ELECTRONIC SPECIFIC HEAT

ELECTRONIC SPECIFIC HEAT

IN DILUTE ALLOYS

By

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SCOPE AND CONTENTS:

The electronic part of the specific heat γ is calculated for dilute alloys at zero temperature. Only alloys where the impurity and the host ions have the same valence are considered. We take into account two mechanisms which change the value of γ of the pure metal. First the impurities affect the band structure and therefore the Fermi level density of states $\rho(E_F)$. Second they also influence the electron-phonon interaction and hence the mass renormalization. We calculate γ from first principles using the Born-von Kármán lattice dynamics theory, electron-ion pseudopotentials and phonon Green's functions. The various corrections to γ are evaluated for NaK and KNa using the Ashcroft pseudopotential form factors. It is found that the change in the mass renormalization is more important than that in $\rho(E_F)$ in calculating the electronic specific heat for the alloy.

À JOSÉE

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CHAPTER I

INTRODUCTION

It is well known from experiments that the low temperature
electronic specific heat shows a strong deviation from the free
electron model behaviour as the coefficient of the linear temperature
part is sometimes bigger, sometimes smaller than its free electron
value. At the international conference on the Fermi surface held at
Cooperstown in 1960, Quinn suggested a mechanism of enhancement of
the electronic specific heat. On the other hand, Stern (1965)
proposed a mechanism which lowers it.

Since the experiments are carried out in dilute alloys, Stern
developed a theory to calculate the change in the Fermi level density
of states due to impurities. He considered an alloy where the host
and the impurity have the same valence. The charge distribution around
an impurity is not the same as around a host due to screening. He
exploited this fact to argue that the density of states at the Fermi
level decreases in the alloy from the pure metal. He calculated its
change using second order perturbation theory.

Quinn (1960) suggested that the electronic part of the specific
heat could be enhanced significantly due to the renormalization of the
electronic mass as a result of the electron-phonon interaction. It
appears that an electron of momentum $\hbar\underline{k}$ and energy $\varepsilon_{\underline{k}}$ can scatter to
an electron state of momentum $\hbar\underline{k}'$ and energy $\varepsilon_{\underline{k}'}$ with the emission of

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a phonon of momentum $\hbar(\underline{k}-\underline{k}')$ and energy $\hbar\omega(\underline{k}-\underline{k}')$. This is a virtual scattering process because the energy is not conserved. It raises the energy of the system and therefore the specific heat. This change in the specific heat has been calculated by various authors. Among them is Migdal (1958) who used a Green's function technique. Wilkins (1968) showed how one can obtain the same result from a self-consistent second order perturbation theory. Ashcroft and Wilkins (1965) estimated the mass enhancement from first principles, as did Pytte (1967), Janak (1968), Trofimenkoff, Carbotte and Dynes (1968), Clune and Green (1970) and Carbotte, Truant and Dynes (1970).

Our purpose is to incorporate the two mechanisms which change the electronic specific heat in a global theory, in order to discuss their relative importance in a dilute alloy. Taylor (1969) has already tried to consider both the electron-phonon interaction and the impurities. He evaluates in a crude way the contribution from the emission or absorption of phonons at impurity sites. Our theory is more complete than his. We obtain more terms and estimate them with greater accuracy. We use a self-consistent perturbation theory approach following Wilkins in order to facilitate the comparison with Stern's theory. We also consider only alloys where impurities and hosts have the same valence.

We write down the Hamiltonian of the system in the second chapter. The concentration of impurities that we have in mind is of the order of 1% or less. We may therefore neglect clustering and impurity-impurity interactions. We obtain the potential energy from a knowledge of lattice dynamics and electron-ion pseudopotential. The

pseudopotential of an impurity is different from that of a host; this will give rise to Stern's term as well as additional corrections. We use second order perturbation theory to calculate the ground state energy of the alloy at zero temperature. It contains the electron-phonon interaction term of the pure metal, an impurity term which we call Stern's term, and two additional cross terms. Correlations between the ion displacements from equilibrium are treated by a phonon Green's function technique. We average over all possible configurations of impurities to obtain a physical answer. Since we do not know the necessary Green's functions, we approximate the phonons by the perfect crystal ones. We calculate these phonons from a Born-von Kármán force constant model.

In Chapter III we find the energy of a quasiparticle of momentum $\hbar p$ propagating through the lattice. We present Stern's theory, learn from him how to calculate the decrease in the density of states at the Fermi level due to the impurities, and compare the expressions obtained for a specific heat. From the electron-phonon interaction terms we obtain m^*/m in a fashion similar to that of Carbotte and Dynes (1968). We combine the results of each mechanism to get the total change of the electronic part of the specific heat. We cannot however evaluate this formula numerically; we make three more approximations to rewrite it in a convenient form. We use a local pseudopotential, assume a spherical Fermi surface and use one plane wave as the zeroth order wave function of the electrons. These approximations are realistic for alkalis but not for the polyvalent metals.

In the fourth chapter we present the results of numerical calculations done for KNa and NaK alloys. They are alkalis, thus the approximations should be valid. We use the Ashcroft form of the pseudopotential form factor and the random phase approximation for the dielectric function. This form factor is similar to those obtained by other methods. It has the advantage of containing only one parameter which has in fact been fixed from a consideration of the electrical resistivity.

On the basis of these calculations we compare the importance, in alkalis, of the two mechanisms which affect the electronic specific heat in the fifth chapter. We discuss the relative importance of each electron-phonon term. We relate our results to Taylor's work (1969) and compare the validity of Stern's theory and ours in different alloys.

We would like to mention that we assume knowledge of the phonon Green's function method presented in Marshall and Lovesey (1971).

CHAPTER II

IMPURITIES AND ELECTRON-PHONON INTERACTION

2.1 Hamiltonian

We are considering a crystal composed of N ions of which about 1% or less are impurities. The host and the impurity have the same valence. The crystal is a metal. Therefore the Hamiltonian must contain the kinetic energy of the ions and of the conduction electrons, and the potential energy of the alloy which can be divided into three kinds of interaction energy: electron-electron, ion-ion and electron-ion. We are studying a dilute alloy to avoid taking into account any clustering effect or interaction between impurities.

The solution of the Hamiltonian including only the kinetic energy and ·the potential energy of the ions is known. Therefore we shall use perturbation theory to calculate the ground state energy of the system at T=0. We would get the same result using a Green's functions technique. Nakajima and Watabe (1963) discuss the electron-phonon interaction with Green's functions and get the same formula as obtained by perturbation theory.

The unperturbed Hamiltonian is written in this way:

$$(2.1) \quad H_0 = \sum_{k\sigma} \epsilon_k f_{k\sigma} + \frac{1}{2} \sum_{\ell,\alpha}^{3N} M_\ell \dot{u}_\alpha^2(\ell,t) + \phi_0 + \frac{1}{2} \sum_{\substack{\ell,\ell' \\ \alpha,\beta}}^{9N^2} \phi_{\alpha\beta}(\ell,\ell') u_\alpha(\ell,t) u_\beta(\ell',t).$$

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To obtain this equation, we expand the ion-ion potential energy ϕ in terms of the small displacements of the ions $u_\alpha(\ell,t)$ and stop at second order. We also use the following definitions:

$$\epsilon_{\underline{k}} = \frac{\hbar^2 k^2}{2m}$$

$$f_{\underline{k}\sigma} = 1 \quad \text{if} \quad k < k_F$$
$$= 0 \quad \text{if} \quad k > k_F$$

$$\phi_{\alpha\beta}(\ell,\ell') = \frac{\partial\phi}{\partial u_\alpha(\ell,t)\partial u_\beta(\ell',t)}$$

(2.2) $R_{\underline{\ell}}(t) = \underline{\ell} + \underline{u}(\ell,t)$

where k_F is the Fermi momentum; σ is the spin; M_ℓ is the mass of the ion located at site $R_{\underline{\ell}}$; $u_\alpha(\ell,t)$ is the displacement of the ion at the ℓ'th site at time t; $\underline{\ell}$ is the equilibrium position; α, β, γ are the cartesian coordinates and ϕ_0 is the equilibrium potential energy.

It must be borne in mind that the unperturbed Hamiltonian describes the perturbed phonons. In Eq. (2.1) we take into account the difference between the host and impurity masses. We neglect however any change in the force constants.

The perturbed part of the Hamiltonian describes the electron-ion interaction in the adiabatic approximation. This means that we suppose that the electrons propagate independently of the velocity

of the ions since the ions are moving slowly compared to the electrons. The electron-ion interaction is expressed as a sum of pseudopotentials, each one due to an ion located at site R_ℓ.

$$(2.3) \quad W(\underline{r}) = \sum_\ell^N w_\ell(\underline{r}-\underline{R}_\ell) \ .$$

The pseudopotential is weak because it involves the repulsive effect of the bound state electrons as well as the attraction of the Hartree fields. The total potential energy is the sum over all conduction electrons which becomes, in the second quantization notation,

$$\int d^3r \psi^+(\underline{r})W(\underline{r})\psi(\underline{r}) \ .$$

$\psi(\underline{r})$ ($\psi^+(\underline{r})$) is the annihilation (creation) field operator which can be written

$$\psi(\underline{r}) = \sum_{k\sigma} \phi_k(\underline{r})|\sigma>C_{k\sigma}$$

$$\psi^+(\underline{r}) = \sum_{k\sigma} \phi_k^*(\underline{r})|\sigma>C_{k\sigma}^+ \ .$$

$C_{k\sigma}$ ($C_{k\sigma}^+$) annihilates (creates) an electron of spin σ in the state of momentum $\underline{k}$. $\phi_k(\underline{r})$ is a pseudowave function. It should be close to a plane wave since $W(\underline{r})$ is weak. Actually it is a superposition of a few plane waves. Only specific ones however are mixed by the crystal potential. In the m-plane wave approximation:

$$\phi_{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{\Omega}} \sum_{g=1}^{m} a_{\underline{k}}(\underline{Kg}) e^{i(\underline{k}+\underline{Kg})\cdot\underline{r}}$$

where Ω is the crystal volume and $\underline{Kg}$ is a reciprocal lattice vector. The coefficients $a_{\underline{k}}(\underline{Kg})$ are found by solving the Schroedinger equation.

To shorten the presentation of the calculations, we take into account only one plane wave. The generalization to the m-plane wave approximation is straightforward but tedious. The general equations are given at the beginning of Chapter III. For the rest of this chapter we consider

$$(2.4) \qquad \phi_{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{\Omega}} e^{i\underline{k}\cdot\underline{r}}$$

The perturbed Hamiltonian is then

$$(2.5) \qquad H' = \sum_{\underline{k}'\underline{k}\sigma} \langle\phi_{\underline{k}'}|W|\phi_{\underline{k}}\rangle C_{\underline{k}'\sigma}^{+} C_{\underline{k}\sigma}$$

where the matrix element

$$(2.6) \qquad \langle\phi_{\underline{k}'}|W|\phi_{\underline{k}}\rangle = \int d^3r \phi_{\underline{k}'}^{*}(\underline{r}) W(\underline{r}) \phi_{\underline{k}}(\underline{r})$$

$$= \sum_{\ell} e^{-i(\underline{k}'-\underline{k})\cdot R_{\ell}} \frac{\langle\underline{k}'|w_{\ell}|\underline{k}\rangle}{N}$$

after use of the Eqs. (2.3), (2.4) and the following definition

$$\langle\underline{k}'|w_{\ell}|\underline{k}\rangle = \frac{1}{\Omega_0} \int d^3y \, e^{-i\underline{k}'\cdot\underline{y}} w_{\ell}(\underline{y}) e^{i\underline{k}\cdot\underline{y}}$$

where Ω_0 is the volume per ion.

Thus the Hamiltonian is given by

$$(2.7) \quad H = 2 \sum_{\underline{k}} \varepsilon_{\underline{k}} f_{\underline{k}} + \frac{1}{2} \sum_{\ell,\alpha}^{3N} M_\ell \dot{u}_\alpha^2(\ell,t) + \frac{1}{2} \sum_{\substack{\ell,\ell' \\ \alpha,\beta}}^{9N^2} \phi_{\alpha\beta}(\ell,\ell')u_\alpha(\ell,t)u_\beta(\ell',t)$$
$$+ \phi_0 + \sum_{k'\underline{k}\,\ell} \ldots e^{-i(k'-\kappa)\cdot R_\ell} \frac{<k'|w_\ell|k>}{N} C_{\underline{k}'}^+ C_{\underline{k}}$$

from Eqs. (2.1), (2.5) and (2.6). We omitted the spin σ, as it is

understood that σ cannot change since there is no interaction in this

Hamiltonian that could flip the spin, and the expectation value of

$C_{\underline{k}'\sigma'}^+ C_{\underline{k}\sigma}$ in a given state is zero unless $\sigma' = \sigma$.

At this point we would like to mention that we are thinking of

doing the calculations for the real Fermi sea which includes the effect

of the crystal potential. Therefore Bragg reflections should not be

included in H' and we shall discard the terms where the Bragg effects

come in.

2.2 Ground State Energy

To calculate the energy of the ground state we use

perturbation theory

$$(2.8) \quad E_i = E_i^0 + <i|H'|i> + \sum_f{}' \frac{|<i|H'|f>|^2}{E_i-E_f} + \ldots$$

where $\{f\}$ is a complete set of eigenstates of H^0, i.e. unperturbed

electrons and perturbed phonons eigenstates. The prime on the sum

means that we restrict the sum to states where $\mathscr{E}_i \neq E_f$. We stop at second order. This gives the same result as is obtained using a Green's function technique. We do not use Green's functions in order to facilitate the comparison with Stern's theory (1965).

The first order correction vanishes for 3 reasons. First, the Bragg reflections are to be thought of as included in the calculation of E_i^0. Second, the electron-phonon interaction does not give any contribution because there are no phonons in the ground state. Third, the impurities do not change anything to first order. We consider the case where the impurity has the same valence as the host, so the long wavelength limits of the pseudopotentials are the same: $W(q=0) = -2\epsilon_F/3$, ϵ_F being the Fermi energy in the host. This means that $\langle \underline{k} | w_{imp} - w_{host} | \underline{k} \rangle = 0$ where "imp" stands for impurity. In summary then we can consider $\langle i | H' | i \rangle = 0$.

The second order term can be written as

$$(2.9) \qquad T^2 = \sum_f{}' \int_0^\infty d(\hbar\omega) \, \frac{|\langle i | H' | f \rangle|^2}{e_i - e_f - \hbar\omega} \, \delta(\hbar\omega + P_i - P_f) \ .$$

Here we separate the energy E_i into an electron part e_i and a phonon part P_i. The integral over ω is restricted to positive values since there is no phonon in the ground state. Using the equality

$$(2.10) \qquad \delta(\hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt \, e^{-i\omega t}$$

as well as Eqs. (2.5) and (2.6) we obtain

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$$(2.11) \quad T^2 = \sum_f{}' \int_0^\infty \frac{d(\hbar\omega)}{\epsilon_i - \epsilon_f - \hbar\omega} \int_{-\infty}^{+\infty} \frac{dt}{2\pi\hbar} e^{-i\omega t}$$

$$\times \langle i | \sum_{\underline{k}'\underline{k}} \sum_\ell e^{-i(\underline{k}-\underline{k}')\cdot R_\ell} \frac{\langle \underline{k} | w_\ell | \underline{k}' \rangle}{N} c_{\underline{k}}^+ c_{\underline{k}'} | f \rangle$$

$$\times \langle f | \sum_{\underline{K}'\underline{K}} \sum_{\ell'} e^{\frac{iP_f t}{\hbar}} e^{-i(\underline{K}'-\underline{K})\cdot R_{\ell'}} e^{-\frac{iP_i t}{\hbar}} \frac{\langle \underline{K}' | w_\ell | \underline{K} \rangle}{N} c_{\underline{K}'}^+ c_{\underline{K}} | i \rangle .$$

In order to get

$$\langle i | c_{\underline{k}}^+ c_{\underline{k}'} | f \rangle \langle f | c_{\underline{K}'}^+ c_{\underline{K}} | i \rangle \neq 0$$

we need $k' = K' > k_F$ and $k = K < k_F$. This means that for all the virtual transitions from $|i\rangle$ to $|f\rangle$ we create a hole in the state of momentum $\hbar\underline{k}$ and a particle in the state of momentum $\hbar\underline{k}'$. So

$$e_i - e_f = \epsilon_{\underline{k}} - \epsilon_{\underline{k}'} .$$

We use the phonon energy to introduce the Heisenberg operator $R_\ell(t)$

$$R_\ell(t) \equiv e^{+iP_f t/\hbar} R_\ell(0) e^{-iP_i t/\hbar} .$$

Now the subscript f does not appear explicitly any more and we take advantage of the completeness of the states $|f\rangle$. Equation (2.11) becomes

$$T^2 = \sum_{\underline{k}'\underline{k}}{}' f_{\underline{k}}(1-f_{\underline{k}'}) \int_0^\infty \frac{d(\hbar\omega)}{\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} - \hbar\omega} \int_{-\infty}^{+\infty} \frac{dt}{2\pi\hbar} e^{-i\omega t}$$

$$\times \sum_{\ell\ell'} \frac{\langle \underline{k} | w_\ell | \underline{k}' \rangle \langle \underline{k}' | w_{\ell'}' | \underline{k} \rangle}{N^2} \langle i | e^{-i(\underline{k}-\underline{k}')\cdot R_\ell(0)} e^{-i(\underline{k}'-\underline{k})\cdot R_{\ell'}(t)} | i \rangle .$$

We expand the exponents in terms of the displacement $\underline{u}(\ell,t)$ defined in Eq. (2.2). We keep the first order term only, neglecting higher orders. Keeping in mind that there are no phonons in the ground state, we obtain

$$
T^2 = \sum_{\underline{k}'\underline{k}}' f_{\underline{k}}(1-f_{\underline{k}'}) \int_0^\infty \frac{d(\hbar\omega)}{\epsilon_{\underline{k}}-\epsilon_{\underline{k}'}-\hbar\omega} \int_{-\infty}^{+\infty} \frac{dt}{2\pi\hbar} e^{-i\omega t}
$$

$$
\times \sum_{\ell\ell'} \frac{\langle\underline{k}|w_\ell|\underline{k}'\rangle\langle\underline{k}'|w_{\ell'}|\underline{k}\rangle}{N^2} e^{-i(\underline{k}'-\underline{k})\cdot(\underline{\ell}-\underline{\ell}')}
$$

$$
\times [1+(\underline{k}'-\underline{k})\cdot\langle i|\underline{u}(\ell,0)\underline{u}(\ell',t)|i\rangle\cdot(\underline{k}'-\underline{k})] .
$$

$\langle i|\underline{u}(\ell,0)u(\ell',t)|i\rangle$ measures the correlation between the displacement of the ion ℓ' at time t and the displacement of the ion ℓ at time 0. From this, one sees that

$$
(2.12) \quad \langle i|\underline{u}(\ell,0)\underline{u}(\ell',-t)|i\rangle = \langle i|\underline{u}(\ell,t)\underline{u}(\ell',0)|i\rangle .
$$

This correlation function is related to a Green's function. In the limit as the temperature goes to zero, one has (see Marshall and Lovesey, 1971)

$$
(2.13) \quad \int_{-\infty}^{+\infty} \frac{dt}{2\pi\hbar} e^{i\omega t}\langle i|u_\alpha(\ell,t)u_\beta(\ell',0)|i\rangle = -\frac{1}{\pi} \text{Im} G_{\alpha\beta}(\ell,\ell',\omega)
$$

where α, β are the cartesian coordinates. If one transforms (t) to $(-t)$ and uses Eqs. (2.10), (2.12) and (2.13), the second order term becomes

$$(2.14) \quad T^2 = \sum_{\underline{k}'\underline{k}}' f_{\underline{k}}(1-f_{\underline{k}'}) \int_0^\infty \frac{d(\hbar\omega)}{\epsilon_{\underline{k}}-\epsilon_{\underline{k}'}-\hbar\omega} \sum_{\ell\ell'} \frac{\langle\underline{k}|w_\ell|\underline{k}'\rangle\langle\underline{k}'|w_{\ell'}|\underline{k}\rangle}{N^2}$$

$$\times e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')}[\delta(\hbar\omega) - \sum_{\alpha\beta}\frac{K_\alpha K_\beta}{\pi} ImG_{\alpha\beta}(\ell,\ell',\omega)]$$

where we set $\underline{k}'-\underline{k} = \underline{K}$ for simplicity.

Until now we have assumed a specific configuration of the hosts and impurities. We would like to average over all possible configurations to get the physical result. For this we need the following definitions:

$$w_\ell = w + P_\ell \Delta w \qquad\qquad \Delta w \equiv w_{imp} - w_{host}$$

$$w \equiv w_{host} \qquad\qquad P_\ell \equiv 1 \text{ if there is an impurity at site } R_\ell$$
$$\equiv 0 \text{ otherwise .}$$

Then

$$(2.15) \quad \langle \sum_{\ell\ell'} \langle\underline{k}|w_\ell|\underline{k}'\rangle\langle\underline{k}'|w_{\ell'}|\underline{k}\rangle e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')}G_{\alpha\beta}(\ell,\ell',\omega)\rangle$$

$$= |\langle\underline{k}|w|\underline{k}'\rangle|^2 \langle \sum_{\ell\ell'} e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')}G_{\alpha\beta}(\ell,\ell',\omega)\rangle$$

$$+ 2Re\{\langle\underline{k}|w|\underline{k}'\rangle\langle\underline{k}'|\Delta w|\underline{k}\rangle\} \langle \sum_{\ell\ell'} P_\ell e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')}G_{\alpha\beta}(\ell,\ell',\omega)\rangle$$

$$+ |\langle\underline{k}|\Delta w|\underline{k}'\rangle|^2 \langle \sum_{\ell\ell'} P_\ell P_{\ell'} e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')}G_{\alpha\beta}(\ell,\ell',\omega)\rangle$$

where $\langle \ \rangle$ means a configuration average. We shall explain in detail only the calculation of the most difficult configuration average and quote the others. We first draw attention to the following: the

configuration average restores the translational symmetry of the crystal. This means that the impurities can be anywhere in the crystal and that $<G_{\alpha\beta}(\ell,\ell',\omega)>$ can be expanded in terms of the eigenvectors of the force constant matrix. These eigenvectors $\underline{\sigma}^j(q)$ are the polarization vectors.

$$(2.16) \quad <G_{\alpha\beta}(\ell,\ell',\omega)> = \frac{1}{N} \sum_{\substack{q \\ F.B.Z.}}^{N} e^{-i\underline{q}\cdot\underline{\ell}} \overline{G_{\alpha\beta}}(q,\omega) e^{i\underline{q}\cdot\underline{\ell}'}$$

$$(2.17) \quad \overline{G_{\alpha\beta}}(q,\omega) = \frac{1}{M} \sum_{j}^{3} \sigma_\alpha^j(q)\sigma_\beta^j(q)\overline{G^j}(q,\omega)$$

$$\frac{1}{M} \sum_{\ell',\beta}^{3N} \phi_{\alpha\beta}(\ell,\ell') e^{i\underline{q}\cdot(\underline{\ell}'-\underline{\ell})}\sigma_\beta^j(\underline{q}) = \omega_j^2(\underline{q})\sigma_\alpha^j(\underline{q})$$

where j is the mode index. We assume that there is no short-range order in the system, i.e. that there is no correlation between impurities at sites $\underline{\ell}$ and $\underline{\ell}'$. "c" is the probability that a lattice site is occupied by an impurity. We are now ready to calculate a configuration average.

$$< \sum_{\ell\ell'} P_\ell e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')} G_{\alpha\beta}(\ell,\ell',\omega)>$$

$$= \sum_\ell <P_\ell G_{\alpha\beta}(\ell,\ell',\omega)> + \sum_\ell \sum_{\ell'\neq\ell} <P_\ell G_{\alpha\beta}(\ell,\ell',\omega)> e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')} \; .$$

We average keeping ℓ and ℓ' constant.

$$= c \sum_\ell <G_{\alpha\beta}^{dd}(\ell,\ell',\omega)> + \sum_\ell \sum_{\ell'\neq\ell} [c^2<G_{\alpha\beta}^{dd}(\ell,\ell',\omega)>+c(1-c)<G_{\alpha\beta}^{dh}(\ell,\ell',\omega)>] e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')}.$$

where $G_{\alpha\beta}^{dd}$ measures the correlation between two impurities and $G_{\alpha\beta}^{dh}$ means that ℓ is an impurity site and ℓ' a host site. From (2.16),

$$= \frac{c}{N} \sum_{q} \sum_{\ell} G_{\alpha\beta}^{dd}(q,\omega) + \sum_{q} \sum_{\ell} \sum_{\ell'\neq\ell} [\frac{c^2}{N} G_{\alpha\beta}^{dd}(q,\omega) + \frac{c(1-c)}{N} G_{\alpha\beta}^{dh}(q,\omega)] e^{i(\underline{K}-\underline{q})\cdot(\underline{\ell}-\underline{\ell}')}$$

We had to separate the terms where $\ell' = \ell$ and $\ell' \neq \ell$ because, even if we assume no correlation between ℓ' and ℓ, the site ℓ is "correlated" with itself. For convenience, we lift the restriction on the second sum.

(2.18)

$$= \frac{c}{N} \sum_{q} \sum_{\ell} G_{\alpha\beta}^{dd}(q,\omega) + \sum_{q} \sum_{\ell\ell'} [\frac{c^2}{N} G_{\alpha\beta}^{dd}(q,\omega) + \frac{c(1-c)}{N} G_{\alpha\beta}^{dh}(q,\omega)] [e^{i(\underline{K}-\underline{q})(\underline{\ell}-\underline{\ell}')} - \delta_{\ell\ell'}]$$

$$= c \sum_{q} G_{\alpha\beta}^{dd}(q,\omega) + c^2 \sum_{q} G_{\alpha\beta}^{dd}(q,\omega) [N\delta_{\underline{K}-\underline{q}-\underline{Kg}} - 1]$$

$$+ c(1-c) \sum_{q} G_{\alpha\beta}^{dh}(q,\omega) [N\delta_{\underline{K}-\underline{q}-\underline{Kg}} - 1]$$

where $\underline{Kg}$ is a reciprocal lattice vector. The other configuration averages give:

$$(2.19) \quad < \sum_{\ell\ell'} e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')} > = N^2 \delta_{\underline{K}-\underline{Kg}}$$

$$(2.20) \quad < \sum_{\ell\ell'} P_{\ell} e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')} > = cN^2 \delta_{\underline{K}-\underline{Kg}}$$

$$(2.21) \quad < \sum_{\ell\ell'} P_{\ell} P_{\ell'} e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')} > = Nc(1-c) + N^2 c^2 \delta_{\underline{K}-\underline{Kg}}$$

$$(2.22) \quad \left\langle \sum_{\ell\ell'} e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')} G_{\alpha\beta}(\ell,\ell',\omega)\right\rangle = N \sum_{\underline{q}} \overline{G}_{\alpha\beta}(q,\omega)\delta(\underline{K}-\underline{q}-\underline{Kg})$$

$$(2.23) \quad \left\langle \sum_{\ell\ell'} P_{\ell}P_{\ell'} e^{i\underline{K}\cdot(\underline{\ell}-\underline{\ell}')} G_{\alpha\beta}(\ell,\ell',\omega)\right\rangle = \sum_{\underline{q}} G_{\alpha\beta}^{dd}(q,\omega)[c(1-c)+c^2 N\delta_{\underline{K}-\underline{q}-\underline{Kg}}]$$

Note that $\overline{G_{\alpha\beta}}(\underline{q},\omega)$ is an average Green's function which does not specify whether it correlates impurities, hosts or both.

Combining Eqs. (2.14) to (2.23), and using

$$\int_0^\infty d(\hbar\omega)\,\frac{\delta(\hbar\omega)}{\varepsilon_{\underline{k}}-\varepsilon_{\underline{k}'}-\hbar\omega} = \frac{1}{\varepsilon_{\underline{k}}-\varepsilon_{\underline{k}'}}\ ,$$

the second order term of the perturbation theory becomes

$$(2.24) \quad T^2 = \sideset{}{'}\sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'})\,\frac{|\langle\underline{k}|w|\underline{k}'\rangle|^2}{\varepsilon_{\underline{k}}-\varepsilon_{\underline{k}'}}\,\delta_{\underline{k}'-\underline{k}-\underline{Kg}}$$

$$+ \sideset{}{'}\sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'})\,\frac{2\mathrm{Re}\{\langle\underline{k}|w|\underline{k}'\rangle\langle\underline{k}'|\Delta w|\underline{k}\rangle\}}{\varepsilon_{\underline{k}}-\varepsilon_{\underline{k}'}}\,c\delta_{\underline{k}'-\underline{k}-\underline{Kg}}$$

$$+ \sideset{}{'}\sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'})\,\frac{|\langle\underline{k}|\Delta w|\underline{k}'\rangle|^2}{\varepsilon_{\underline{k}}-\varepsilon_{\underline{k}'}}\,[\frac{c(1-c)}{N}+c^2\delta_{\underline{k}'-\underline{k}-\underline{Kg}}]$$

$$- \sideset{}{'}\sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'})\int_0^\infty \frac{d(\hbar\omega)}{\varepsilon_{\underline{k}}-\varepsilon_{\underline{k}'}-\hbar\omega}\,\frac{1}{M}\,\underset{\mathrm{F.B.Z.}}{\overset{N}{\underset{\underline{q}}{\sum}}}\,\sum_j^3\,\frac{|(\underline{k}'-\underline{k})\cdot\underline{\sigma}^j(\underline{q})|^2}{\pi}$$

$$\times \mathrm{Im}\{|\langle\underline{k}|w|\underline{k}'\rangle|^2 \overline{G}^j(q,\omega)\delta_{\underline{k}-\underline{q}-\underline{Kg}}$$

$$+ 2\mathrm{Re}[\langle\underline{k}|w|\underline{k}'\rangle\langle\underline{k}'|\Delta w|\underline{k}\rangle]\,[G^{dd,j}(\underline{q},\omega)(\frac{c}{N}+c^2\delta_{\underline{K}-\underline{q}-\underline{Kg}}-\frac{c^2}{N})$$

$$+ G^{dh,j}(\underline{q},\omega)\,\frac{c(1-c)}{N}\,(N\delta_{\underline{K}-\underline{q}-\underline{Kg}}-1)]$$

$$+ |\langle\underline{k}|\Delta w|\underline{k}'\rangle|^2 G^{dd,j}(\underline{q},\omega)[\frac{c(1-c)}{N}+c^2\delta_{\underline{K}-\underline{q}-\underline{Kg}}]\}\ .$$

To go any further, we need to know the Green's functions $\overline{G^j}(q,\omega)$, $G^{dd,j}(q,\omega)$ and $G^{dh,j}(q,\omega)$. However, they have not been calculated for the system that we are interested in. So at this point we are going to neglect the change in the dispersion curve due to the impurities and we shall use the perfect crystal Green's function $P^j(q,\omega)$. Carbotte et al. (1970) showed that this is a good approximation. One can easily imagine that the accoustic phonons which have long wavelengths are very little perturbed by a few impurities.

By convention we evaluate the imaginary part of $P^j(q,\omega)$ by giving a small positive imaginary part δ to ω and taking the limit as δ goes to zero

$$P^j(q,\omega) = \lim_{\delta \to 0^+} \frac{1}{(\omega+i\delta)^2 - \omega_j^2(q)}$$

$$(2.25) \quad \text{Im}P^j(q,\omega) = \frac{-\pi}{2\omega_j(q)} [\delta(\omega-\omega_j(q)) - \delta(\omega+\omega_j(q))] .$$

The perfect crystal Green's function has been calculated by Dawber and Elliott (1963). From Eq. (2.25)

$$\int_0^\infty d\omega \, \frac{\text{Im}P^j(q,\omega)}{\varepsilon_{\underline{k}}-\varepsilon_{\underline{k}'}-\hbar\omega} = -\frac{\pi}{2\omega_j(q)} \times \frac{1}{\varepsilon_{\underline{k}}-\varepsilon_{\underline{k}'}-\hbar\omega_j(q)}$$

and Eq. (2.24) becomes

(2.26)

$$T^2 = \sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'}) \frac{|<\underline{k}|w|\underline{k}'>|^2}{\epsilon_{\underline{k}}-\epsilon_{\underline{k}'}} \delta_{\underline{k}'-\underline{k}-\underline{Kg}}$$

$$+ \sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'}) \frac{2Re[<\underline{k}|w|\underline{k}'><\underline{k}'|\Delta w|\underline{k}>]}{\epsilon_{\underline{k}}-\epsilon_{\underline{k}'}} c\delta_{\underline{k}'-\underline{k}-\underline{Kg}}$$

$$+ \sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'}) \frac{|<\underline{k}|\Delta w|\underline{k}'>|^2}{\epsilon_{\underline{k}}-\epsilon_{\underline{k}'}} [\frac{c(1-c)}{N} + c^2\delta_{\underline{k}'-\underline{k}-\underline{Kg}}]$$

$$- \sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'}) \sum_{\substack{qj \\ F.B.Z.}} \frac{\hbar|(\underline{k}'-\underline{k})\cdot\underline{\sigma}^j(\underline{q})|^2}{2MN\omega_j(\underline{q})} \frac{|<\underline{k}|w|\underline{k}'>|^2}{\epsilon_{\underline{k}}-\epsilon_{\underline{k}'}-\hbar\omega_j(\underline{q})} \delta_{(\underline{k}'-\underline{k}-\underline{q}-\underline{Kg})}$$

$$- \sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'}) \sum_{\substack{qj \\ F.B.Z.}} \frac{\hbar|(\underline{k}'-\underline{k})\cdot\underline{\sigma}^j(\underline{q})|^2}{2MN\omega_j(\underline{q})} \frac{2Re[<\underline{k}|w|\underline{k}'><\underline{k}'|\Delta w|\underline{k}>]}{\epsilon_{\underline{k}}-\epsilon_{\underline{k}'}-\hbar\omega_j(\underline{q})} c\delta_{(\underline{k}'-\underline{k}-\underline{q}-\underline{Kg})}$$

$$- \sum_{\underline{k}'\underline{k}} f_{\underline{k}}(1-f_{\underline{k}'}) \sum_{\substack{qj \\ F.B.Z.}} \frac{\hbar|(\underline{k}'-\underline{k})\cdot\underline{\sigma}^j(\underline{q})|^2}{2MN\omega_j(\underline{q})} \frac{|<\underline{k}|\Delta w|\underline{k}'>|^2}{\epsilon_{\underline{k}}-\epsilon_{\underline{k}'}-\hbar\omega_j(\underline{q})} [\frac{c(1-c)}{N}$$

$$+ c^2\delta_{(\underline{k}'-\underline{k}-\underline{q}-\underline{Kg})}] \ .$$

We would like to discuss each of these terms. The first one describes Bragg scattering from the static lattice. We shall forget about it for the reason mentioned earlier. The second one is a cross term between the Bragg term and the impurity term. We must discard it too. The third term is related to what Stern (1965) calculated. He thinks that it is the main factor in the change of the Fermi density of states and consequently in the specific heat. The fourth one is due to the electron-phonon interaction. It has been calculated by Ashcroft and Wilkins (1965). They believe that this is the important influence on the specific heat. The two last terms are due to the electron-phonon interaction together with the influence of the impurities.

CHAPTER III

ELECTRONIC SPECIFIC HEAT

3.1 Quasiparticle

So far we know the ground state energy of a system of N ions and N conduction electrons. However we are interested in the energy of the low lying excited states of the conduction electrons. To get these we proceed as follows: we calculate the energy of an excited state of momentum $\hbar p$ of a system of N+1 electrons from which we subsract our previous value for the ground state energy of N electrons. This gives the energy of a quasiparticle (electron dressed with phonons) of momentum $\hbar p$ propagating in the crystal. Letting its momentum go to $\hbar k_F$ we should have a good evaluation of the energy of the quasiparticles involved in the specific heat.

For simplicity we write the energy of the system of N electrons in the following way:

$$(3.1) \quad E_0^N = 2\sum_{\underline{k}} \epsilon_{\underline{k}} f_{\underline{k}} + \sum'_{\underline{k}'\underline{k}} \cdot \frac{|i_{\underline{k}'\underline{k}}|^2}{\epsilon_{\underline{k}} - \epsilon_{\underline{k}'}} f_{\underline{k}}(1-f_{\underline{k}'})$$

$$+ \sum'_{\underline{k}'\underline{k}} \sum_{j} \frac{|g_{\underline{k}'\underline{k}j}|^2}{\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} - \hbar\omega_j(\underline{k}'-\underline{k})} f_{\underline{k}}(1-f_{\underline{k}'})$$

$$+ \sum'_{\underline{k}'\underline{k}} \sum_{j} \cdot \frac{|h_{\underline{k}'\underline{k}j}|^2}{\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} - \hbar\omega_j(\underline{k}'-\underline{k})} f_{\underline{k}}(1-f_{\underline{k}'})$$

$$+ \sum'_{\underline{k}'\underline{k}} \sum_{\underline{q}j} \frac{|f_{\underline{k}'\underline{k}\underline{q}j}|^2}{\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} - \hbar\omega_j(\underline{q})} f_{\underline{k}}(1-f_{\underline{k}'})$$

where

(3.2) $\quad |1_{\underline{k}'\underline{k}}|^2 = \frac{c}{N} |<\underline{k}|\Delta w|\underline{k}'>|^2$

(3.3) $\quad |g_{\underline{k}'\underline{k}j}|^2 = \frac{\hbar}{2MN\omega_j(\underline{k}'-\underline{k})} |(\underline{k}'-\underline{k})\cdot\underline{\sigma}^j(\underline{k}'-\underline{k})|^2 |<\underline{k}|w|\underline{k}'>|^2$

(3.4) $\quad |h_{\underline{k}'\underline{k}j}|^2 = \frac{\hbar}{2MN\omega_j(\underline{k}'-\underline{k})} |(\underline{k}'-\underline{k})\cdot\underline{\sigma}^j(\underline{k}'-\underline{k})|^2 \, 2cRe[<\underline{k}|w|\underline{k}'><\underline{k}'|\Delta w|\underline{k}>]$

(3.5) $\quad |f_{\underline{k}'\underline{k}qj}|^2 = \frac{\hbar}{2MN\omega_j(\underline{q})} |(\underline{k}'-\underline{k})\cdot\underline{\sigma}^j(\underline{q})|^2 \frac{c}{N} |<\underline{k}'|\Delta w|\underline{k}>|^2 \; .$

We neglect the terms proportional to c^2 since we have in mind that c is less than 1%. In the m-plane wave approximation, the coupling constants are:

$$|1_{\underline{k}'\underline{k}}|^2 = \frac{c}{N} \cdot \sum_{n'n}^{m^2} a_{\underline{k}}(\underline{K}_n)^* a_{\underline{k}'}(\underline{K}_{n'}) \sum_{n'\eta}^{m^2} a_{\underline{k}'}(\underline{K}_{\eta'})^* a_{\underline{k}}(\underline{K}_\eta)$$

$$\times <\underline{k}'+\underline{K}_{n'}|\Delta w|\underline{k}+\underline{K}_n><\underline{k}+\underline{K}_\eta|\Delta w|\underline{k}'+\underline{K}_{\eta'}>$$

$$|g_{\underline{k}'\underline{k}j}|^2 = -\frac{\hbar}{2MN\omega_j(\underline{k}'-\underline{k})} \sum_{n'n}^{m^2} a_{\underline{k}}(\underline{K}_n)^* a_{\underline{k}'}(\underline{K}_{n'}) \sum_{n'\eta}^{m^2} a_{\underline{k}'}(\underline{K}_\eta)^* a_{\underline{k}}(\underline{K}_{-\eta})$$

$$\times (\underline{k}'+\underline{K}_{n'},-\underline{k}-\underline{K}_n)\cdot\underline{\sigma}^j(\underline{k}'-\underline{k}) (\underline{k}'+\underline{K}_\eta,-\underline{k}-\underline{K}_\eta)\cdot\underline{\sigma}^j(\underline{k}'-\underline{k})$$

$$\times <\underline{k}'+\underline{K}_{n'}|w|\underline{k}+\underline{K}_n><\underline{k}+\underline{K}_\eta|w|\underline{k}'+\underline{K}_{\eta'}>$$

$$|f_{\underline{k}'\underline{k}qj}|^2 = -\frac{c}{N} \frac{\hbar}{2MN\omega_j(\underline{q})} \sum_{n'n}^{m^2} a_{\underline{k}}(\underline{K}_n)^* a_{\underline{k}'}(\underline{K}_{n'}) \sum_{n'\eta}^{m^2} a_{\underline{k}'}(\underline{K}_{\eta'})^* a_{\underline{k}}(\underline{K}_\eta)$$

$$\times (\underline{k}'+\underline{K}_{n'},-\underline{k}-\underline{K}_n)\cdot\underline{\sigma}^j(\underline{q}) (\underline{k}'+\underline{K}_\eta,-\underline{k}-\underline{K}_\eta)\cdot\underline{\sigma}^j(\underline{q})$$

$$\times <\underline{k}'+\underline{K}_{n'}|\Delta w|\underline{k}+\underline{K}_n><\underline{k}+\underline{K}_\eta|\Delta w|\underline{k}'+\underline{K}_{\eta'}> \; .$$

$|h_{\underline{k}'\underline{k}j}|^2$ is obtained from $|g_{\underline{k}'\underline{k}j}|^2$ replacing $<\underline{k}'+\underline{K}_\eta,|w|\underline{k}+\underline{K}_\eta><\underline{k}+\underline{K}_\eta|w|\underline{k}'+\underline{K}_\eta,>$

by $2c\,Re[<\underline{k}'+\underline{K}_\eta,|w|\underline{k}+\underline{K}_\eta><\underline{k}+\underline{K}_\eta|\Delta w|\underline{k}'+\underline{K}_\eta,>]$.

We easily calculate the energy of a system of N+1 electrons where the added electron has momentum $\hbar\underline{p}$. The additional electron propagates in the crystal and polarizes it in its vicinity. The electron plus its cloud of phonons is a quasiparticle whose energy is given by·

$$
\begin{aligned}
E_{\underline{p}} &= \left(E_{\underline{p}}^{N+1}\right) - E_0^N \\[1em]
(3.6)\quad E_{\underline{p}} &= \epsilon_{\underline{p}} + \Sigma'_{\underline{k}}\,\frac{|i_{\underline{k}\underline{p}}|^2}{\epsilon_{\underline{p}}-\epsilon_{\underline{k}}} \\[1em]
&+ \Sigma'_{\underline{k}j}\,|g_{\underline{k}\underline{p}j}|^2\left\{\frac{-f_{\underline{k}}}{\epsilon_{\underline{k}}-\epsilon_{\underline{p}}-\hbar\omega_j(\underline{p}-\underline{k})} - \frac{(1-f_{\underline{k}})}{\epsilon_{\underline{k}}-\epsilon_{\underline{p}}+\hbar\omega_j(\underline{p}-\underline{k})}\right\} \\[1em]
&+ \Sigma'_{\underline{k}j}\,|h_{\underline{k}\underline{p}j}|^2\left\{\frac{-f_{\underline{k}}}{\epsilon_{\underline{k}}-\epsilon_{\underline{p}}-\hbar\omega_j(\underline{p}-\underline{k})} - \frac{(1-f_{\underline{k}})}{\epsilon_{\underline{k}}-\epsilon_{\underline{p}}+\hbar\omega_j(\underline{p}-\underline{k})}\right\} \\[1em]
&+ \Sigma'_{\underline{k}\underline{q}j}\,|f_{\underline{k}\underline{p}\underline{q}j}|^2\left\{\frac{-f_{\underline{k}}}{\epsilon_{\underline{k}}-\epsilon_{\underline{p}}-\hbar\omega_j(\underline{q})} - \frac{(1-f_{\underline{k}})}{\epsilon_{\underline{k}}-\epsilon_{\underline{p}}+\hbar\omega_j(\underline{q})}\right\}.
\end{aligned}
$$

The first part of the curly brackets reflects the fact that the state of momentum $\hbar\underline{p}$ is now occupied and cannot be used in the virtual transitions while the second part comes because it is now possible to create a hole of momentum $\hbar\underline{p}$. We are ready to calculate the change in the specific heat.

3.2 Stern's Theory

Stern (1965) has given a theory of the effect of fixed impurities

on the specific heat. It seems appropriate at this point to derive his theory and relate it to ours.

Stern takes a starting point different from ours. His zeroth approximation to the alloy potential is the average crystal potential. He is mainly interested in the noble metal alloys. He notes that experiments have shown that the area of contact of the Fermi surface neck with the Brillouin zone boundaries varies linearly from pure silver to pure gold. He then assumes that the whole Fermi surface changes linearly from silver to gold which implies that it can be calculated from an average potential and that the specific heat also varies linearly from silver to gold in zeroth approximation. The average potential has the periodicity of the lattice. He treats the difference between the real alloy potential and the average one as a perturbation which does not have the periodicity of the lattice. Stern calculates the energy levels from second order perturbation theory.

The average potential is

$$V_p(\underline{r}) = cV_{1p}(\underline{r}) + (1-c)V_{2p}(\underline{r})$$

where c is the atomic fraction of atoms 1, V_{1p} and V_{2p} are respectively the periodic potentials of type 1 and type 2 ions, i.e.

$$V_{jp}(\underline{r}) = \sum_g V_j(\underline{Kg})e^{i\underline{Kg}\cdot\underline{r}} .$$

The alloy potential is a sum over all lattice sites $\underline{R_n}$

$$V(\underline{r}) = \sum_n V(\underline{r}-\underline{R}_n)$$

where $V(\underline{r}-\underline{R}_n)$ may be V_1 or V_2, the potential of the particular ion located at the nth site. The perturbation is the difference between them

$$(3.7) \quad V_s(\underline{r}) = \sum_n \{V(\underline{r}-\underline{R}_n) - [cV_{1p}(\underline{r}-\underline{R}_n) + (1-c)V_{2p}(\underline{r}-\underline{R}_n)]\}$$

with the condition

$$V_s(\underline{Kg}) = 0 .$$

Starting with the Hamiltonian

$$H = 2 \sum_{\underline{k}} \varepsilon_{\underline{k}} f_{\underline{k}} + V_p(\underline{r}) + V_s(\underline{r})$$

second order perturbation theory gives

$$(3.8) \quad E_{\underline{k}} = E(\underline{k}) + E_2(\underline{k})$$

and

$$(3.9) \quad E_2(\underline{k}) = \sum_{\underline{k}'}' \frac{|\langle \underline{k}'|V_s|\underline{k}\rangle|^2}{E(\underline{k})-E(\underline{k}')}$$

where the energies $E(\underline{k})$ are the same as for a pure metal with the periodic potential V_p. One calculates the matrix elements $\langle \underline{k}'|V_s|\underline{k}\rangle$ from Eq. (3.7) and the following definition:

$$\Delta V(\underline{r}) = V_1(\underline{r}) - V_2(\underline{r}) \; .$$

It gives

$$\langle \underline{k}'|V_s|\underline{k}\rangle = \frac{\langle \underline{k}'|\Delta V|\underline{k}\rangle}{N} \; \Sigma_j \; e^{i(\underline{k}-\underline{k}')\cdot \underline{R}_j}$$

where the sum extends only over the atom-1 sites. Stern is thus distributing the difference of potentials over the atom-1 sites. Substituting this expression for $\langle \underline{k}'|V_s|\underline{k}\rangle$ in Eq. (3.9), we get

$$(3.10) \quad E_2(\underline{k}) = \frac{1}{N^2} \; \Sigma'_{\underline{k}'} \; \frac{|\langle \underline{k}'|\Delta V|\underline{k}\rangle|^2}{E(\underline{k})-E(\underline{k}')} \; |\Sigma_j \; e^{i(\underline{k}-\underline{k}')\cdot \underline{R}_j}|^2 \; .$$

We are interested in the configuration average of $|\Sigma_j \; e^{i(\underline{k}-\underline{k}')\cdot \underline{R}_j}|^2$ because this is the physical quantity.

$$\langle |\Sigma_j \; e^{i(\underline{k}-\underline{k}')\cdot \underline{R}_j}|^2 \rangle = Nc(1-c) + N^2 c^2 \delta(\underline{k}-\underline{k}'-\underline{Kg}) \; .$$

Using the condition $V_s(\underline{Kg}) = 0$; this equation reduces to

$$\langle |\Sigma_j \; e^{i(\underline{k}-\underline{k}')\cdot \underline{R}_j}|^2 \rangle = Nc(1-c) \; .$$

Equation (3.10) becomes

$$E_2(\underline{k}) = \frac{c(1-c)}{N} \; \Sigma'_{\underline{k}'} \; \frac{|\langle \underline{k}'|\Delta V|\underline{k}\rangle|^2}{E(\underline{k})-E(\underline{k}')} \; .$$

At this point we see that his term is a bit different from ours (Eq. (3.2)).

Stern's term does not include the periodic part of ΔV because he has introduced it in the unperturbed Hamiltonian.

He calculates the specific heat in the following way. Using Eq. (3.8) and the definition of the density of states at the energy level $E_{\underline{k}}$, one obtains

$$\rho(E_{\underline{k}}) = \frac{2\Omega}{(2\pi)^3} \int \frac{dS_\epsilon}{\nabla_{\underline{k}}[E(\underline{k}) + E_2(\underline{k})]} \cdot$$

He assumes that $E_2(\underline{k})$ depends only on $E(\underline{k})$ since $|<\underline{k}|\Delta V|\underline{k}'>|^2$ does not vary much for $\underline{k}'$ close to $\underline{k}$.

$$\rho(E_{\underline{k}}) = \frac{2\Omega}{(2\pi)^3} \int \frac{dS_\epsilon}{\nabla_{\underline{k}}(E(\underline{k}))[1 + \partial E_2(\underline{k})/\partial E(\underline{k})]} \cdot$$

Then he expands $[1 + \partial E_2(\underline{k})/\partial E(\underline{k})]^{-1}$ in a Taylor series and keeps only the first term. The first derivative is small ($\sim 10^{-3}$) and so that is a good approximation. Therefore

$$\rho(E_{\underline{k}}) = \rho_0(E(\underline{k}))[1 - \frac{\partial E_2(\underline{k})}{\partial E(\underline{k})}]$$

where $\rho_0(E(\underline{k}))$ is the zeroth order density of states at $E(\underline{k})$. Since the electronic part of the specific heat is proportional to the density of states at the Fermi level, we obtain

$$\gamma = \gamma_0[1 - \frac{\partial E_2(\underline{k})}{\partial E(\underline{k})}]\Big|_{|\underline{k}|=k_F}$$

or

$$\frac{\gamma - \gamma_0}{\gamma_0} = Kc(1-c)$$

where $K = \frac{1}{N} \left(\frac{\partial}{\partial E(\underline{k})} \left[\sum_{\underline{k}'}' \frac{|<\underline{k}'|\Delta V|\underline{k}>|^2}{E(\underline{k})-E(\underline{k}')} \right] \right) \bigg|_{|\underline{k}|=k_F}$

and γ_0 is the linearly interpolated result between the specific heat of the pure metal of type 1 and that of the pure metal of type 2.

This linear behaviour is introduced by Stern because he uses the virtual crystal (average potential) approximation as his starting point and builds in the disorder as a perturbation on the average potential. On the other hand, we start with the pure metal so that in the zeroth approximation it is γ_0 for $c=0$ that comes in and we build in the alloy nature as a perturbation on the pure metal. Stern's theory, as $c \to 0$, reduces appropriately to ours neglecting the contributions from the electron-phonon interaction.

If we go back to Eq. (3.6), consider the first two terms and proceed as Stern does, we get

$$\rho(E_{\underline{p}}) = \rho_0(\varepsilon_{\underline{p}}) \left[1 - \frac{\partial}{\partial \varepsilon_{\underline{p}}} \sum_{\underline{k}}' \frac{|i_{\underline{kp}}|^2}{\varepsilon_{\underline{p}}-\varepsilon_{\underline{k}}} \right] .$$

We neglect the variation of $|i_{\underline{kp}}|^2$ for $\underline{k}$ close to $\underline{p}$ which is the region of interest. Then

$$\rho(E_{\underline{p}}) = \rho_0(\varepsilon_{\underline{p}}) \left[1 + \sum_{\underline{k}}' \frac{|i_{\underline{kp}}|^2}{(\varepsilon_{\underline{p}}-\varepsilon_{\underline{k}})^2} \right]$$

so

(3.11) $\gamma = \gamma_0(c=0)[1 + \lambda_s]$

where λ_s is an average over the Fermi surface since all the states at the Fermi level contribute to the specific heat.

$$(3.12) \quad \lambda_s = \frac{\displaystyle\int_{S_F} \frac{dS_{\underline{p}}}{\hbar |v_{\underline{p}}|} \, {\sum_{\underline{k}}}' \, \frac{|i_{\underline{kp}}|^2}{(\varepsilon_{\underline{p}} - \varepsilon_{\underline{k}})^2}}{\displaystyle\int_{S_F} \frac{dS_{\underline{p}}}{\hbar |v_{\underline{p}}|}} \; .$$

3.3 Mass Renormalization

We now want to calculate the contributions to the specific heat due to the electron-phonon interaction. We consider Eq. (3.6) neglecting Stern's term and, in particular, we look at the energy denominators. Since the electron-phonon interaction is most important near the Fermi surface, we define

$$\tilde{\varepsilon}_{\underline{k}} = \varepsilon_{\underline{k}} - \varepsilon_F$$

$$\tilde{E}_{\underline{k}} = E_{\underline{k}} - \varepsilon_F \; .$$

The denominators become $\tilde{\varepsilon}_{\underline{k}} - \tilde{\varepsilon}_{\underline{p}} + \hbar\omega_j(\underline{p}-\underline{k})$ and $\tilde{\varepsilon}_{\underline{k}} - \tilde{\varepsilon}_{\underline{p}} + \hbar\omega_j(\underline{q})$. We shall let $\tilde{\varepsilon}_{\underline{p}}$ go to zero because we are interested in the behaviour of the low lying states of the conduction electrons. Typical phonon energies and Fermi energies are respectively of the order of 10 meV and 1 eV. Therefore the dominant contribution to those terms comes from small $\varepsilon_{\underline{k}}$'s or states near the Fermi surface.

Over this range the functions $|g_{\underline{kp}j}|^2$, $|h_{\underline{kp}j}|^2$ and $|f_{\underline{kpq}j}|^2$ do not vary significantly and we approximate them by their value for $\underline{k}$ lying on the Fermi surface.

Each term is treated in the same way so, for conciseness, we shall only go through the calculations for the term proportional to

$|g_{\underline{k}\underline{p}j}|^2$. Let us go back to Eq. (3.6) and treat $\underline{k}$ as a continuous variable.

$$\sum_{\underline{k}} \rightarrow \frac{\Omega}{(2\pi)^3} \int \frac{dS_{\underline{k}}}{\hbar|v_{\underline{k}}|} \, d\varepsilon_{\underline{k}}$$

where Ω is the crystal volume, then

$$\tilde{E}_{\underline{p}} = \tilde{\varepsilon}_{\underline{p}} + \sum_j \int_{S_F} \frac{dS_{\underline{k}}}{\hbar|v_{\underline{k}}|} \frac{\Omega}{(2\pi)^3} |g_{\underline{k}\underline{p}j}|^2 \int_{-\infty}^{+\infty} d\tilde{\varepsilon}_{\underline{k}} \left\{ \frac{-f_{\underline{k}}}{\tilde{\varepsilon}_{\underline{k}}-\tilde{\varepsilon}_{\underline{p}}-\hbar\omega_j(\underline{p}-\underline{k})} - \frac{(1-f_{\underline{k}})}{\tilde{\varepsilon}_{\underline{k}}-\tilde{\varepsilon}_{\underline{p}}+\hbar\omega_j(\underline{p}-\underline{k})} \right\} .$$

The first integral extends over the Fermi surface. The second one extends from $-\varepsilon_F$ to 0 for the first part of the bracket and from 0 to ∞ for the second part. Since only the small $\varepsilon_{\underline{k}}$'s make an important contribution, we extend the interval $[-\varepsilon_F, 0]$ to $[-\infty, 0]$. The electron-phonon term becomes

$$\sum_j \int_{S_F} \frac{dS_{\underline{k}}}{\hbar|v_{\underline{k}}|} \frac{\Omega}{(2\pi)^3} |g_{\underline{k}\underline{p}j}|^2 \int_0^{\infty} d\tilde{\varepsilon}_{\underline{k}} \left\{ \frac{1}{-\tilde{\varepsilon}_{\underline{k}}-\tilde{\varepsilon}_{\underline{p}}-\hbar\omega_j(\underline{p}-\underline{k})} - \frac{1}{\tilde{\varepsilon}_{\underline{k}}-\tilde{\varepsilon}_{\underline{p}}+\hbar\omega_j(\underline{p}-\underline{k})} \right\} .$$

The renormalized mass is given by

$$\frac{\hbar^2 k_F}{m^*} = \left. \frac{dE_{\underline{p}}}{d_{\underline{p}}} \right|_{p=k_F} .$$

The electron-phonon term is however more a function of $\tilde{\varepsilon}_{\underline{p}}$ than $\underline{p}$ and we expand it in terms of $\tilde{\varepsilon}_{\underline{p}}$.

$$\tilde{E}_{\underline{p}} = \tilde{\varepsilon}_{\underline{p}} + \Delta E_{\underline{p}}(0) + \left. \frac{\partial}{\partial \varepsilon_{\underline{p}}} \Delta E_{\underline{p}}(\tilde{\varepsilon}_{\underline{p}}) \right|_{\tilde{\varepsilon}_{\underline{p}}=0} \tilde{\varepsilon}_{\underline{p}} + \cdots$$

(3.13) $\tilde{E}_{\underline{p}} = \tilde{\varepsilon}_{\underline{p}} - \lambda_{\underline{p}} \tilde{\varepsilon}_{\underline{p}}$

since the quantity in the curly brackets goes to zero as $\bar{\epsilon}_{\underline{p}}$ goes to zero. We consider only the first order term.

$$\lambda_{\underline{p}} = \sum_j \int_{S_F} \frac{dS_{\underline{k}}}{\hbar |v_{\underline{k}}|} \frac{\Omega}{(2\pi)^3} |g_{\underline{kpj}}|^2 \int_0^\infty d\bar{\epsilon}_{\underline{k}}$$

$$\times \left[\frac{\partial}{\partial \bar{\epsilon}_{\underline{p}}} \left\{ \frac{1}{-\bar{\epsilon}_{\underline{k}} - \bar{\epsilon}_{\underline{p}} - \hbar\omega_j (\underline{p}-\underline{k})} + \frac{1}{\bar{\epsilon}_{\underline{k}} - \bar{\epsilon}_{\underline{p}} + \hbar\omega_j (\underline{p}-\underline{k})} \right\} \right] \Bigg|_{\bar{\epsilon}_{\underline{p}}=0}$$

We differentiate with respect to $\bar{\epsilon}_{\underline{k}}$ instead of $\bar{\epsilon}_{\underline{p}}$. Afterwards we set $\bar{\epsilon}_{\underline{p}}$ and $\bar{\epsilon}_{\underline{k}}$ equal to zero which means that we set k and p equal to k_F.

$$\lambda_{\underline{p}} = \sum_j \int_{S_F} \frac{dS_{\underline{k}}}{\hbar |v_{\underline{k}}|} \frac{\Omega}{(2\pi)^3} |g_{\underline{kpj}}|^2 \frac{2}{\hbar\omega_j (\underline{p}-\underline{k})} .$$

We write $\lambda_{\underline{p}}$ in a more convenient form using the equality

$$1 = \int_0^\infty d\omega \delta(\omega - \omega_j (\underline{p}-\underline{k})) .$$

Then $\lambda_{\underline{p}}$ equals

$$(3.14) \quad \lambda_{\underline{p}} = 2 \int_0^\infty \frac{d\omega}{\hbar\omega} \sum_j \int_{S_F} \frac{dS_{\underline{k}}}{\hbar |v_{\underline{k}}|} \frac{\Omega}{(2\pi)^3} |g_{\underline{kpj}}|^2 \delta(\omega - \omega_j (\underline{p}-\underline{k})) .$$

We define $\alpha_{\underline{p}}^2(\omega)F(\omega)$ by the equation

$$(3.15) \quad \lambda_{\underline{p}} = 2 \int_0^\infty \frac{d\omega}{\omega} \alpha_{\underline{p}}^2(\omega)F(\omega) .$$

It is defined this way to emphasize the fact that it looks like a frequency distribution. It is in fact a weighted phonon frequency

distribution. It is a measure of the importance of the phonon of frequency ω in the electron-phonon interaction. It is however directional and applies to a particular electron. We are interested in the Fermi surface average of $\alpha_p^2(\omega)F(\omega)$ as all the conduction electrons on the Fermi surface contribute to the specific heat. We define

$$(3.16) \quad \alpha^2(\omega)F(\omega) = \frac{\displaystyle\int_{S_F} \frac{dS_p}{\hbar|v_p|} \, \alpha_p^2(\omega)F(\omega)}{\displaystyle\int_{S_F} \frac{dS_p}{\hbar|v_p|}} .$$

This function contains all the information about lattice dynamics and the electron-phonon interaction (without impurities) that we need to calculate the renormalization of the electronic mass. It also determines superconductivity in the Eliashberg (1960) formulation of pairing theory.

Naturally, we will be interested in knowing λ

$$(3.17) \quad \lambda = 2 \int_0^\infty \frac{d\omega}{\omega} \, \alpha^2(\omega)F(\omega) .$$

Its values range between a few tenths to more than unity. It can clearly be quite large and it is therefore not valid to use second order perturbation theory. It is necessary to go to a higher order. However, as we mentioned, perturbation theory does give the result obtained by Green's function techniques provided we use the Brillouin-Wigner perturbation theory. This is a self-consistent procedure which

consists in replacing the $\tilde{\varepsilon}$'s by the $\tilde{E}$'s. This way we sum up terms of higher order in $|g_{\underline{kpj}}|^2$.

According to this prescription, Eq. (3.13) becomes

$$\tilde{E}_{\underline{p}} = \tilde{\varepsilon}_{\underline{p}} - \lambda_{\underline{p}}\tilde{E}_{\underline{p}}$$

or

$$\tilde{E}_{\underline{p}}(1+\lambda_{\underline{p}}) = \tilde{\varepsilon}_{\underline{p}}$$

and

$$\frac{m^*_{\underline{p}}}{m} = 1 + \lambda_{\underline{p}}$$

Again we want to average $\lambda_{\underline{p}}$ over the Fermi surface. Therefore

$$(3.18) \quad \frac{m^*}{m} = 1 + \lambda$$

λ being defined in Eq. (3.17). This result is very close to the one obtained by using a Green's function method. In fact Migdal (1958) showed that Eq. (3.18) is correct up to a term of order $(m/M)^{\frac{1}{2}}$ if one neglects Umklapp processes and assumes a spherical Fermi surface.

The most difficult part in a calculation of m* is now done. We next put together the other terms involved in the mass renormalization. From Eqs. (3.6) and (3.14) to (3.17), one finds

$$(3.19) \quad \frac{m^*}{m} = 1 + \lambda_{w^2} + \lambda_{w\Delta w} + \lambda_{\Delta w^2}$$

where

$$\lambda_{w^2} = \lambda$$

$$(3.20) \quad \lambda_{w\Delta w} = 2 \int_0^\infty d\omega \, \frac{\alpha'^2(\omega)F(\omega)}{\omega}$$

$$(3.21) \quad \alpha'^2(\omega)F(\omega) = \frac{\int_{S_F} \frac{dS_p}{\hbar|v_p|} \sum_j \int_{S_F} \frac{dS_k}{\hbar|v_k|} \frac{\Omega}{(2\pi)^3} \frac{|h_{kpj}|^2}{\hbar} \delta(\omega - \omega_j(p-k))}{\int_{S_F} \frac{dS_p}{\hbar|v_p|}}$$

$$(3.22) \quad \lambda_{\Delta w^2} = 2 \int_0^\infty \frac{\alpha''^2(\omega)F(\omega)}{\omega} \, d\omega$$

$$(3.23) \quad \alpha''^2(\omega)F(\omega) = \frac{\int_{S_F} \frac{dS_p}{\hbar|v_p|} \sum_{qj} \int_{S_F} \frac{dS_k}{\hbar|v_k|} \frac{\Omega}{(2\pi)^3} \frac{|f_{kpqj}|^2}{\hbar} \delta(\omega - \omega_j(q))}{\int_{S_F} \frac{dS_p}{\hbar|v_p|}} .$$

All that is left is to combine the results of Sections 3.2 and 3.3. Since

$$\rho(\varepsilon) = \frac{3N}{\varepsilon} \propto m$$

and the linear coefficient of the specific heat

$$\gamma = \frac{2\pi^2}{3} k_B^2 \rho(\varepsilon_F) \frac{m^*}{m}$$

k_B being the Boltzmann constant, we get from Eqs. (3.11) and (3.19)

$$(3.24) \quad \gamma = \gamma_0^0 [1 + \lambda_s + \lambda_{w^2} + \lambda_{w\Delta w} + \lambda_{\Delta w^2}]$$

where γ_0^0 is the specific heat of the pure crystal at zero temperature

ignoring the electron-phonon renormalization.

3.4 Approximations

So far we have neglected the change in the phonons and we have
assumed that the matrix elements $|g_{kpj}|^2$, $|h_{kpj}|^2$ and $|f_{kpqj}|^2$ do not
vary very much with $\underline{k}$ for $k \approx k_F$. To facilitate the numerical calculations,
we shall make three more approximations.

We use a local pseudopotential, we assume a spherical Fermi
surface and we approximate the zeroth order wave function of an
electron by a single plane wave. These approximations are quite
reasonable for the alkalis because the conduction electrons act very
much like free electrons. The Fermi sea occupies half of the Brillouin
zone. The Fermi surface is therefore far from the Brillouin zone
boundary and is almost spherical. These approximations are obviously
not as realistic for polyvalent metals.

Nevertheless we are going to use these approximations to bring
Eqs. (3.12) (λ_s), (3.22) and (3.23) ($\lambda_{\Delta w^2}$) to more convenient
expressions. Let us consider (3.12)

$$\lambda_s = \frac{\displaystyle\int_{S_F} \frac{dS_p}{\hbar|v_p|} \sum_k{}' \frac{|i_{kp}|^2}{(\epsilon_p - \epsilon_k)^2}}{\displaystyle\int_{S_F} \frac{dS_p}{\hbar|v_p|}} .$$

We substitute for $|i_{kp}|^2$ the formula (3.2), go to the limit of a
continuous $\underline{k}$ and change the variable of integration foom $\underline{k}$ to $\underline{q} = \underline{k} - \underline{p}$.

$$\lambda_s = \frac{\int\limits_{S_F} \frac{dS_p}{\hbar|v_p|} \frac{c}{N} \frac{\Omega}{(2\pi)^3} P\int d^3q \frac{\Delta w(q)^2}{(\epsilon_p - \epsilon_{p+q})^2}}{\int\limits_{S_F} \frac{dS_p}{\hbar|v_p|}}$$

where "P" means principal part. In this step we have assumed a local pseudopotential and used one plane wave (Eq. (2.4)). For the following one, we suppose a spherical Fermi surface

$$\lambda_s = \frac{\int\limits_{S_F} \frac{dS_p}{\hbar v_F} \frac{c}{N} \frac{\Omega}{(2\pi)^3} P\int d^3q \left(\frac{2m}{\hbar^2}\right)^2 \frac{\Delta w(q)^2}{(2k_F q\mu + q^2)^2}}{\int\limits_{S_F} \frac{dS_p}{\hbar v_F}}$$

where μ is the cosine of the angle between p and q. The integral over q is independent of the direction of p, so we do not need to average over the Fermi surface. The integration over angles gives:

$$(3.25) \quad \lambda_s = \frac{c}{N} \frac{\Omega}{(2\pi)^3} \left(\frac{m}{\hbar^2 k_F}\right)^2 P\int\limits_0^\infty dq \Delta w(q)^2 \left\{\frac{1}{1 - q/2k_F} + \frac{1}{1 + q/2k_F}\right\} .$$

We had to be careful in integrating over the variable μ since there was a singularity at $q = 2k_F$. Time dependent perturbation theory tells us what to do in that case. If we define the perturbed potential as $Ve^{i\alpha t}$ and let α go to zero, one can prove the following equation (see Appendix A).

$$(A.3) \quad E = E_0 + \langle i|V|i\rangle + \lim_{\alpha \to 0^+} \sum_f \frac{|\langle i|V|f\rangle|^2}{E_i - E_f + i\alpha} + \ldots .$$

This indicates to us that one can avoid the singularity by going in the complex plane. This is how we got Eq. (3.25) which can be integrated without difficulty.

Let us now consider Eqs. (3.22) and (3.23) and use one plane wave (Eq. (2.4))

$$(3.26) \quad \lambda_{\Delta w}^2 = 2 \int_0^\infty d\omega \, \frac{\Omega}{(2\pi)^3}$$

$$\int_{S_F} \frac{dS_p}{\hbar |v_p|} \int_{S_F} \frac{dS_k}{\hbar |v_k|} |<\underline{k}|\Delta w|\underline{p}>|^2 \, \frac{c}{N} \sum_{\underline{q},j} \frac{|(\underline{k}-\underline{p})\cdot \underline{\sigma}^j(\underline{q})|^2}{2MN\omega^2} \delta(\omega-\omega_j(\underline{q}))$$

$$\times \left[\frac{}{\int_{S_F} \frac{dS_p}{\hbar |v_p|}} \right]$$

Next we assume a local pseudopotential and a spherical Fermi surface. We prove in the Appendix B:

$$(B.3) \quad \int_{S_F} \frac{dS_k}{\hbar |v_k|} \int \frac{dS_{k'}}{\hbar |v_{k'}|} \, f(\underline{k}'-\underline{k}) = \frac{2\pi m^2}{\hbar^4} \int_{<2k_F} d^3q \, \frac{f(\underline{q})}{q}$$

where the integral over $\underline{q}$ extends over a sphere of radius $2k_F$. Using this equation, one obtains

$$(3.27) \quad \int_{S_F} \frac{dS_p}{\hbar |v_p|} \int_{S_F} \frac{dS_k}{\hbar |v_k|} |\Delta w(\underline{k}-\underline{p})|^2 |(\underline{k}-\underline{p})\cdot \underline{\sigma}^j(\underline{q})|^2$$

$$= \frac{2\pi m^2}{\hbar^4} \int_{<2k_F} d^3q' \, \frac{\Delta w(\underline{q}')^2}{q'} |\underline{q}'\cdot \underline{\sigma}^j(\underline{q})|^2 .$$

Let us define μ as being the cosine of the angle between $\underline{\sigma}^j(\underline{q})$ and $\underline{q}'$. The right hand side of Eq. (3.27) becomes

$$\frac{(2\pi)^2 m^2}{\hbar^4} \int_0^{2k_F} q'dq' \Delta w(q')^2 \int_{+1}^{-1} d\mu q'^2 \mu^2$$

or

$$(3.28) \quad \frac{2}{3} \frac{\pi m^2}{\hbar^4} \int_{<2k_F} q'd^3q' \Delta w(q')^2 \ .$$

$\underline{\sigma}^j(\underline{q})$ does not appear any more because its norm is equal to one. Using the following definition of the frequency distribution

$$F(\omega) = \frac{1}{N} \sum_{\substack{\underline{q},j \\ F.B.Z.}} \delta(\omega-\omega_j(\underline{q}))$$

and Eqs. (3.26) to (3.28), we obtain for $\lambda_{\Delta w^2}$

$$(3.29) \quad \lambda_{\Delta w^2} = c \frac{m}{48\pi^3 \hbar^2 n M k_F} \int_{<2k_F} qd^3q \Delta w(q)^2 \int_0^\infty d\omega \frac{F(\omega)}{\omega^2}$$

where n is the ion concentration (N/Ω).

We are now ready to do numerical calculations.

CHAPTER IV

NUMERICAL CALCULATIONS AND RESULTS

In this chapter we describe how we calculate the pseudopotential form factor. We indicate where we get the phonon frequency distribution functions: $F(\omega)$, $\alpha^2(\omega)F(\omega)$, $\alpha'^2(\omega)F(\omega)$ and we present the results.

Following Hayman and Carbotte (1971) we use the Ashcroft model of the pseudopotential form factor. In real space it is defined as

$$w^0(r) = 0 \quad \text{for} \quad r < R_c$$

$$= -\frac{e^2}{r} \quad \text{for} \quad r > R_c .$$

R_c is a parameter of the order of the ion radius. The idea is to cancel the Hartree field of the ions and the repulsive effect of the core electrons (due to Pauli's principle) inside a core radius R_c. This is a simple model but it gives results similar to what has been obtained using the Heine-Abarenkov or the Shaw form of the pseudopotential for the calculation of λ. It certainly is a good description of the real potential for large r's and small q's. It is not as realistic for big q's.

In reciprocal space

$$w^0(q) = -\frac{1}{\Omega_0} \frac{4\pi e^2}{q^2} \cos(qR_c)$$

where Ω_0 is the volume per ion. Actually the potential is screened by the conduction electrons and we write

$$w(q) = -\frac{1}{\Omega_0} \frac{4\pi e^2}{q^2} \frac{\cos(qR_c)}{\epsilon(q)}$$

where $\epsilon(q)$ is the dielectric function. We choose for this the Lindhard form which is quite simple:

$$\epsilon(q) = 1 + \frac{k_F e^2}{q^2 \pi} \{1 + \frac{1}{qk_F} [k_F^2 - \frac{q^2}{4}] \ln\left|\frac{q+2k_F}{q-2k_F}\right|\} .$$

So all we need to know is R_c, the lattice parameter and k_F at zero temperature.

They have been evaluated by Hayman et al. (1971) for sodium and potassium. They fixed R_c by fitting the electrical resistivity at a certain temperature. In the case of sodium they fitted the constant pressure (atmospheric) electrical resistivity at 90°K. They used the phonon dispersion curve measured by Woods et al. (1962) at 90°K and analysed according to the Born-von Kármán force constant model. In the case of potassium, they fitted the constant volume (zero temperature) electrical resistivity at 90°K. Here they used the phonon dispersion curve measured by Cowley et al. (1966) at 9°K. In doing so they neglected the difference between the lattice volumes at 0°K and 9°K. This method however leads to two values of R_c. For each of them they calculated the constant volume electrical resistivity as a function of of temperature. They got rid of the ambiguity by comparing their results with experiments. The chosen values are given in Table 1.

The R_c values that we use are those of the pure metal. We should use those appropriate of the alloys electron density but one does not know how to calculate these from experimental measurements. Choosing the values of the pure metal we do a consistent calculation which enables us to compare the relative size of each term entering the specific heat.

The frequency distributions that we need have been calculated by Kus et al. (1974). The method used is described in detail by Carbotte and Dynes (1968) and Carbotte, Dynes and Trofimenkoff (1969). The force constants between ions are obtained from the phonon dispersion curves measured by inelastic neutron scattering. Then the dynamical matrix is constructed and the polarization vectors $\underline{\sigma}^j(q)$, are calculated at every point of the first Brillouin zone. With these values, the dispersion curve and the pseudopotential form factor, $\alpha^2(\omega)F(\omega)$ and $\alpha'^2(\omega)F(\omega)$, are computed. The van Hove singularities are resolved by using the computer technique developed by Gilat and Raubenheimer (1966). We have plotted $F(\omega)$, $\alpha^2(\omega)F(\omega)$ and $\alpha'^2(\omega)F(\omega)$ for the alloys $\underline{K}Na$ and $\underline{Na}K$ in Figs. 1 and 2.

Having these data, we were able to evaluate λ, $\lambda_{w\Delta w}$, $\lambda_{\Delta w^2}$, λ_s and γ with the help of Eqs. (3.17), (3.20) to (3.24) and (3.12). There is however one point that we should mention about the evaluation of λ_s. The Ashcroft pseudopotential form factor is not a good approximation for big values of q, due to the drastic condition imposed on $w(r)$ for small values of r. At zero, $w(q) = -2\epsilon_F/3$, then as q increases, the pseudopotential increases, it becomes positive, crosses the q axis again and oscillates. We do not want to take into account

the oscillations, so we stop the integration over q at the second node of w_{Na}. The second node of w_K occurs at a smaller value of q than the second node of w_{Na}: q^*. Therefore, Eq. (3.12) is modified to:

$$\lambda_s = \frac{c}{N} \frac{\Omega}{(2\pi)^2} (\frac{m}{\hbar^2 k_F})^2 P \int_0^{q^*} dq \Delta w(q)^2 \{\frac{1}{1 - q/2k_F} + \frac{1}{1 + q/2k_F}\} .$$

The final results are given in Table 2.

Table 1:   Data taken from Hayman and Carbotte (1971) and used

to calculate the Ashcroft form of the pseudopotential

form factor for sodium and potassium.

Table 2:   The contributions to the heat capacity enhancement due

to electron-phonon interactions and the impurities for

$\underline{Na}K$ and $\underline{K}Na$.   The underlined metal is the host.   The

star means that γ is evaluated for a concentration of

1%. $\Delta\lambda = \lambda_{w\Delta w} + \lambda_{\Delta w^2}$.

TABLE 1

Metal	Lattice parameter at $T=0°K$ ($\overset{\circ}{A}$)	Fermi momentum at $T=0°K$ ($\overset{\circ}{A}^{-1}$)	R_c ($\overset{\circ}{A}$)
Na	4.2268	0.9222	0.8282
K	5.2275	0.7456	1.0353

TABLE 2

	$\underline{NaK}$	$\underline{KNa}$
λ	0.185	0.134
$\lambda_{w\Delta w}/c$	−0.158	0.092
$\lambda_{\Delta w^2}/c$	0.166	0.091
$\Delta\lambda/c$	0.008	0.183
λ_s/c	−0.003	−0.004
γ/γ_0^0	1.185+c(0.005)	1.134+c(0.179)
$(\gamma/\gamma_0^0)*$	1.185	1.136

Figure 1: The phonon frequency distributions $F(\nu)$ (———),
$\alpha^2(\nu)F(\nu)$ ($\cdots\cdots$), and $\alpha'^2(\nu)F(\nu)$ (——–) are
plotted as a function of frequency ν for $\underline{K}Na$.
$\alpha^2(\nu)F(\nu)$ and $\alpha'^2(\nu)F(\nu)$ are scaled up by a
factor of 10 and 100 respectively. ν is in units
of 10^{12} Hz.
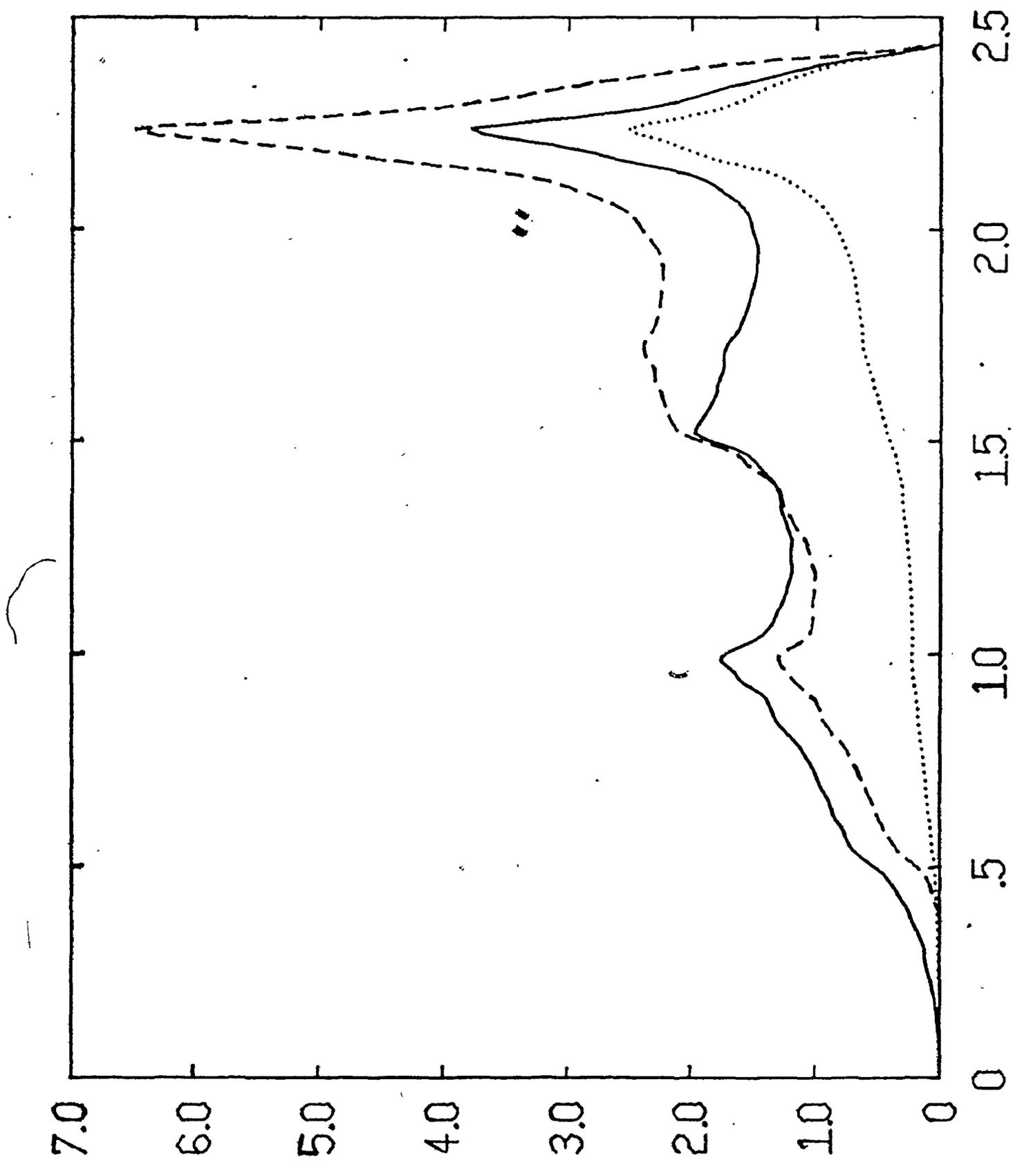
Figure 2: The phonon frequency distributions $F(\nu)$ (———),
$\alpha^2(\nu)F(\nu)$ (·····), and $\alpha'^2(\nu)F(\nu)$ (-----) are
plotted as a function of frequency ν for $\underline{Na}K$.
The latter two distributions are scaled up by a
factor of 10. In addition $\alpha'^2(\nu)F(\nu)$ is
multiplied by (-1). ν is in units of 10^{12} Hz.
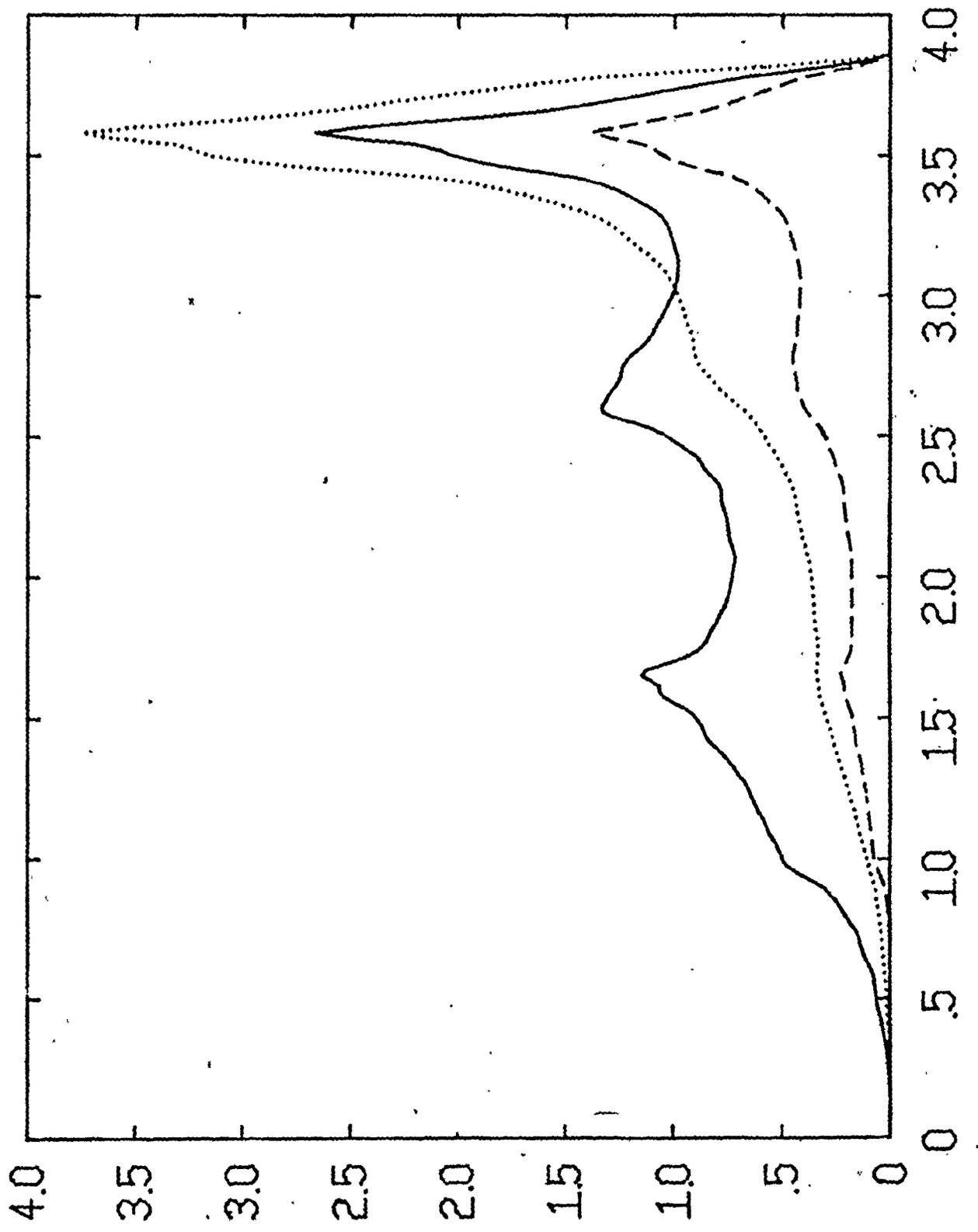
CHAPTER V

DISCUSSION AND CONCLUSION

5.1 Discussion

We have calculated the electronic part of the specific heat of a dilute alloy at zero temperature. We have considered two mechanisms: the change in the Fermi level density of states and the electronic mass renormalization. The former is due to the addition of impurities in the pure metal; the latter comes from the electron-phonon interaction and the impurities. It was found that:

$$(3.24) \quad \gamma = \gamma_0^0 [1 + \lambda_{w^2} + \lambda_{w\Delta w} + \lambda_{\Delta w^2} + \lambda_s] \ .$$

We have evaluated the different corrections for two alloys NaK and KNa. The addition of a low concentration of impurities (1% or less) has very little effect on γ. One percent of impurities causes a change of less than 1% in the value of γ including the electron-phonon interaction of the pure metal. λ_s is negligible compared to $\lambda_{w\Delta w}$ and $\lambda_{\Delta w^2}$ which indicates that the effect of the impurities on the electron-phonon interaction is a more important cause of change in the electronic specific heat than Stern's mechanism. $|\lambda_{w\Delta w}|$ is of the same size as $\lambda_{\Delta w^2}$. In the case of KNa they add up while for NaK they almost cancel. One would need more calculations to see if this is a general result when Δw is negative.

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For example, one does not know how $\lambda_{w\Delta w}$ and $\lambda_{\Delta w^2}$ change with R_c. It might be that $|\lambda_{w\Delta w}|$ is bigger than $\lambda_{\Delta w^2}$ and γ could decrease or increase as impurities are added. Experimentalists could investigate the behaviour of γ in this kind of system.

In any case our calculations show that Taylor (1969) should not have neglected $\lambda_{w\Delta w}$. He considered only $\lambda_{\Delta w^2}$ which he estimated to be .09c in KNa. This is equal to our result which is purely accidental because Taylor makes many approximations. For example, he uses the Debye model to evaluate

$$\sum_{q} \left(\frac{1}{\hbar\omega(q)}\right)^2$$

and he approximates

$$\sum_{\underline{k}'} \frac{2\pi N(1-c)}{\hbar} \left|V_{imp}(\underline{k}'-\underline{k})\right|^2 (1-\cos\theta_{\underline{k}'\underline{k}})\delta(\epsilon_{\underline{k}'}-\epsilon_{\underline{k}})$$

by $1/\tau$ where τ is the relaxation time of the electrical resistivity, $\theta_{\underline{k}'\underline{k}}$ the angle between $\underline{k}'$ and $\underline{k}$ and V_{imp}, the scattering potential of a single impurity. Doing so he considers only the longitudinal modes of the crystal while he should also take into account the transverse modes.

Our numerical results for NaK and KNa show that the electronic mass renormalization is a more important mechanism than the change in the Fermi level density of states proposed by Stern. Stern's theory however certainly has the proper qualitative behaviour for the electronic specific heat in the case of a gold impurity in silver-gold

alloys (see Green and Valladares (1966), Martin (1968), Davis and
Rayne (1972)). The experiments show that γ first decreases with the
addition of gold to silver, then starts increasing when the
concentration of gold reaches about 30% and finally goes up to the
pure gold value. In our theory γ can decrease only if $\Delta w < 0$, i.e.
γ could decrease for the addition of gold to pure silver if the
pseudopotential of gold were less than that of silver and the screening
should be very important and complicated to make the pseudopotential
of silver less than that of gold in a crystal where gold is the host.
One should not be surprised that our theory cannot explain the
variation of γ in silver-gold alloys because the noble metals have a
very complicated Fermi surface. There are necks which means that the
electrons at the Fermi level are far from being free electrons. In
this case the use of pseudopotentials is not valid.

If one neglects the electron-phonon interaction, Stern's theory
reduces to ours for low concentration. If Stern's mechanism is the
important one, we would expect that it is also important in the
sodium-potassium alloys and we should see this in our calculations for
a low concentration of impurities. This is not the case and it leads
us to think that Stern's mechanism is not the important one. His
calculations are crude: he assumes that $|<\underline{k}|V_{12}|\underline{\ell}>|^2$ is constant and
does not couple the states at the Fermi level to the d-states. He
neglects clustering, impurity-impurity interactions and claims that
his theory is valid for any c provided that $|<\underline{k}|V_{12}|\underline{\ell}>|^2\times[E(\underline{k})-E(\underline{\ell})]^{-1}$
is small. He uses a "virtual crystal" as his starting point without
much justification. In his paper with McAlister and McGroody (1965) he

admits that this assumes that the amplitude of the alloy wave function

for the electronic states near the Fermi energy is nearly equal on each

constituent. This is generally not true but he believes that it is

valid for silver and gold since their potentials are similar. To

summarize, at this point we do not believe that any simple theory can

explain the change in the electronic specific heat in silver-gold alloys

because they have a very complicated Fermi surface. We think that if

the addition of impurities would cause a major change in the Fermi

level density of states of the Ag-Au alloys, it would be the same in

sodium-potassium alloys and we should have found this in our

calculations.

5.2 Conclusion

We have evaluated the change in the electronic specific heat

in NaK and KNa at zero temperature. It is found that the electron-

phonon interaction causes the major change. The addition of impurities

does not modify significantly the situation existing in the pure metals

either through a direct change in the Fermi level density of states or

their interactions with phonons.

We made a few approximations to arrive at this conclusion but

they should be realistic for alkalis. We avoided uncertainties by using

the Ashcroft form of the pseudopotential form factor since it is fitted

to electrical resistivity experiments. If one knew the necessary phonon

Green's functions, one could easily introduce them in the theory (Eq.

(2.24)) and make more accurate calculations. One could also evaluate

the various corrections without assuming a spherical Fermi sphere and using a single plane wave as the zeroth order wave function of the electrons. It would take however a lot of computing time and we believe that it would not change the results by very much.

Stern's theory does explain qualitatively the results of experiments on silver-gold alloys while ours would require the additional assumption that Δw be negative for both the pure gold and pure silver ends of the alloy series and that $|\lambda_{w\Delta w}|$ is bigger than $\lambda_{\Delta w^2}$. We do not believe however that Stern's theory is more realistic than ours because the noble metals have a Fermi surface which is too complicated to be described by simple theories.

APPENDIX A

Time-dependent perturbation theory is described in Kittel (1963), Chapter 1. We will write down his results and calculate the second order contribution to the energy.

The Hamiltonian is

$$H = H_0 + Ve^{-\alpha t}$$

where α is positive. The exact wave function of the ground state ψ can be expressed in terms of the ψ_n's, solutions of H_0. $n=0$ corresponds to the ground state.

(A.1) $\quad \psi = \psi_0 + \sum_n a_n^{(1)} \psi_n + \sum_n a_n^{(2)} \psi_n + \ldots$

where

(A.2) $\quad a_n^{(1)} = \dfrac{\langle \psi_n | V | \psi_0 \rangle}{E_0 - E_n + i\alpha}$

and $\quad a_n^{(2)} = \sum_k \dfrac{\langle \psi_n | V | \psi_k \rangle \langle \psi_k | V | \psi_0 \rangle}{(E_0 - E_n + 2i\alpha)(E_0 - E_k + i\alpha)}$

for $n \neq k$. Kittel also proves that

$$E = E_0 + \dfrac{\langle \psi_0 | V | \psi \rangle}{\langle \psi_0 | \psi \rangle}$$

or

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$$E = E_0 + \frac{\langle \psi_0 | V | \psi \rangle}{1 + a_0^{(1)} + a_0^{(2)} + \ldots}$$

since the eigenstates of H_0 are orthogonal to each other. The a_n's must be small coefficients otherwise V is big compared to H_0 and perturbation theory is not valid. So we expand:

$$E = E_0 + \langle \psi_0 | V | \psi \rangle [1 - a_0^{(1)} - a_0^{(2)} \ldots] \; .$$

Using (A.1)

$$E = E_0 + \langle \psi_0 | V | \psi_0 \rangle + \langle \psi_0 | V | \sum_n a_n^{(1)} \psi_n \rangle + \ldots [1 - a_0^{(1)} - a_0^{(2)} - \ldots] \; .$$

We keep the first and second order terms only:

$$E = E_0 + \langle \psi_0 | V | \psi_0 \rangle - a_0^{(1)} \langle \psi_0 | V | \psi_0 \rangle + \sum_n a_n^{(1)} \langle \psi_0 | V | \psi_n \rangle + \ldots \; .$$

After use of (A.2), we get

$$(A.3) \quad E = E_0 + \langle \psi_0 | V | \psi_0 \rangle + \sum_{n \neq 0} \frac{|\langle \psi_0 | V | \psi_n \rangle|^2}{E_0 - E_n + i\alpha} + \ldots \; .$$

APPENDIX B

The proof can be divided into two parts. First one writes that

$$\int d^3k \int d^3k' f(\underline{k}'-\underline{k}) \delta(\epsilon_{\underline{k}}-\epsilon_F) \delta(\epsilon_{\underline{k}'}-\epsilon_F)$$

$$= \int \frac{dS_{\underline{k}}}{\hbar|v_{\underline{k}}|} \int \frac{dS_{\underline{k}'}}{\hbar|v_{\underline{k}'}|} \int d\epsilon_{\underline{k}} \int d\epsilon_{\underline{k}'} f(\underline{k}'-\underline{k}) \delta(\epsilon_{\underline{k}}-\epsilon_F) \delta(\epsilon_{\underline{k}'}-\epsilon_F)$$

or

(B.1) $$\int d^3k \int d^3k' f(\underline{k}'-\underline{k}) \delta(\epsilon_{\underline{k}}-\epsilon_F) \delta(\epsilon_{\underline{k}'}-\epsilon_F)$$

$$= \int_{S_F} \frac{dS_{\underline{k}}}{\hbar|v_{\underline{k}}|} \int_{S_F} \frac{dS_{\underline{k}'}}{\hbar|v_{\underline{k}'}|} f(\underline{k}'-\underline{k}) \ .$$

The integrals on the right hand side of the equation extend over the Fermi surface: on the left hand side however, they extend over all space. This allows us to define $\underline{q}$ as $\underline{k}'-\underline{k}$ and write

$$\int d^3k \int d^3k' f(\underline{k}'-\underline{k}) \delta(\epsilon_{\underline{k}}-\epsilon_F) \delta(\epsilon_{\underline{k}'}-\epsilon_F)$$

$$= \int d^3k \int d^3q f(\underline{q}) \delta(\epsilon_{\underline{k}}-\epsilon_F) \delta(\epsilon_{\underline{k}+\underline{q}}-\epsilon_F) \ .$$

Assuming a spherical Fermi surface, the right hand side becomes equal to

$$\int d^3k \int d^3q f(\underline{q}) \delta(\epsilon_{\underline{k}}-\epsilon_F) \delta[\frac{\hbar^2}{2m}(k^2+q^2-2kq\mu) - \epsilon_F]$$

where μ is the cosine of the angle between $\underline{k}$ and $\underline{q}$. It can be rewritten as:

$$\int d^3q f(\underline{q}) \int k^2 dk \delta(\varepsilon_{\underline{k}} - \varepsilon_F) \int d\mu d\phi \frac{2m}{\hbar^2} \delta(q^2 - 2kq\mu) \ .$$

Using again the assumption of a spherical Fermi surface and the delta function $\delta(\varepsilon_{\underline{k}} - \varepsilon_F)$, we can specify $|\underline{k}| = k = k_F$. The integration over dk becomes easy: we change the variable k to ε_k to obtain:

$$\int d^3q f(\underline{q}) \frac{4\pi m}{\hbar^2} \int \frac{d_k \sqrt{2m^3 \varepsilon_k}}{\hbar^3} \delta(\varepsilon_{\underline{k}} - \varepsilon_F) \int d\mu \frac{\delta(q/2k_F - \mu)}{2k_F q} \ .$$

We get after integration

$$(B.2) \quad \int d^3k \int d^3k' f(\underline{k}' - \underline{k}) \delta(\varepsilon_{\underline{k}} - \varepsilon_F) \delta(\varepsilon_{\underline{k}'} - \varepsilon_F)$$

$$= \frac{2\pi m^2}{\hbar^4} \int_{<2k_F} d^3q \frac{f(\underline{q})}{q} \ .$$

The norm q is restricted to values smaller than $2k_F$ because μ varies in the interval $[-1, +1]$ and we need the delta function $\delta(q/2k_F - \mu)$ to be non-zero.

Combining Eqs. (B.1) and (B.2), we get the desired result:

$$(B.3) \quad \int \frac{dS_{\underline{k}}}{\hbar|v_{\underline{k}}|} \int \frac{dS_{\underline{k}'}}{\hbar|v_{\underline{k}'}|} f(\underline{k}' - \underline{k}) = \frac{2\pi m^2}{\hbar^4} \int_{<2k_F} d^3q \frac{f(\underline{q})}{q} \ .$$

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