTMANN,
       C      PHYS. REV. B, VOL. 1, 1486. THE HEAT CAPACITY IS GRAPHED AND PRINTED IN
       C      MILLIJOULES PER MOLE-DEGREE KELVIN,FROM 1 TO 100 DEGREES KELVIN.
       C
10     C
              DIMENSION P(2,16,100)
              DIMENSION X(100)
              DIMENSION THETA(100)
              DIMENSION CV(100)
15            REAL NUMAX
              REAL KELVIN
              COMPLEX PC
              SINH(X)=(EXP(X)-EXP(-X))/2.0
              COTH(X)=1.0+2.0/(EXP(2.0*X)-1.0)
20            PI=3.14159265358979
              NUMAX=8.0E12
              NUMAX=NUMAX*428/343
       C      RATIO OF DEBYE TEMPERATURES RESCALES FREQUENCIES
              PLANCK=6.62559E-27
25            BOLTZ=1.38054E-16
              C=NUMAX*PLANCK/(2.*BOLTZ)
              CONC=0.0095
              READ (5) P
       C      P IS PERFECT XL GREENS FUNCTION
30            WT DEFCT = 107.870
              WT HOST = 26.9815
              E=1.0-WTDEFCT/WTHOST
              DO 1 K=1,100
              X(K)=(K-0.5)/100.
35     C      X(K) ARE 100 FREQUENCY BINS BETWEEN 0. AND 1.
              PC=CMPLX(P(1,1,K),P(2,1,K))
              THETA(K)=AIMAG(CLOG(1.-E*X(K)*X(K)*PC))
       1      CONTINUE
              KELVIN=1
40            DO 3 J=1,100
              HC=0.
              B=C/KELVIN
              DO 2 K=1,100
              HC=HC+X(K)*THETA(K)*(1.-B*X(K)*COTH(B*X(K)))/(SINH(B*X(K))**2)
45     2      CONTINUE
              CV(J)=6./(   PI)*B*B*HC*CONC*0.01*8.31434E3
              CALL PLOTPT (KELVIN,CV(J),4)
              KELVIN=KELVIN+1
       3      CONTINUE
50            CALL OUTPLT
              PRINT 500
              PRINT 510, CV
       500    FORMAT (1H1)
       510    FORMAT (1X,1P,10E12.5)
55            END
```

```
        PROGRAMMETST (INPUT,OUTPUT,TAPE5=INPUT)
   C
   C
   C    THIS PROGRAMME COMPARES PHONON ENTROPY TO CONFIGURATIONAL ENTROPY AT 500
   C    DEGREES KELVIN FOR .01 TO 1 PER CENT CONC OF GOLD ATOMS IN COPPER.
   C
   C
        DIMENSION P(2,16,100)
        DIMENSION X(100)
        DIMENSION THETA(100)
        DIMENSION S(21)
        DIMENSION Z(21)
        DIMENSION SBX2(100)
        REAL NUMAX
        REAL N,KELVIN
        COMPLEX PC
        SINH(X)=(EXP(X)-EXP(-X))/2.0
        PI=3.14159265358979
        NUMAX=8.0E12
        PLANCK=6.62539E-27
        BOLTZ=1.38054E-16
        C=NUMAX*PLANCK/(2.*BOLTZ)
        KELVIN=500.
        B=C/KELVIN
        CONC=0.0001
        WT HOST = 63.54
        READ (5) P
   C    P IS PERFECT XL GREENS FUNCTION
        DO 1 K=1,100
        X(K)=(K-0.5)/100.
   C    X(K) ARE 100 FREQUENCY BINS BETWEEN 0. AND 1.
        SBX2(K)= SINH( B*X(K) ) **2
      1 CONTINUE
        DO 4 L=1,100
        A=-CONC*ALOG(CONC)-(1.-CONC)*ALOG(1.-CONC)
   C    A IS THE CONFIGURATIONAL ENTROPY.
        WTDEFCT=WTHOST+0.001
        DO 3 J=1,21
        E=1.0-WTDEFCT/WTHOST
        N=0.
        DO 2 K=1,100
        PC=CMPLX(P(1,1,K),P(2,1,K))
        THETA(K)=AIMAG(CLOG(1.-E*X(K)*X(K)*PC))
        N=N+X(K)*THETA(K)/SBX2(K)
      2 CONTINUE
        S(J)=-3./(        PI)*3*B*N*CONC*0.01
   C    S IS THE PHONON ENTROPY
        Z(J)=S(J)/(A+S(J))*100.
   C    Z IS THE PER CENT OF PHONON ENTROPY TO PHONON PLUS CONFIGURATIONAL ENTPOPY
        WTDEFCT=WTDEFCT+0.15*WTHOST
      3 CONTINUE
        PRINT 510, CONC*100.,A
        PRINT 500, S
        PRINT 500
        PRINT 500, Z
        PRINT 500
        PRINT 500
```

66

```
              PROGRAMMETST (INPUT,OUTPUT,TAPE5=INPUT)
        C
        C
        C     CALCULATION OF ENTROPY (S) BETWEEN 1 AND 1401 DEGREES KELVIN AT 25 DEGREE
        C     INTERVALS. IT ARISES FROM THE ADDITION OF .1 PER CENT CONC OF GOLD ATOMS
        C     TO A PERFECT COPPER CRYSTAL.
        C
        C
              DIMENSION P(2,16,100)
              DIMENSION X(100)
              DIMENSION THETA(100)
              DIMENSION S(56)
              REAL NUMAX
              REAL KELVIN
              COMPLEX PC
              SINH(Y)=(EXP(X)-EXP(-X))/2.0
              PI=3.141592653589790
              NUMAX=6.0E12
              PLANCK=6.62559E-27
              BOLTZ=1.38054E-16
              C=NUMAX*PLANCK/(2.*BOLTZ)
              CONC=0.01
              READ (5) P
        C     P IS PERFECT XL GREENS FUNCTION
              WT DEFCT = 196.67
              WT HOST = 63.54
              E=1.0-WTDEFCT/WTHOST
              DO 1 K=1,100
              X(K)=(K-0.5)/100.
        C     X(K) ARE 100 FREQUENCY BINS BETWEEN 0. AND 1.
              PC=CMPLX(P(1,1,K),P(2,1,K))
              THETA(K)=AIMAG(CLOG(1.-E*X(K)*X(K)*PC))
        1     CONTINUE
              KELVIN=1
              DO 3 J=1,56
              N=0.
              B=C/KELVIN
              DO 2 K=1,100
              N=N+X(K)*THETA(K)/(SINH(B*X(K))**2)
        2     CONTINUE
              S(J)=-3./(          PI)*B*B*N*CONC*0.01
              CALL PLOTPT (KELVIN,S(J),4)
              KELVIN=KELVIN+25
        3     CONTINUE
              CALL OUTPLT
              PRINT 500
              PRINT 520, S
        500   FORMAT (1H1)
        520   FORMAT (1X,1P,4E25.5)
              END
```

```
               PROGRAMMETST (INPUT,OUTPUT,TAPE5=INPUT)
       C
       C
       C       THIS PROGRAMME COMPARES A GREENS FUNCTION HIGH TEMPERATURE ENTROPY (S)
       C       WITH A SIMPLE MINDED FORMULA (Z)
       C
       C
               DIMENSION P(2,16,100)
               DIMENSION X(100)
               DIMENSION THETA(100)
               DIMENSION S(21)
               DIMENSION Z(21)
               DIMENSION SBX2(100)
               REAL NUMAX
               REAL N,KELVIN
               COMPLEX PC
               SINH(X)=(EXP(X)-EXP(-X))/2.0
               PI=3.14159265358979
               NUMAX=3.0E12
               PLANCK=6.62559E-27
               BOLTZ=1.38054E-16
               C=NUMAX*PLANCK/(2.*BOLTZ)
               KELVIN=1200.
               B=C/KELVIN
               CONC=0.01
               WT HOST = 63.54
               READ (5) P
       C       P IS PERFECT XL GREENS FUNCTION
               DO 1 K=1,100
               X(K)=(K-0.5)/100.
       C       X(K) ARE 100 FREQUENCY BINS BETWEEN 0. AND 1.
               SBX2(K)= SINH( B*X(K) ) **2
       1       CONTINUE
               WTDEFCT=WTHOST+0.001
               DO 3 J=1,21
               E=1.0-WTDEFCT/WTHOST
               N=0.
               DO 2 K=1,100
               PC=CMPLX(P(1,1,K),P(2,1,K))
               THETA(K)=AIMAG(CLOG(1.-E*X(K)*X(K)*PC))
               N=N+X(K)*THETA(K)/SBX2(K)
       2       CONTINUE
               S(J)=-3./(          PI)*B*B*N*CONC*0.01
               A=WTDEFCT/WTHOST
               Z(J)=3./2.*ALOG(A)*CONC
               CALL PLOTPT (A,S(J),4)
               CALL PLOTPT (A,Z(J),2)
               WTDEFCT=WTDEFCT+0.15*WTHOST
       3       CONTINUE
               CALL OUTPLT
               PRINT 510
               PRINT 500, S
               PRINT 500, Z
       500     FORMAT (1X,1P,10E12.3)
       510     FORMAT (1H1)
               END
```

```
         PRINT 500
         CONC=CONC+0.0001
60     4   CONTINUE
     500   FORMAT (1X,1P,10E12.3)
     510   FORMAT (29X,*CONC=*,1PE10.3,45X,1PE10.3,/)
         END
```