TRANSPORT IN DILUTE ALLOYS

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SCOPE AND CONTENTS:

The effect of a small concentration of nonmagnetic impurities or defects on the transport properties of a simple metal is investigated.

The correction to the Friedel Sum Rule, or displaced charge sum rule, due to the relaxation of the ions around an impurity, is calculated, and related to the volume change induced by the relaxation.

The finite temperature resistivity of dilute alloys of simple metals is studied in terms of the deviations from Matthiessen's Rule. An approximate theory, similar to the two band model, is presented. Detailed calculations based on this approximate theory as well as the complete expressions of a scattering time formalism for the resistivity, to include the effect of anisotropy in the electron-phonon interaction, are given for some alkali and aluminum alloys. The results are compared with experimental data and the predictions of other theories.

A simple theory for the finite temperature resistivity of a dilute alloy, which includes the effect of the strain field or relaxation of the ions around an impurity at finite temperature, is presented.

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CHAPTER I

SCOPE OF THE THESIS

The properties of an alloy are in general more difficult from a theoretical point of view than those of a pure metal (1,2). The break in the translational invariance of the system due to the impurities causes the conduction electrons to be scattered even at zero temperature. Friedel (1) has derived a sum rule relating the phase shifts due to the defect scattering to the difference in valence between the host ions and the impurity. Since the potential between the host and impurity ions is in general different from one between two host ions, there is a net force tending to drive the host ions surrounding the impurity off their perfect lattice equilibrium positions to new, relaxed equilibrium positions. In Chapter II the extra scattering due to these displaced host ions will be introduced as a correction to the Friedel or displaced charge sum rule. This correction has been related phenomenologically to the volume change induced by the displaced ions (3,4) and, also in Chapter II, this volume change will be calculated completely microscopically. It will be shown that this volume change is indeed related to the correction to the displaced charge sum rule, thus showing that the theory is consistent. Some numerical estimates of the correction are given for the case of alkali impurities or vacancies in alkali metals as well as a discussion of how the correction is related to the residual resistivity.

At finite temperature, the conduction electrons are scattered not only by lattice defects and impurities but also by the vibrating ions or phonons. There are also scattering effects associated with the fact that the impurities are also vibrating so that they present a different scattering cross section than if they were static, and they may have a different mass from the host ions. In Section 3.1 the theory of the finite temperature resistivity appropriate to a dilute alloy of substitutional nonmagnetic impurities in non-transition metal hosts is presented as a generalization of the scattering time formalism for the solution of the Boltzmann transport equation introduced by Robinson and Dow (37). This is to be contrasted with the usual variational method (33) for deriving the resistivity from the Boltzmann equation. The scattering time solution, in which a scattering time $\tau_a(\underline{k})$ appropriate to the alloy is defined in terms of $\tau_0(\underline{k})$, the scattering time for the pure metal, as well as additional scattering times for the various other scattering mechanisms, is favoured because of its mathematical simplicity and the direct physical insight it gives into the results. $\tau_0(\underline{k})$, where $\underline{k}$ refers to an electron in a state described by the wave vector $\underline{k}$, will be found to be very anisotropic even over a spherical Fermi surface. This anisotropy is due to the anisotropy in the phonon spectrum and, more important, in the electron-phonon interaction, particularly where this involves umklapp processes for which the electron momentum transfer exceeds the largest phonon momentum.

The central quantity of interest in the resistivity is the deviation from Matthiessen's Rule $^{(38)}$ (D.M.R.) denoted by $\Delta(T,c)$ where T is the temperature and c is the impurity concentration. Matthiessen's rule states that the resistivity of an alloy at any temperature T, is simply the sum of the pure metal resistivity at that temperature plus the residual resistivity of the alloy which is independent of temperature but depends linearly on c.

Experimentally this rule is rarely obeyed exactly $^{(39)}$ and, especially at low temperature, the additional term, $\Delta(T,c)$, in the total alloy resistivity can be quite large and have a very nonlinear dependence on the concentration. In Section 3.2 a simple, approximate theory for $\Delta(T,c)$ is presented and compared with the exact theory. At low temperature and for very dilute alloys, the scattering time formalism, particularly in its approximate form, shows the importance of the anisotropy in $\tau_0(\underline{k})$ and the effect on it of the impurities, represented to a first approximation by τ_R which is the scattering time related to the residual resistivity. The nonlinear dependence of $\Delta(T,c)$ on c as well as the temperature at which this will occur can be clearly seen. Calculations are presented for the dilute alloys of the alkalis, especially potassium where there are recent experimental results (44,45).

More detailed results for very dilute alloys of lithium as well as more concentrated ($c \lesssim 1\%$) Li-Mg and Li-Ag alloys are presented in Section 3.3, including also the effect of the additional scattering due to vibrating impurities and the different mass of the impurities plus the modification of the impurity resistivity introduced by including the Debye-Waller factor in the scattering cross sections. The Debye-Waller factor, familiar from X-ray and neutron diffraction (43), takes account of the modification of the cross sections with increasing temperature. Calculations of $\Delta(T,c)$ in a series of dilute alloys of aluminum are presented in Section 3.[illegible] including all the scattering mechanisms mentioned above. Detailed comparison of the calculated values of $\Delta(T,c)$ with the experimental ones shows that the physical ideas and mathematical techniques used here are probably adequate for the explanation of the D.M.R. for the simple systems considered in this thesis. Discrepancies with the experimental results can be identified, usually by the temperature range in which they occur, and the appropriate deficiency could be corrected in future calculations. Also, since the effect of the various scattering processes is now clearer, further experiments, using certain concentrations and in certain temperature ranges, to study the effect of the various mechanisms may be made.

In Chapter IV, a simple theory to include the effect of the strain fields or lattice relaxation around an impurity on the finite temperature resistivity in a metal is presented. Just as at zero temperature, there is additional scattering of the conduction electrons by the displaced host atoms, so at finite temperature there is an additional scattering mechanism due to the fact that the displaced host atoms are undergoing thermal vibrations about equilibrium positions which do not form a perfectly periodic array in the crystal.

In Chapter V, the results of the theories and calculations presented in this thesis are summarized and some conclusions are drawn. Finally, some suggestions of other properties of dilute alloys to which the ideas and techniques presented here may be applied are given.

CHAPTER II

MODIFICATION OF THE DISPLACED CHARGE SUM RULE FOR LATTICE RELAXATION

2.1 Introduction

A fundamental property of a pure metal is its translational invariance. This means that the environment at any point $\underline{r}$ is the same as at $\underline{r} + \underline{R}_\ell^0$ where $\underline{R}_\ell^0$ gives the equilibrium position of the ℓ^{th} atom in the crystal. This periodicity implies that $V(\underline{r}) = V(\underline{r} + \underline{R}_\ell^0)$ where $V(\underline{r})$ is the crystal potential at the point $\underline{r}$. The eigenstates of the system are Bloch states $\phi_{\underline{k}}$ with energy $\varepsilon_{\underline{k}}$ for an electron in a state specified by the wave vector $\underline{k}$. At T = 0°K and in the absence of applied fields the conduction electrons propagate freely throughout the crystal, maintaining the same wave vector $\underline{k}$.

The introduction of defects or impurities into the metal causes a breakdown of this translational invariance, leading to the scattering of an electron in a state specified by $\underline{k}$ to one specified by $\underline{k}'$. This scattering is due to the net difference between the host potential and the potential of the impurity ion when it is placed in the matrix of the host material. The Bloch states are no longer eigenstates of the system and this can be represented by allowing the energy $\varepsilon_{\underline{k}}$ to become complex

$$\varepsilon_{\underline{k}} \rightarrow E_{\underline{k}} + i\Gamma_{\underline{k}}$$

where the energy of the electron in the state $\underline{k}$ in the alloy is $E_{\underline{k}}$. $\Gamma_{\underline{k}}$ represents the scattering out of the state $\underline{k}$ with a lifetime of the order of $(2\Gamma_{\underline{k}})^{-1}$.

The lack of the simplification of translational invariance in the alloy makes it much harder to calculate any of its properties. Many approximations are inevitably necessary. To check the validity of a given approximation, it is very helpful to have some simple exact results against which the approximation may be compared. One such result is the Friedel Sum Rule (1) (F.S.R.) or displaced charge sum rule which relates the conduction electron phase shifts to the total displaced charge, ΔZ, caused by the impurity

$$\frac{2}{\pi} \sum_{\ell} (2\ell+1)\delta_{\ell}(k_F) = \Delta Z \quad . \qquad (2.1)$$

Here $\delta_{\ell}(k_F)$ is the phase shift of the ℓ^{th} partial wave, evaluated at the Fermi wave vector k_F, and ΔZ is the valence difference between the host and impurity ions. Physically this means that the conduction electrons redistribute themselves around the impurity so as to completely shield it in a distance of the order of the lattice spacing. For very dilute alloys, the Fermi energy is the same as it is in the pure metal (1).

The above result assumes that the volume of the crystal is not changed by the alloying. When this volume change is considered the perturbation due to the impurity is no longer localized (2). Although the excess charge introduced by the impurity is localized by the screening, there is a long range effect from the strain perturbation due to the possible volume mismatch between the host ion and the impurity ion placed into the host material substitutionally. As discussed by Eshelby (3) this causes a change in the volume of the crystal but only about one third of the total change comes from a uniform change or dilatation of the crystal, the rest occurs in the vicinity of the impurity, causing a distortion of the lattice around the impurity. However, with a random distribution of impurities this shearing strain cancels out on the average so that, macroscopically, a cubic lattice remains cubic.

To take account of this volume change Blatt (4) proposed a suitable modification of the F.S.R. so that (2.1) is replaced by

$$\frac{2}{\pi} \sum_{\ell} (2\ell+1)\delta_{\ell}(k_F) = \Delta Z - Z_H \frac{\Delta\Omega}{\Omega_0} \qquad (2.2)$$

where Z_H is the valence of a host ion, $\Delta\Omega$ is the part of the volume change associated with the distortion and Ω_0 is the volume of a unit cell in the pure metal. The above modification is based on the fact that the impurity causes the host ions around it to be displaced and this displaces a certain amount of ionic charge in the region occupied by the impurity. In the approximation of an infinite isotropic elastic continuum the ionic charge density in the remainder of the lattice is unchanged, the strain being a pure shear and contributing no dilatation. However, the effective charge which the scattering center presents to the conduction electrons is no longer ΔZ but $\Delta Z - Z_H \, \Delta\Omega/\Omega_0$ where $\Delta\Omega/\Omega_0$ is the fractional change in size of the cell occupied by the impurity. Blatt's approach is phenomenological in that he makes use of experimental values for the macroscopic volume change, but, as mentioned above, not all of the volume change induced by the impurity causes extra scattering of the electrons. Béal-Monod and Kohn $^{(5)}$ used a discrete model for the ions instead of an elastic displacement field, but they did not attempt any detailed estimate of the actual ion displacements. Instead they used an isotropic approximation for the displacement $\underline{u}_\ell$ of the ℓ^{th} ion (with equilibrium coordinate $\underline{R}_\ell^0$)

$$\underline{u}_\ell = \alpha_0 \frac{\underline{R}_\ell^0}{|\underline{R}_\ell^0|^3} \tag{2.3}$$

with α_0 determined again from the volume change using the relation

$$\alpha_0 = \frac{3}{4\pi\gamma_E} \left(\frac{\delta a}{a}\right) \Omega_0 \tag{2.4}$$

where γ_E is given in terms of Poisson's ratio by $\gamma_E = 3(1-\sigma)/(1+\sigma)$ and $\delta a/a$ is the fractional change in lattice constant per unit atomic concentration of impurities. This leads to a correction to the F.S.R. of[5]

$$Z_H \frac{\Delta\Omega}{\Omega_0} = -\frac{3}{\gamma_E}\left(\frac{\delta a}{a}\right) Z_H . \tag{2.5}$$

It is the purpose of this chapter to present a completely microscopic discussion of the effect of lattice relaxation on the displaced charge sum rule.

2.2 Scattering Caused by the Displaced Host Ions

The relaxation of the lattice around a defect can be calculated in terms of the defect driving force and the phonon dispersion relations and polarization vectors using the method of lattice statics (6,7). Since a defect interacts with a host atom via a different potential than that between two host atoms, there will in general be an unbalanced force $\underline{F}_\ell$ on the ℓ^{th} host atom around the defect which is usually considered to be at the origin, and this force will drive this atom off its perfect lattice equilibrium site, $\underline{R}_\ell^0$, to a new equilibrium site $\underline{R}_\ell$ given by

$$\underline{R}_\ell = \underline{R}_\ell^0 + \underline{u}_\ell \quad . \tag{2.5}$$

Here $\underline{u}_\ell$ is the displacement of the ℓ^{th} host atom which is determined by $\underline{F}_\ell$ from the basic equation of lattice statics (6,7)

$$\underline{F}_\ell = \sum_{\ell' \neq \ell} \underline{\Phi}(\ell,\ell')\underline{u}_{\ell'} \quad . \tag{2.6}$$

In Eq. (2.6) $\underline{\Phi}(\ell,\ell')$ is the force constant matrix whose component $\Phi_{\alpha\beta}(\ell,\ell')$ is the force in the direction α on ion ℓ due to a unit displacement in the direction β of ion ℓ'. In lattice statics the force constants are those of the unperturbed perfect lattice, while $\underline{F}_\ell$ is evaluated at the new equilibrium positions $\underline{R}_\ell$.

To determine the displacements, the $\underline{u}_\ell$ are expanded in terms of Fourier coefficients

$$\underline{u}_\ell = \frac{1}{N}\sum_{\underline{k}\lambda}^{B.Z.} e^{-i\underline{k}\cdot\underline{R}_\ell^0}\,\underline{\varepsilon}(\underline{k}\lambda)\,\phi_\lambda(\underline{k}) \tag{2.7}$$

where the $\underline{k}$ sum is over the first Brillouin zone (B.Z.), λ is the phonon polarization branch index, N is the number of ions, $\underline{\varepsilon}(\underline{k}\lambda)$ is the polarization vector and $\phi_\lambda(\underline{k})$ is given below. Equations (2.6) and (2.7) give

$$\frac{1}{M}\sum_\ell \underline{F}_\ell\, e^{-i\underline{k}\cdot\underline{R}_\ell^0} = \sum_\lambda \underset{\sim}{D}(\underline{k})\,\underline{\varepsilon}(\underline{k}\lambda)\,\phi_\lambda(\underline{k}) \tag{2.8}$$

where M is the host mass and $\underset{\sim}{D}(\underline{k})$ is the dynamical matrix

$$\underset{\sim}{D}(\underline{k}) = \frac{1}{M}\sum_\ell e^{-i\underline{k}\cdot\underline{R}_\ell^0}\,\underset{\sim}{\Phi}(\ell,0) \tag{2.9}$$

which gives the phonon eigenfrequencies $\omega(\underline{k}\lambda)$

$$\omega^2(\underline{k}\lambda)\,\underline{\varepsilon}(\underline{k}\lambda) = \underset{\sim}{D}(\underline{k})\,\underline{\varepsilon}(\underline{k}\lambda) \quad . \tag{2.10}$$

Thus (2.8) becomes

$$\frac{1}{M}\sum_\ell \underline{F}_\ell\, e^{-i\underline{k}\cdot\underline{R}_\ell^0} = \sum_\lambda \omega^2(\underline{k}\lambda)\,\underline{\varepsilon}(\underline{k}\lambda)\,\phi_\lambda(\underline{k}) \quad . \tag{2.11}$$

Multiplication of both sides of Eq. (2.11) by $\underline{\varepsilon}(\underline{k}\lambda)$ and using the orthogonality relationship of the polarization vectors

$$\sum_{\lambda} \varepsilon_{\alpha}(\underline{k}\lambda)\,\varepsilon_{\beta}(\underline{k}\lambda) = \delta_{\alpha\beta}$$

gives an explicit expression for $\phi_{\lambda}(\underline{k})$

$$\phi_{\lambda}(\underline{k}) = \frac{1}{M\omega^{2}(\underline{k}\lambda)}\,\underline{\varepsilon}(\underline{k}\lambda)\cdot\sum_{\ell'} \underline{F}_{\ell'}\, e^{-i\underline{k}\cdot\underline{R}^{0}_{\ell'}} \tag{2.12}$$

Substituting Eq. (2.12) into Eq. (2.7) gives the basic expression for $\underline{u}_{\ell}$

$$\underline{u}_{\ell} = \frac{1}{MN} \sum_{\underline{k}\lambda}^{B.Z.} e^{i\underline{k}\cdot\underline{R}^{0}_{\ell}}\, \frac{\underline{\varepsilon}(\underline{k}\lambda)}{\omega^{2}(\underline{k}\lambda)} \sum_{\ell'} \underline{\varepsilon}(\underline{k}\lambda)\cdot\underline{F}_{\ell'}\, e^{-i\underline{k}\cdot\underline{R}^{0}_{\ell'}} . \tag{2.13}$$

To describe the scattering of the electrons by the ions, pseudopotential theory is used$^{(8)}$. The interaction of the conduction electrons with a system of free conduction electrons is given by the total pseudopotential W of the system of N ions

$$W(\underline{r}) = \sum_{\ell} w_{\ell}(\underline{r}-\underline{R}_{\ell}) \tag{2.14}$$

where $w_{\ell}(\underline{r}-\underline{R}_{\ell})$ is the pseudopotential associated with the ℓ^{th} ion. In many applications, e.g., in transport theory and in the P.S.R., one is interested in Fermi surface matrix elements of this potential

$$\langle \underline{k}+\underline{q}|W|\underline{k}\rangle = \frac{1}{N}\sum_{\ell} e^{-i\underline{q}\cdot\underline{R}_{\ell}} \langle \underline{k}+\underline{q}|w_{\ell}|\underline{k}\rangle \tag{2.15}$$

where $\langle \underline{k}+\underline{q}|w_{\ell}|\underline{k}\rangle$ is the electron-ion pseudopotential form factor associated with the ℓ^{th} ion. Let w_{ℓ} be denoted by w_H when ($\ell \neq 0$) is a host ion and by w_I for $\ell = 0$, i.e., for a single impurity ion at the origin. For a perfect crystal there is only Bragg scattering but this does not lead to any resistivity (8)

$$\langle \underline{k}+\underline{q}|W_p|\underline{k}\rangle = \frac{1}{N}\sum_{\ell} e^{-i\underline{q}\cdot\underline{R}^0_{\ell}} \langle \underline{k}+\underline{q}|w_H|\underline{k}\rangle \quad . \tag{2.16}$$

If the displacements caused by the defect are small, then

$$e^{-i\underline{q}\cdot\underline{R}_{\ell}} \approx e^{-i\underline{q}\cdot\underline{R}^0_{\ell}} (1 - iq\cdot\underline{u}_{\ell}) \quad . \tag{2.17}$$

Transport properties such as the residual resistivity (8,9) can then be calculated from the matrix elements of the difference potential

$$\langle \underline{k}+\underline{q}|W-W_p|\underline{k}\rangle = \frac{1}{N} \langle \underline{k}+\underline{q}|\Delta w|k\rangle$$
$$- \frac{i}{N}\sum_{\ell} \underline{q}\cdot\underline{u}_{\ell}\, e^{-i\underline{q}\cdot\underline{R}^0_{\ell}} \langle \underline{k}+\underline{q}|w_H|\underline{k}\rangle \tag{2.18}$$

where Δw denotes ($w_I - w_H$). Since Δw and w_H are spherically symmetric to a good approximation, their Fermi surface matrix elements will only depend on the magnitude of the momentum transfer, $\hbar q$, where $\hbar$ is Planck's constant divided by 2π. q is related to the scattering angle θ by

$$q = 2k_F \sin(\theta/2) \quad . \tag{2.19}$$

If lattice distortion effects are neglected, in the Born approximation of small phase shifts the perturbing potential $\Delta w(q)$ is related to the phase shifts by (10)

$$-\frac{2\pi\hbar^2}{mk_F\Omega_0}\sum_\ell (2\ell+1)\delta_\ell(k_F)P_\ell(\cos\theta) = \Delta w(q) \tag{2.20}$$

where m is the electron mass and P_ℓ is the ℓ^{th} Legendre polynomial. The F.S.R. in the Born approximation is obtained simply by taking the $q \to 0$ limit of Eq. (2.20)

$$\frac{2}{\pi}\sum_\ell (2\ell+1)\delta_\ell = Z_I - Z_H$$

$$= -\frac{mk_F\Omega_0}{\pi^2\hbar^2}\lim_{q\to 0}\Delta w(q) \tag{2.21}$$

where Z_I is the valence of the impurity, i.e., $\Delta Z = Z_I - Z_H$. It is important to note that although the Born approximation was used to derive Eq. (2.21), the F.S.R. actually holds for a strong potential (1). It will, however, be necessary to use the Born approximation when calculating the effect of the displaced host ions. For consistency the Born approximation is used also for the defect scattering.

When lattice relaxation is included, the defect potential is no longer spherically symmetric. Following Béal-Monod and Kohn (5), the quantity corresponding to the right hand side of Eq. (2.21) is replaced by a spherical average to give

$$\Delta Z + Z^* = -\frac{mk_F\Omega_0}{\pi^2\hbar^2}\lim_{q\to 0}\Big[\Delta w(q) - iw_H(q)\int\frac{d\Omega_{\underline{q}}}{4\pi} \times \sum_{\ell}\underline{q}\cdot\underline{u}_{\ell}\, e^{-i\underline{q}\cdot\underline{R}_{\ell}^{0}}\Big] \tag{2.22}$$

where Z^* denotes the correction to the F.S.R.

$$Z^* = \frac{imk_F\Omega_0}{\pi^2\hbar^2}\lim_{q\to 0} w_H(q)\int\frac{d\Omega_{\underline{q}}}{4\pi}\sum_{\ell}\underline{q}\cdot\underline{u}_{\ell}\, e^{-i\underline{q}\cdot\underline{R}_{\ell}^{0}} \; . \tag{2.23}$$

Later it will be proved that Z^* is indeed the displaced ionic charge associated with the displaced volume caused by the lattice distortion, thus indicating that the model used is consistent.

Substituting Eq. (2.13) into (2.23), the expression for Z^* may be simplified by using the fact that for small $\underline{q}$ and $\underline{k}$ restricted to the first B.Z.

$$\frac{1}{N}\sum_{\ell} e^{i(\underline{k}-\underline{q})\cdot\underline{R}_{\ell}^{0}} = \delta_{\underline{k},\underline{q}} \; . \tag{2.24}$$

Furthermore, in the limit of small q

$$e^{-i\underline{q}\cdot\underline{R}_\ell^0} \approx 1 - i\underline{q}\cdot\underline{R}_\ell^0 \quad . \tag{2.25}$$

This gives

$$Z^* = \frac{mk_F\Omega_0}{M\pi^2\hbar^2} \lim_{q\to 0} w_H(q) \sum_\lambda \int \frac{d\Omega_{\underline{q}}}{4\pi} \frac{(\underline{q}\cdot\underline{\varepsilon}(\underline{q}\lambda))}{\omega^2(\underline{q}\lambda)} \times \sum_\ell (\underline{\varepsilon}(\underline{q}\lambda)\cdot\underline{F}_\ell)(\underline{q}\cdot\underline{R}_\ell^0) \tag{2.26}$$

since by inversion symmetry

$$\sum_\ell \underline{F}_\ell = 0 \quad .$$

Following Flinn and Maradudin (11), in the limit of small q the phonon eigenvalues and eigenvectors may be written

$$\omega(\underline{q}\lambda) = A_\lambda(\theta\phi)q$$

$$\underline{\varepsilon}(\underline{q}\lambda) = \underline{\varepsilon}_\lambda(\theta\phi)$$

where $(\theta\phi)$ are the angles of $\hat{q} = \underline{q}/q$ and $A_\lambda(\theta\phi)$ is the sound velocity for the branch λ in the direction $(\theta\phi)$. Finally, using

$$\lim_{q\to 0} \frac{m\Omega_0 k_F}{M\pi^2\hbar^2} w_H(q) = -\frac{1}{M} Z_H \tag{2.27}$$

and the notation

$$\langle f(\theta\phi)\rangle = \frac{1}{4\pi}\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi f(\theta\phi) \qquad (2.28)$$

the result for Z* is obtained

$$Z^* = -\frac{Z_H}{M}\sum_{\lambda} \left\langle \frac{\hat{q}\cdot\underline{\varepsilon}_{\lambda}(\theta\phi)}{A_{\lambda}^2(\theta\phi)} \sum_{\ell} \underline{\varepsilon}_{\lambda}(\theta\phi)\cdot\underline{F}_{\ell}\ \hat{q}\cdot\underline{R}_{\ell}^0 \right\rangle \ . \qquad (2.29)$$

Although it is possible to evaluate Eq. (2.29) as it is, it is desirable to have a simpler expression, especially if one wishes to compare this result with the usual one (4,5). To this end, it is assumed that the transverse phonons are perfectly transverse and the longitudinal phonons perfectly longitudinal, i.e.,

$$\hat{q}\cdot\underline{\varepsilon}_{\lambda}(\theta\phi) = \begin{cases} 0 & \lambda = 2,\ 3 \\ 1 & \lambda = 1 \ . \end{cases} \qquad (2.30)$$

If $\underline{F}_{\ell}$ can be derived from a central potential U

$$\underline{F}_{\ell} = -\nabla U_{\ell} = -\frac{\underline{R}_{\ell}^0}{R_{\ell}^0}\frac{dU}{dR_{\ell}^0} \qquad (2.31)$$

and, also, the angular dependence of $A_1(\theta\phi)$ is neglected so that the angular integrations in Eq. (2.29) may be done, the following result is obtained

$$Z^* = \frac{Z_H}{M} \frac{1}{\bar{A}^2} \sum_{\ell} \frac{1}{3} R_\ell^0 \frac{dU}{dR_\ell^0} \quad . \tag{2.32}$$

$\bar{A}$ can be interpreted as the average longitudinal sound velocity. Equation (2.32) will be useful for making rough estimates of Z*, but it should be emphasized that the simplifying assumptions leading from Eq. (2.29) to (2.32) are not necessary for the discussion in the next section of the interpretation of Z* in terms of the displaced volume.

2.3 Displaced Volume

As mentioned earlier there are two distinct volume changes associated with the relaxation about a defect: one referring only to relaxation in the bulk of the material which gives the strain field and the other, including surface effects and a uniform dilatation of the crystal. The scattering of electrons or the F.S.R. is only affected by the former.

The displacement field $\underline{u}_\ell$ is, of course, only defined at the ionic sites, but the expression in Eq. (2.13) can be continued to all space, and written as

$$\Delta\underline{R} = \frac{1}{MN} \sum_{\underline{k}\lambda}^{B.Z.} e^{i\underline{k}\cdot\underline{R}} \frac{\underline{\varepsilon}(\underline{k}\lambda)}{\omega^2(\underline{k}\lambda)} \sum_{\ell'} \underline{\varepsilon}(\underline{k}\lambda)\cdot\underline{F}_{\ell'}\, e^{-i\underline{k}\cdot\underline{R}^0_{\ell'}} \qquad (2.33)$$

to get a smoothly varying function which agrees with the true displacement field at the ionic sites. The volume change can then be defined to be

$$\Delta\Omega = \lim_{R\to\infty} R \int d\Omega_{\underline{R}}\ \underline{R}\cdot\Delta\underline{R} \quad . \qquad (2.34)$$

Substituting Eq. (2.33) into (2.34) and carrying out the angular integrations over $\underline{R}$ gives

$$\Delta\underline{R} = \lim_{R\to\infty} \frac{i\Omega_0}{2\pi^2 M} \int d\Omega_{\underline{q}} \int dq \sum_{\ell\lambda} \frac{(\underline{\varepsilon}(\underline{q}\lambda)\cdot\underline{F}_\ell)}{\omega^2(\underline{q}\lambda)}\, e^{-i\underline{q}\cdot\underline{R}^0_\ell}$$

$$\times\ (\underline{q}\cdot\underline{\varepsilon}(\underline{q}\lambda)\left[\frac{\sin(qR)}{q} - R\cos(qR)\right] \quad . \qquad (2.35)$$

The Fourier integral theorem states

$$\lim_{R\to\infty}\int_0^\infty f(q)\,\frac{\sin(qR)}{q}\,dq = \frac{\pi}{2}\lim_{q\to 0} f(q)$$
$$\lim_{R\to\infty}\int_0^\infty f(q)\,R\cos(qR)\,dq = 0 \quad . \tag{2.36}$$

Using the same notation and approximations as before, this is reduced to

$$\frac{\Delta\Omega}{\Omega_0} = \frac{1}{M}\sum_\lambda \left< \frac{\hat{q}\cdot\underline{\varepsilon}_\lambda(\theta\phi)}{A_\lambda^2(\theta\phi)} \sum_\ell \underline{\varepsilon}_\lambda(\theta\phi)\cdot\underline{F}_\ell\ \hat{q}\cdot\underline{R}_\ell^0 \right> \quad . \tag{2.37}$$

Comparing Eq. (2.29) and (2.37), it is seen that the displaced charge sum rule is expressible in terms of the volume change through

$$Z^* = - Z_H \frac{\Delta\Omega}{\Omega_0} \tag{2.38}$$

which is formally the same as that used by Blatt (4) and Béal-Monod and Kohn (5) but whereas they related ΔΩ to macroscopically measured quantities, which automatically include the surface effects, the ΔΩ defined above includes only the relevant part of the volume change and must be calculated using microscopic parameters of the alloy.

In order to calculate the correction to the F.S.R. or the displaced volume it is necessary to know the force, or potential, causing the relaxation. The interionic potential V(r) in a metal can be written in the form given by Shyu and Gaspari (12)

$$V(r) = \frac{Z_H^2 e^2}{r} - \frac{2Z_H^2 e^2}{\pi} \int_0^\infty G(q) \frac{\sin(qr)}{qr} dq \qquad (2.39)$$

where the first term is the direct Coulomb interaction between bare ions and the second term is the indirect interaction via the electrons. G(q) is given by

$$G(q) = \left| \frac{w_H^0(q)}{-4\pi Z_H e^2/\Omega_0 q^2} \right|^2 \left(1 - \frac{1}{\varepsilon(q)}\right) \qquad (2.40)$$

$w_H^0(q)$ is the bare ion pseudopotential which will be approximated by the Ashcroft form (13)

$$w_H^0 = - \frac{4\pi Z_H e^2}{\Omega_0 q^2} \cos(qR_c a_0) \qquad (2.41)$$

where R_c is an adjustable parameter representing an effective radius of the ionic core and a_0 is the Bohr radius. For the alkalis R_c has been fitted by Shyu et al. (14) to the force constants and by Price et al. (15) to the phonons. The dielectric function $\varepsilon(q)$ is given by

$$\varepsilon(q) = 1 + \frac{Q_0(q)}{1 - f(q) Q_0(q)} \qquad (2.42)$$

where $Q_0(q)$ is the Lindhard electron polarizability times $-4\pi e^2/q^2$

$$Q_0(q) = \frac{k_{FT}^2}{q^2} F(\frac{q}{k_F}) \qquad (2.43)$$

with

$$F(x) = \frac{1}{2} + (\frac{4-x^2}{8x}) \ell n \left|\frac{2+x}{2-x}\right| \qquad (2.44)$$

and

$$k_{FT}^2 = \frac{m^*}{m} \frac{4k_F}{a_0\pi} . \qquad (2.45)$$

The effects of the band structure on the conduction electrons have been included in an approximate way by introducing an effective mass m*. The function f(q) in Eq. (2.42) accounts for exchange and correlation effects among the electrons; it has been evaluated by Singwi et al.(16) in a self consistent treatment and has the form

$$f(q) = A[1 - \exp(-B(q/k_F)^2)] \qquad (2.46)$$

where A and B are parameters which depend on the electron density r_s.

For the case of a vacancy in a metal the perturbing potential is taken to be

$$U(r) = - V(r) \qquad (2.47)$$

while for an impurity, with the same valence as the host atoms, the perturbing potential is

$$U(r) = -\frac{2Z_H^2e^2}{\pi}\int_0^\infty \overline{G}(q)\,\frac{\sin(qr)}{qr}\,dq \quad . \tag{2.48}$$

$\overline{G}(q)$ is obtained from $G(q)$ by replacing $|w_H^0(q)|^2$ by $w_H^0(q)(w_I^0(q) - w_H^0(q))$ and $w_I^0(q)$ is the bare pseudopotential for the impurity but with the atomic volume appropriate for the host. The screening is according to the dielectric function for the host. The parameter R_c for the impurity is taken to be the one the impurity would have in its own bulk, e.g., any energy dependence in R_c is neglected.

In Fig. 1 a plot is given of $V(r)$ for the pure metals Na, K and Rb as well as $U(r)$ for the case of K impurities in Rb and Rb impurities in K. The perturbing forces are derived from the first derivative of these potentials which should be evaluated at the relaxed lattice positions (7) but for simplicity this complication will be ignored since it would entail doing a complete lattice statics calculation. For the case of vacancies, it is also possible to get the required forces directly from the neutron-derived Born-von Kármán pure metal force constants (see, for example, Woods et al. (17)). Further, instead of performing the complete average over the anisotropic longitudinal sound velocities, the value of the sound velocity S_L in the (100) direction was used. It is given by

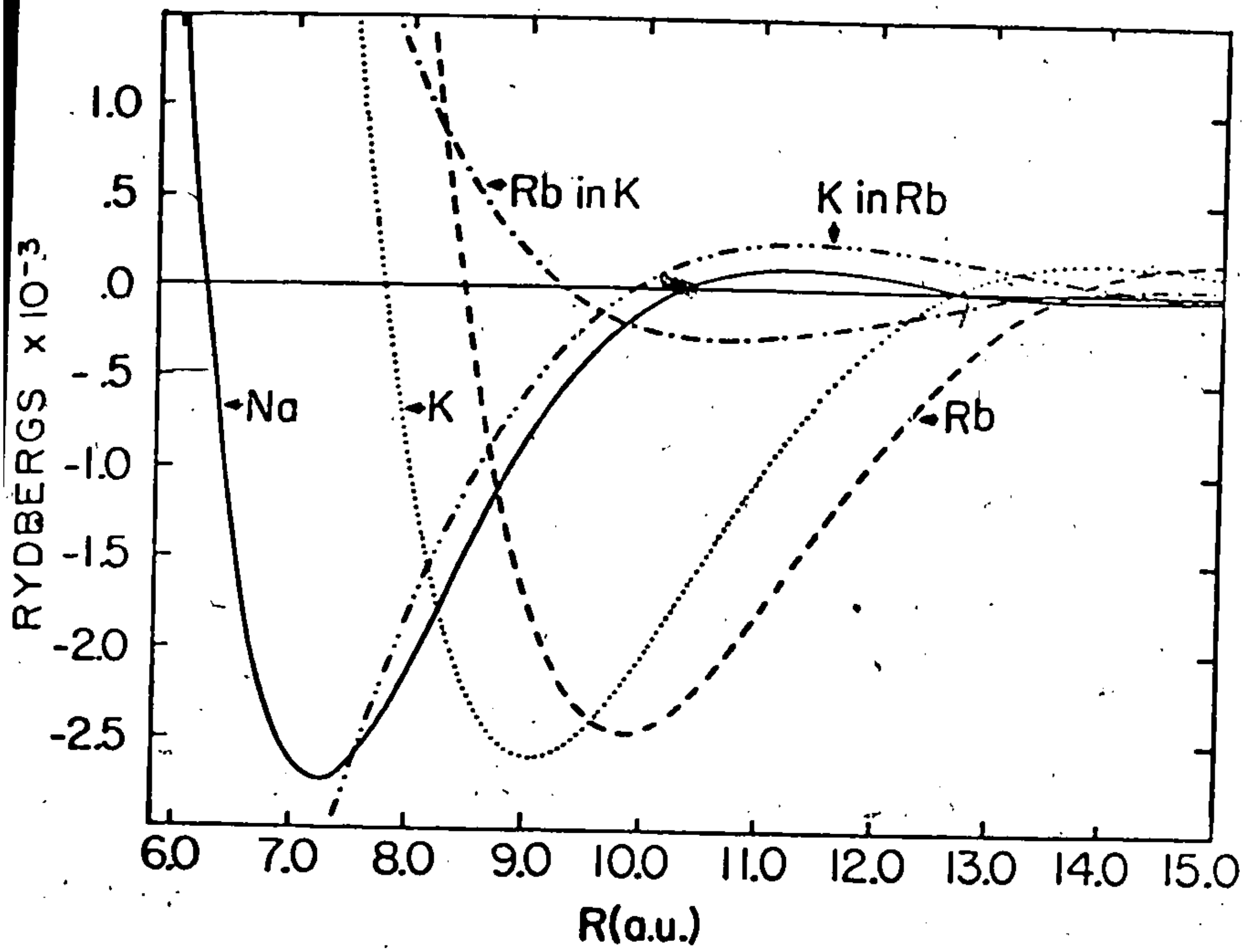


Fig. 1: Interionic potentials in Na, K and Rb, and the perturbing potentials for the dilute solutions K in Rb and Rb in K.

$$C_{11} = S_L^2 \rho \qquad (2.49)$$

where ρ is the metal density and C_{11} an elastic constant. The results for Eq. (2.32) are presented in Table 1, along with the values of r_s, the values of A and B suggested by Singwi et al. (16) as well as the Ashcroft core radius suggested by Shyu et al. (14). The effective masses suggested by these authors were also used. For vacancies the sum in Eq. (2.32) has been quoted using only experimental force constants. An alternative approach is to employ the potential given by Eq. (2.39). When this is done there is a question of convergence of the sum in Eq. (2.32) for very distant neighbours. This problem does not arise when the experimental force constants are used since they are cut off at some finite neighbour distance during the fitting procedure to neutron data. For large r the potential exhibits Friedel oscillations. The asymptotic form of the potential is in fact (8)

$$V(r) \underset{r \to \infty}{\rightarrow} \frac{9\pi Z_H^2 |w_H(2k_F)|^2}{E_F} \frac{\cos(2k_F r)}{(2k_F r)^3} \qquad (2.50)$$

where E_F is the Fermi energy. The forces from the potential were evaluated out to 12 neighbours and the sum performed out to that point. An estimate of the sum from 12 neighbours to infinity was added using the asymptotic form. The required sums for the asymptotic potential have been done by

Shaw (18). This gives about a 10% correction and is taken as evidence that it is reasonable to ignore the very distant neighbours.

The results for Z* using the theoretical expression for the vacancy potential and including the asymptotic contribution differ from those quoted in Table 1 by 20-30%. In the case of vacancies only the results based on measured force constants are quoted since it is well known that it is difficult to obtain good agreement between theoretical and experimental force constants.

In the case of impurities, the theoretical expression (2.48) must be used and to be consistent with the treatment of vacancies the sums were limited to 5 neighbours which is the same as the number of neighbours included in the fitting to neutron data.

TABLE 1

VALUES OF THE PARAMETERS USED IN THE CALCULATION AND THE CALCULATED VALUES OF Z*

SYSTEM	r_s	A	B	R_c (a.u.)	m*/m	$C_{11}\times10^{10}$ (dynes/cm^2)	$\sum_\ell R_\ell^0 dU/dR_\ell^0\times10^{-12}$ (dynes/cm)	Z*
FOR VACANCIES								
Na	3.931	0.995	0.2625	1.694	1.0	8.45^a	2.27^d	0.238
K	4.862	1.007	0.249	2.226	0.93	4.16^b	1.22^e	0.137
Rb	5.197	1.008	0.247	2.45	0.89	3.25^c	1.91^f	0.225
FOR IMPURITIES								
Rb in K	4.862	1.007	0.249	2.45 2.226	0.93	4.16^b	-1.91	-0.215
K in Rb	5.197	1.008	0.247	2.226 2.45	0.89	3.25^c	1.66	0.195

The experimental values were taken from the following sources:

[a] Diederich and Trivisonno (19)

[b] Marquart and Trivisonno (20)

[c] Gutman and Trivisonno (21)

[d] Woods et al. (17)

[e] Cowley et al. (22)

[f] Copley et al. (23)

2.4 Discussion

From Table 1 the correction, Z*, to the F.S.R. is appreciable especially for the case of the impurities where the F.S.R. without the Z* correction would require, since there is no valence difference,

$$\frac{2}{\pi}\sum_{\ell}(2\ell+1)\delta_{\ell}(k_F) = 0 \quad .$$

Similarly, for the case of the vacancies, where there is in effect a valence difference, the Z* is still appreciable. It should be reemphasized that we have used the Born approximation and linear screening theory which are probably not adequate to describe the scattering since these approximations require small fractional changes in the electron density whereas if there is a valence change associated with the defect the electron density has a large change $^{(24)}$. Another way of seeing this is to consider the F.S.R. for, say, $\Delta Z = 1$. Then

$$\frac{2}{\pi}\sum_{\ell}(2\ell+1)\delta_{\ell}(k_F) = 1$$

and since in most cases only the first few phase shifts contribute significantly, this requires at least one of the δ_{ℓ} to be of the order of $\pi/2$ whereas the Born approximation requires $\delta_{\ell} \ll 1$. Thus it is expected that these approximations will work best for isovalent impurities or a lattice distorted by phonons as in the finite temperature resistivity (25).

It is the above mentioned ability of the Z* correction to the F.S.R. to distinguish between the detailed properties of different impurities which makes it so useful in practice, especially in discussions of the residual resistivity ρ_R of isovalent impurities (4,26) such as Ag in Cu, Cu in Ag, Cu in Au and Ag in Au where the F.S.R. alone is not able to distinguish between Cu or Ag in Au. Care must be taken in using the F.S.R. to determine the phase shifts to be used in a calculation of the residual resistivity. In the Born approximation, as emphasized by Ziman (27), the F.S.R. only fixes the $q \rightarrow 0$ limit of the scattering amplitude while the expression for the resistivity involves all q values from 0 to $2\ k_F$. In calculations of the resistivity in which the phase shifts are chosen to satisfy the F.S.R. (4,27), a simple square well potential is often used to represent the impurity but the exact, not Born approximation, phase shifts are then used. However, as well as not being as physical as the pseudopotential, the square well involves 2 parameters: the depth and width of the well. The latter is usually chosen to be about the ionic radius while the former is then adjusted to fit the F.S.R. The effect of the lattice distortion is included by modifying the width of the square well by a factor of $(1 + \Delta\Omega/\Omega_0)^{1/3}$ (4)

and then demanding that the resulting phase shifts satisfy the modified F.S.R.

Calculations of ρ_R using the Born approximation and pseudopotential theory, and including explicitly the effect of lattice distortion in the q integral have been done (9,29,30) and corrections of the order of 5 to 30% are generally found. As was pointed out above, however, there is no direct relationship between the correction to the F.S.R. and the one to ρ_R since in the former case only the $q \rightarrow 0$ limit of the scattering amplitude enters (8).

CHAPTER III

PHONON-LIMITED RESISTIVITY AND DEVIATIONS FROM MATTHIESSEN'S RULE

3.1 Theory

At finite temperature, the thermal oscillations of the ions in a pure metal cause a conduction electron in a state $\underline{k}$ to be scattered to a state $\underline{k}'$ via the absorption or emission of a phonon with wavevector $\underline{q} = \underline{k}' - \underline{k} + \underline{G}$ where the electron states are on the Fermi surface so that $|\underline{k}| = |\underline{k}'| = k_F$ and $\underline{G}$ is a reciprocal lattice vector which distinguishes between normal ($\underline{G} = 0$) and umklapp processes ($\underline{G} \neq 0$). This is due to the fact that the electron wavevector transfer $(\underline{k}' - \underline{k})$ can exceed the magnitude of the largest phonon wavevector in the first B.Z.. The transition probability for the scattering is given by the Fermi Golden Rule

$$P_{\underline{k}}^{\underline{k}'}(\omega) = \frac{2\pi}{\hbar} \sum_{i,f} \frac{e^{-\beta\omega_i}}{Z_p} |\langle f,\underline{k}'|H'|\underline{k},i\rangle|^2 \delta(\hbar\omega-\hbar\omega_{fi}) \quad . \tag{3.1}$$

Here i and f refer to initial and final lattice states. $\hbar\omega_i$ and $\hbar\omega_f$ are the corresponding energies of the lattice and $\omega_{fi} = \omega_f - \omega_i$, and Z_p is the partition function

$$Z_p = \sum_i e^{-\beta\omega_i}$$

with $\beta = \hbar/k_BT$ where k_B is the Boltzmann constant and T is the temperature. The factor $e^{-\beta\omega_i}/Z_p$ is the probability of finding the lattice in a state i in thermal equilibrium, and the δ function conserves energy, i.e., the change in the energy of the lattice, ω_{fi}, must equal the change in the electron energy, ω. The perturbation Hamiltonian causing the scattering is the electron-ion coupling which in pseudopotential theory is given by

$$H' = \sum_{\ell} w_\ell(r - R_\ell) \quad . \tag{3.2}$$

For the case of a pure metal, using plane waves for the conduction electron states with energy $E_k = \hbar^2k^2/2m$

$$\langle r|\underline{k}\rangle = \frac{1}{\sqrt{\Omega}}\, e^{i\underline{k}\cdot\underline{r}}$$

where Ω is the total volume of the system, this reduces to, in the Born approximation

$$P_{\underline{k}}^{\underline{k}'}(\omega) = \frac{2\pi}{\hbar}\, |w(|\underline{k}-\underline{k}'|)|^2\, S(\underline{k}-\underline{k}',\omega) \tag{3.3}$$

where $S(\underline{q}\omega)$ is the dynamic structure factor containing all the information about the lattice. In the harmonic approximation it is given by (31,32)

$$S(\underline{q}\omega) = \sum_{\lambda} \frac{2\pi N}{M2\omega(\underline{q}\lambda)} |\underline{q}\cdot\underline{\varepsilon}(\underline{q}\lambda)|^2$$

$$\times [(1+n(\omega(\underline{q}\lambda)))\delta(\omega-\omega(\underline{q}\lambda))+n(\omega(\underline{q}\lambda))\delta(\omega+\omega(\underline{q}\lambda))] \quad (3.4)$$

where $n(\omega) = [e^{\beta\omega} - 1]^{-1}$ is the Bose-Einstein factor which gives the thermal population of phonons, and all phonon variables are understood to be reduced to the first B.Z.. The phonons will be considered to be always in equilibrium, i.e., phonon drag effects $^{(33)}$, which may be expected to be significant at very low temperature, are neglected.

To calculate the resistivity for the pure metal, the general formula is $^{(34)}$

$$\rho_0(T) = [-\frac{e^2}{\Omega} \sum_{\underline{k}} \underline{v}(\underline{k})\cdot\underline{\Lambda}_{\underline{k}} \frac{\partial f_0}{\partial E_{\underline{k}}}]^{-1} \quad (3.5)$$

where $\underline{v}(\underline{k})$ is the electron velocity in the state $\underline{k}$ which is proportional to $\underline{k}$ for a spherical Fermi surface, $\underline{\Lambda}_{\underline{k}}$ is the electron mean free path and $f_0(E_{\underline{k}}) = [e^{\beta E_{\underline{k}}} - 1]^{-1}$ is the Fermi-Dirac function which gives the electron occupation of the state $\underline{k}$. In a cubic system the conductivity is isotropic. Since the vector mean free path $\underline{\Lambda}_{\underline{k}}$ is approximately parallel to the electron velocity $v(\underline{k})$, a temperature dependent scattering time $\tau_0(\underline{k}T)$ may be defined by $^{(34)}$

$$\underline{\Lambda}_{\underline{k}} = \tau_0(\underline{k})\underline{v}(\underline{k}) \quad (3.6)$$

where the temperature dependence has been suppressed.

To get an explicit expression for the resistivity $\rho_0(T)$, the mean free path must be determined. The Boltzmann equation is used to relate the change of the electron occupation of a state $\underline{k}$, $f_{\underline{k}}$, due to an electric field to the change caused by the scattering by phonons. In the steady state

$$\left(\frac{\partial f_k}{\partial t}\right)_{\text{scat.}} + \left(\frac{\partial f_k}{\partial t}\right)_{\text{field}} = 0 \ . \tag{3.7}$$

The scattering term is the difference between scattering into and out of a state $\underline{k}$ by the emission and absorption of phonons (31,33)

$$\left(\frac{\partial f_k}{\partial t}\right)_{\text{scat.}} = \sum_{\underline{k}'} \int_{-\infty}^{\infty} d\omega\,\delta(E - E' - \hbar\omega)\,|w(q)|^2$$
$$\times [f'(1-f)S(\underline{k}'-\underline{k},-\omega)-f(1-f')S(\underline{k}-\underline{k}',\omega)] \tag{3.8}$$

where, to simplify the notation, f, f', E, E' have been used for $f_{\underline{k}}$, $f_{\underline{k}'}$, $E_{\underline{k}}$, $E_{\underline{k}'}$. In the absence of thermal gradients and magnetic fields, the field term appropriate for a unit electric field $\underline{\varepsilon}$ is (33)

$$\left(\frac{\partial f}{\partial t}\right)_{\text{field}} = e\underline{\varepsilon}\cdot\underline{v}(\underline{k})\,\frac{\partial f_0}{\partial E} \ . \tag{3.9}$$

The electron distribution is expanded about the equilibrium Fermi-Dirac distribution f_0 to give

$$f_{\underline{k}} = f_0 - \Phi_{\underline{k}} \frac{\partial f_0}{\partial E} \quad . \qquad (3.10)$$

This is substituted into Eq. (3.8) and only the terms of lowest order in $\Phi_{\underline{k}}$ are kept, leading to the following form for the Boltzmann equation

$$e\underline{\varepsilon}\cdot\underline{v}(\underline{k}) \frac{\partial f_0}{\partial E} = \beta \sum_{\underline{k}'} \int_{-\infty}^{\infty} d\omega\,\delta(E - E' - \hbar\omega) S(\underline{k}-\underline{k}',\omega)$$
$$\times [\Phi_{\underline{k}'} - \Phi_{\underline{k}}] f_0 (1 - f_0') \quad . \qquad (3.11)$$

Ziman (33) discusses in detail the variational solution of Eq. (3.11) and it is sufficient to quote the result

$$\rho_0 = \frac{\frac{1}{2k_BT} \iint d^3k d^3k' [\Phi_{\underline{k}} - \Phi_{\underline{k}'}]^2 \; P_{\underline{k}}^{\underline{k}'} f_0 (1 - f_0')}{\left| \int e\underline{v}(\underline{k}) \Phi_{\underline{k}} \frac{\partial f_0}{\partial E_{\underline{k}}} d^3k \right|^2} \quad . \qquad (3.12a)$$

$P_{\underline{k}}^{\underline{k}'}$ is similar to $P_{\underline{k}}^{\underline{k}'}(\omega)$ used previously except that $E_{\underline{k}} - E_{\underline{k}'}$ is written for $\hbar\omega$.

The lowest order approximation uses $\Phi_{\underline{k}} = \underline{k}\cdot\underline{\varepsilon}$ and this leads to the standard result for the phonon limited resistivity (32)

$$\rho_C^V(T) = \frac{3\Omega_0 \beta m}{16Me^2 v_F^2 k_F^4} \int_{<2k_F} q d^3q |w(q)|^2$$
$$\times \sum_{\lambda} \frac{|\underline{q}\cdot\underline{\varepsilon}(\underline{q}\lambda)|^2}{(e^{\beta\omega(\underline{q}\lambda)} - 1)(1 - e^{-\beta\omega(\underline{q}\lambda)})} \quad . \qquad (3.12b)$$

which involves essentially the integral over $|w(q)|^2\, S(\underline{q},\omega)$, making use of the delta functions.

With the reintroduction of a Dirac delta function, $\delta(\omega-\omega(\underline{q}\lambda))$, and integrating over ω this can be rewritten as

$$\rho_0^v(T) = \frac{4\pi\beta m}{ne^2}\int \frac{d\omega\,\omega\,\alpha_{TR}^2 F(\omega)}{(e^{\beta\omega}-1)(1-e^{-\beta\omega})} \tag{3.13}$$

where n is the conduction electron density and $\alpha_{TR}^2F(\omega)$ is an "effective frequency distribution" for transport (35)

$$\alpha_{TR}^2F(\omega) = \Omega_0 \int \frac{d^3q}{(2\pi)^3}\,\frac{mq}{8\hbar^2k_F^3M}\sum_{\lambda}\frac{|q\cdot\varepsilon(q\lambda)|^2|w(q)|^2\delta(\omega-\omega(q\lambda))}{\omega(\underline{q}\lambda)} \tag{3.14}$$

When the effect of the anisotropy in the electron-phonon scattering is considered, it becomes convenient to consider an anisotropic effective distribution (36) that is intermediate in the derivation of Eq. (3.12)

$$\alpha_{TR}^2F(\underline{k}\omega) = \frac{N(0)}{\hbar}\int_{F.S.}\frac{d\Omega_{k'}}{4\pi}\sum_{\lambda}|g_{\underline{k}\underline{k}'\lambda}|^2$$

$$\times\ (1-\cos(\underline{k},\underline{k}'))\,\delta(\omega-\omega(\underline{k}-\underline{k}'\lambda)) \tag{3.15}$$

where N(0) is the single spin electron density of states at the Fermi surface, and $g_{\underline{k}\underline{k}'\lambda}$ is the electron phonon coupling constant

$$g_{\underline{k}\underline{k}'\lambda} = -\,i\left(\frac{\hbar}{2NM\omega(\underline{k}-\underline{k}'\lambda)}\right)^{1/2} w(|\underline{k}-\underline{k}'|)\,(\underline{k}-\underline{k}')\cdot\underline{\varepsilon}(\underline{k}-\underline{k}'\lambda) \tag{3.16}$$

where $(\underline{k}-\underline{k}')$ is to be reduced to the first B.Z. in all phonon variables.

The angular integral in Eq. (3.15) is over the Fermi surface; and by doing another angular average, $\alpha^2_{TR}F(\underline{k}\omega)$ and $\alpha^2_{TR}F(\omega)$ are related by

$$\alpha^2_{TR}F(\omega) = \int_{F.S.} \frac{d\Omega_{\underline{k}}}{4\pi} \alpha^2_{TR}F(\underline{k}\omega) \tag{3.17}$$

where the double angular integral now in Eq. (3.17) may be converted into a volume integral to give Eq. (3.14). In the expression for the isotropic effective frequency distribution, $F(\omega)$ is the phonon density of states

$$F(\omega) = \frac{1}{N} \sum_{\underline{k}\lambda}^{B.Z.} \delta(\omega - \omega(\underline{k}\lambda)) \tag{3.18}$$

and the effective coupling constant α^2_{TR} is actually a function of ω and $\underline{k}$ but this will be suppressed in the notation.

The resistivity may also be conveniently written in terms of a scattering time $\tau_0(\underline{k})$ as

$$\rho^v_0(T) = \frac{m}{ne^2} \left\langle \frac{1}{\tau_0(\underline{k})} \right\rangle \tag{3.19}$$

where the angular brackets denote a Fermi surface average, and $\tau_0(\underline{k})$ is given by

$$\frac{1}{\tau_0(\underline{k})} = 4\pi\beta \int d\omega R(\omega) \alpha^2_{TR}F(\underline{k}\omega) \tag{3.20}$$

where

$$R(\omega) = \frac{\omega}{(e^{\beta\omega}-1)(1-e^{-\beta\omega})}$$

Robinson and Dow (37) have pointed out that Eq. (3.20) averages over the resistivities of the individual electrons whereas actually the conductivities should be averaged, to give

$$\rho_0^S(T) = \frac{m}{ne^2}\frac{1}{\langle\tau_0(\underline{k})\rangle} \quad . \tag{3.21}$$

That this is more physical can be seen from the basic expression (3.5) where the conductivity is just the reciprocal of the resistivity. These authors give a prescription for calculating $\tau_0(\underline{k})$ directly, in what they call the scattering time approximation, as opposed to the variational method which gives the average in Eq. (3.19) directly. It is interesting to note that if the $\tau_0(\underline{k})$ obtained by Robinson and Dow is averaged according to Eq. (3.19) then one obtains exactly the $\rho_0^V(T)$ as given by the variational formulation. This is not obvious because of the approximations used to obtain $\tau_0(\underline{k})$ by the Robinson and Dow method. The resistivities of the alkalis have been calculated (36) using both Eqs. (3.19) and (3.21) with significant differences obtained at low temperature, while at high temperature they give the same result.

The essential difference between the method of Robinson and Dow (37) and the variational method (33) is that in the latter the unknown function $\Phi_{\underline{k}}$ is expanded in a series of cubic harmonics with arbitrary coefficients which are then determined by the variational procedure to minimize the resistivity. In lowest order, the approximation $\Phi_{\underline{k}} = \underline{k}\cdot\underline{\varepsilon}$ leads to Eq. (3.12). In contrast to this, the scattering time method writes $\Phi_{\underline{k}}$ in terms of the (unknown) mean free path (37)

$$\Phi_{\underline{k}} = e\underline{\Lambda}_{\underline{k}}\cdot\underline{\varepsilon} \tag{3.22}$$

and thus obtains an integral equation by substitution into Eq. (3.11) for $\underline{\Lambda}_{\underline{k}} = \tau_0(\underline{k})\underline{v}(\underline{k})$ which for a spherical fermi surface reduces to (38)

$$\underline{k} = \frac{4\pi\beta}{\hbar}\int d\omega R(\omega)N(0)\int\frac{d\Omega_{\underline{k}'}}{4\pi}\sum_{\lambda}|g_{\underline{k}\underline{k}'\lambda}|^2$$
$$\times\{\tau_0(\underline{k})\underline{k} - \tau_0(\underline{k}')\underline{k}'\}\delta(\omega - \omega(\underline{k}-\underline{k}'\lambda)) \quad . \tag{3.23}$$

In the curly brackets $\tau_0(\underline{k})\underline{k}'$ is added and subtracted to obtain, so that after taking $\underline{k}\cdot$ on sides of the equation

$$1 = \frac{4\pi\beta}{\hbar}\int d\omega R(\omega)N(0)\int\frac{d\Omega_{\underline{k}'}}{4\pi}\sum_{\lambda}|g_{\underline{k}\underline{k}'\lambda}|^2$$
$$\times\{\tau_0(\underline{k})(1-\cos(\underline{k},\underline{k}'))+(\tau_0(\underline{k})-\tau_0(\underline{k}')\frac{\underline{k}\cdot\underline{k}'}{k_F^2}\}\delta(\omega-\omega(\underline{k}-\underline{k}'\lambda)) \quad . \tag{3.24}$$

At this point it is observed that the first term in the curly brackets is always positive while the second term is both positive and negative. In fact, for a general point $\underline{k}$ the second term will go to zero 48 times (if the scattering is elastic) for a cubic crystal, by symmetry, so this term is expected to be small and is thus neglected. Then it is possible to obtain an explicit expression for $\tau_0(\underline{k})$

$$\frac{1}{\tau_0(\underline{k})} = 4\pi\beta \int d\omega R(\omega)\alpha^2_{TR}F(\underline{k}\omega) \quad . \tag{3.25}$$

So far only the ideal, phonon limited resistivity has been considered. In order to compare the results of theoretical calculations with those of experiment it is important to consider the effect of the defects and impurities which are always present even in the purest experimental samples. If the validity of Matthiessen's rule $^{(38)}$ is assumed these effects are easy to include. Matthiessen's rule (M.R.) states that for a dilute alloy, the resistivity $\rho_a(c,T)$ obeys the relation

$$\frac{d\rho_a(cT)}{dT} = \frac{d\rho_0(T)}{dT} \quad . \tag{3.26}$$

If Eq. (3.26) is assumed to apply at all temperatures, then it can be integrated to give

$$\rho_a(cT) = \rho_0(T) + \rho_R(c) \quad . \tag{3.27}$$

According to these equations, the addition of impurities merely adds to the ideal resistivity a constant component, leaving the temperature-dependent component unchanged. Alternatively, to the extent that Eq. (3.27) is exactly valid, this implies that the two scatterers of electrons, i.e., lattice vibrations and impurities, produce contributions which are independent and additive.

In fact neither Eq. (3.26) nor Eq. (3.27) is exactly valid and there are always deviations from Matthiessen's rule (D.M.R.). Then a quantity $\Delta(cT)$, the D.M.R., may be defined such that

$$\rho_a(cT) = \rho_0(T) + \rho_R(c) + \Delta(cT) \quad . \tag{3.28}$$

Non-zero values of $\Delta(cT)$ have been found in a wide variety of systems and under a wide variety of physical conditions, e.g., dilute substitutional alloys, alloys with vacancies and interstitial atoms, plastic deformations and size dependent D.M.R.. An excellent review of both the history of this effect and all relevant theoretical and experimental work is given by Bass (39). In this thesis only the D.M.R. for the dilute nonmagnetic substitutional alloys of simple metals such as the alkalis and aluminum will be considered in detail but some general features of the theory will be found to give a plausible explanation for other metals, such as the noble metals, as well.

The origin of the anisotropy in the scattering times lies partly in the cubic anisotropy of the phonon spectrum and, more importantly, in the geometry of the electron-phonon umklapp processes. The phonon dispersion curves in the different directions in reciprocal space can be quite different. This gives rise to different sound velocities and the energy of a phonon with a given wavevector needed to satisfy the momentum conservation in the normal scattering of an electron from one point on the Fermi surface to another can be quite different depending on the direction of $\underline{k}-\underline{k}'$. At low temperature, the thermal population of phonons is very sensitive to the phonon energy via the Bose-Einstein distribution, so that the lowest energy phonons have the largest population. Thus, if the direction of $\underline{k}-\underline{k}'$ is such that the phonon wavevector $\underline{q}$ needed has a higher energy in that particular direction, the transition will be greatly restricted. At high temperature, phonons with all energies up to the Debye energy are sufficiently populated that the energy restriction becomes unimportant. In the actual calculation of the scattering time this anisotropy is, however, largely averaged over so that it has little effect (41). In any case, it would not explain the very large difference in the anisotropy observed in Li as compared to Na or K (36).

The main cause of the large amount of anisotropy in $\tau_0(\underline{k})$ is the geometry of the electron-phonon umklapp scattering. When the wavevector transfer $\underline{k}-\underline{k}'$ of the electron becomes larger than the maximum phonon wavevector in that direction, it is an umklapp process and a reciprocal lattice vector is needed to make up the wavevector difference and map the scattering back into the first B.Z.. For a given initial point k on the Fermi surface, the same reciprocal lattice vector is required in the scattering to many final points k'. For a completely different starting point k, reciprocal lattice vectors different in direction, and, possibly, magnitude, will be needed. Since so much of the momentum is taken up by the reciprocal lattice vector, the phonon wavevector q can be quite small even if k-k' (= q + G) is large. Thus a great deal of spectral weight can fall in the low energy region of $\alpha^2_{TR}F(\underline{k}\omega)$ (36), and the exact distribution of this weight in energy will depend on the direction k. For the alkali metals, whose Fermi surface lies completely inside the first B.Z., there is a minimum phonon wavevector needed before umklapp processes can occur (33), but for metals like Al whose Fermi surface is cut by the first B.Z. boundary, there is no such minimum so that umklapp processes may contribute all the way down to zero phonon wavevector or energy. The difference in the amount of anisotropy in Li compared to Na or K lies mainly in the larger value of the pseudopotential form factor for large k-k' used in calculating $\alpha^2_{TR}F(\underline{k}\omega)$ for Li. Large values of the pseudopotential at large values of k-k' are greatly weighted by the factor (1 - cosθ) where θ is the angle between $\underline{k}$ and $\underline{k}'$. At low temperature, because of the peaked behaviour of the thermal factors for small ω in the ω integral for $1/\tau_0(\underline{k})$, the values for the scattering time will be very sensitive to differences in the effective frequency distributions for different directions. At high temperature, all of the distributions are completely contributing to their respective $\tau_0(\underline{k})$'s so that the differences in details of the spectral distribution of weight in the $\alpha^2_{TR}F(\underline{k}\omega)$'s becomes less important.

The theory necessary to calculate the D.M.R. is given in its most convenient form by Kagan and Zhernov (40) both for the case of the lowest order trial wavefunction and also, to include the effects of anisotropy in the electron-phonon scattering, for the case of higher order trial wavefunctions in the variational calculation. Their calculations using just the lowest order trial wavefunction give results which are too small to explain the experimental data, often by an order of magnitude. Including the higher order trial wavefunctions gives results in much better agreement but they depend very much on the assumed anisotropy in the model phonon spectrum, on the value of k_F/q_D where q_D is the maximum phonon vector, and on the screened Coulomb scattering potential used in the calculation.

It is the main purpose of this chapter on resistivity to present calculations of the D.M.R. which use realistic phonons and pseudopotentials to represent the lattice and electron-ion interaction respectively, and to demonstrate that a scattering time formalism based on an extension of the work of Robinson and Dow (37) to include the effect of impurities gives essentially the same results as the variational method when higher trial wavefunctions are used (40,41). The effect of the "washing out" of the anisotropy, which will be seen to dominate the D.M.R. and give it its characteristic structure, will be more transparent physically and mathematically in the scattering time formalism.

The theory of the D.M.R. proceeds by allowing a small fraction of the ions, typically less than 1%, in the crystal to have a different electron-ion scattering cross section or pseudopotential and a different mass. As for the case of the phonon limited resistivity considered earlier, the scattering due to both vibrating host ions and the impurities which are also vibrating is calculated using the Fermi Golden Rule and the Born approximation. The calculation is simplified if it is assumed that there is only one impurity located at the origin. The effect of a finite concentration of defects is then accounted for by multiplying the terms explicitly depending on the impurity by the number of impurity atoms, i.e., cN. The perturbing Hamiltonian can then be rewritten, from Eq. (3.2) as

$$H' = \sum_{\ell} w(r - R_{\ell}) + \Delta w(r - R_{\ell}) \tag{3.29}$$

where the notation is the same as in Chapter I. Then the transition probability becomes ($w_H(r) \equiv w(r)$ here).

$$P_{\underline{k}}^{\underline{k}'}(\omega) = \frac{2\pi}{\hbar} \sum_{i=0}^{3} |v_i(|\underline{k}-\underline{k}'|)|^2 \, S_i(\underline{k}-\underline{k}',\omega) \quad . \tag{3.30}$$

If the effect of mass changes is neglected for the moment, then $S_0(\underline{q},\omega)$ is just $S(\underline{q},\omega)$ given in Eq. (3.4) and $|v_0|^2 = |w|^2$; $S_1(\underline{q}\omega)$ is similar to $S_0(\underline{q}\omega)$ but $|v_1|^2 = 2cw\Delta w$. $S_2(\underline{q},\omega)$ is given by

$$S_2(\underline{q},\omega) = \sum_{\underline{k}\lambda}^{B.Z.} \frac{2\pi|\underline{q}\cdot\underline{\varepsilon}(\underline{k}\lambda)|^2}{M2\omega(\underline{k}\lambda)} \times [(n(\omega(\underline{k}\lambda))+1)\delta(\omega-\omega(\underline{k}\lambda)) + n(\omega(\underline{k}\lambda))\delta(\omega+\omega(\underline{k}\lambda))] \tag{3.31}$$

and $|v_2|^2 = c|\Delta w|^2$, and

$$S_3(\underline{q}\omega) = 2\pi\delta(\omega) \, , \tag{3.32}$$

and $|v_3|^2 = c|\Delta w|^2$.

In the variational formalism this leads to a total resistivity given by (40) (using $\phi_{\underline{k}} = \underline{k}\cdot\underline{\varepsilon}$)

$$\rho_a^V(T) = \sum_{i=0}^{3} \rho_i^V(T)$$

where $\rho_0^V(T)$ is given by Eq. (3.12) while $\rho_2^V(T)$ and $\rho_1^V(T)$, which is the interference term between phonon and impurity scattering, are obtained by modifying $\rho_0^V(T)$ as outlined above, and $\rho_3 = \rho_R$ is the residual resistivity. It is possible to write ρ_1 and ρ_2 in a form analogous to ρ_0 in Eq. (3.13) by defining $\alpha_{TR}^{2(1)}F(\omega)$ to be $\alpha_{TR}^2F(\omega)$ with $|w(q)|^2$ replaced by $2cw(q)\Delta w(q)$, i.e.,

$$\alpha_{TR}^{2(1)}F(\omega) = 2c\Omega_0 \int_{<2k_F} \frac{d^3\underline{q}\, mqw(q)\Delta w(q)}{(2\pi)^3\ 8\hbar^2k_F^3M} \times \sum_{\lambda} \frac{|\underline{q}\cdot\underline{\varepsilon}(\underline{q}\lambda)|^2\delta(\omega-\omega(\underline{q}\lambda))}{\omega(\underline{q}\lambda)} ,$$

while ρ_2, which represents incoherent inelastic scattering, may be simplified by noting that the electron momentum transfer coordinate $\underline{q}$ is completely decoupled from the phonon coordinate $\underline{k}$ in Eq. (3.31). The integral involving the angles of $\underline{q}$ may thus be done, yielding

$$\rho_2^V(T) = \frac{c4\pi m\beta}{ne^2}\frac{4\pi}{3}\int_0^{2k_F} dqq^5|\Delta w(q)|^2 \int d\omega \frac{F(\omega)}{(e^{\beta\omega}-1)(1-e^{-\beta\omega})} \qquad (3.33)$$

where $F(\omega)$ is the phonon density of states given in Eq. (3.18).

The effect of mass changes may be included by a consideration of the phonon Green's function$^{(40)}$. For a perfect lattice this is given by [(42)]

$$P(\omega) = \frac{1}{3N}\sum_{\underline{k}\lambda}^{B.Z.} \frac{1}{\omega^2 - \omega^2(\underline{k}\lambda)}$$

$$= \frac{1}{3}⨍_0^{\omega_D} d\omega' \frac{F(\omega')}{\omega^2 - \omega'^2} - \frac{i\pi}{2\omega}\frac{F(\omega)}{3} \tag{3.34}$$

where $⨍$ denotes the principal part integral and ω_D is the maximum phonon frequency. The density of states is simply related to the imaginary part of $P(\omega)$ by

$$F(\omega) = -\frac{6\omega}{\pi} \operatorname{Im} P(\omega) . \tag{3.35}$$

When there is a concentration c of impurity ions whose mass M' is different from the host ion mass, then the perfect lattice Green's function is replaced by

$$\overline{G}(\omega) = \frac{1}{3N}\sum_{\underline{k}\lambda}^{B.Z.} \frac{1}{\omega^2 - \omega^2(\underline{k}\lambda) - cT'(\omega)} \tag{3.36}$$

where

$$T'(\omega) = \frac{\epsilon\omega^2}{1 - \epsilon\omega^2 P(\omega)} \tag{3.37}$$

and $\epsilon = 1 - M'/M$.

Just as one was interested in the density of states or the imaginary part of the $P(\omega)$ for the perfect lattice, so one is interested in the imaginary part of $\overline{G}(\omega)$ when mass defects are included. By noting that $\alpha^2_{TR}F(\omega)$ involves the density of states $F(\omega)$ times a function $\alpha^2_{TR}(\omega)$ which contains an average of the electron-phonon coupling, it is possible to merely modify the calculations done with no mass defect by replacing $F(\omega)$ by $-6\omega \mathrm{Im}\overline{G}(\omega)/\pi$. Thus the term corresponding to Eq. (3.13) now has

$$|w(q)|^2 \sum_{\lambda} |\underline{q}\cdot\underline{\varepsilon}(\underline{q}\lambda)|^2 \delta(\omega - \omega(\underline{q}\lambda))$$

replaced by

$$-\frac{2\omega}{\pi} |w(q)|^2 \sum_{\lambda} |\underline{q}\cdot\underline{\varepsilon}(\underline{q}\lambda)|^2 \, \mathrm{Im}\overline{G}^{\lambda}(\underline{q}) \qquad (3.38)$$

where

$$\overline{G}(\omega) = \frac{1}{3N} \sum_{\underline{k}\lambda} \overline{G}^{\lambda}(\underline{k}) \; .$$

The practical evaluation of the resistivity can be greatly facilitated by observing that for any $f(\omega)$

$$\int d\omega \int d^3\underline{q}\; f(\omega(\underline{q}))\,\delta(\omega - \omega(\underline{q})) = \int \overline{f}(\omega)\,d\omega \qquad (3.39)$$

where

$$\overline{f}(\omega) = \int d^3\underline{q}\; f(\omega(\underline{q}))\,\delta(\omega - \omega(\underline{q})) \; .$$

Similarly

$$\mathrm{Im}\int d\omega \int d^3\underline{q}\, f(\omega(\underline{q}))\,\frac{1}{\omega^2 - \omega^2(\underline{q}) - cT'(\omega)}$$

$$= \mathrm{Im}\int d\omega \int d\omega' \int d^3\underline{q}\, f(\omega(\underline{q}))\,\frac{\delta(\omega' - \omega(\underline{q}))}{\omega^2 - \omega'^2 - cT'(\omega)}$$

$$= \mathrm{Im}\int d\omega \int d\omega'\,\frac{\bar{f}(\omega')}{\omega^2 - \omega'^2 - cT'(\omega)} \tag{3.40}$$

where $f(\omega')$ is defined as above. For the case of the pure metal resistivity, $f(\omega)$ is given by comparison with Eq. (3.13), and similarly for the contribution to the resistivity from the ideal resistivity term modified as above to include the mass change. For the terms which lead to ρ_1 and ρ_2, it is not necessary to include the full lattice Green's function $\bar{G}(\omega)$ since they are already proportional to c [(40)] and contain $T'(\omega)$ as a factor. Thus in ρ_1 and ρ_2, $F(\omega)$ is replaced by $(-6\omega/\pi)\mathrm{Im}[P(\omega)T'(\omega)/\epsilon\omega^2]$. This discussion of the effect of mass changes and different impurity scattering cross sections is formally the same as that used in the theory of inelastic neutron scattering in alloys [(43)]. Because of the factor of q^3 in $\alpha^2_{TR}F(\omega)$, the largest values of momentum transfer, near $2k_F$, are expected to contribute most to the resistivity. Physically, this is the result of the factor of $(1 - \cos\theta) = q^2/2k_F^2$ which represents the change in the electron momentum as it is scattered from a state $\underline{k}$ to $\underline{k}'$ through an angle θ. It shows that large angle scattering is most effective in destroying an electric current and causing resistance.

Kagan and Zhernov (40) point out that a proper derivation of the dynamic structure factor, $S(\underline{q},\omega)$, treating the ionic displacements as quantum mechanical operators throughout, leads to a temperature dependent modification of the scattering cross section, represented by the pseudopotential, by the Debye-Waller factor familiar in the theory of neutron scattering (43). The Debye-Waller $W_{D.W.}(q)$ is given by

$$W_{D.W.}(q) = \frac{\hbar q^2}{4M} \int_0^{\omega_D} d\omega \, \frac{F(\omega)}{3\omega} \, (2n(\omega) + 1) \qquad (3.41)$$

for a host ion and, for an impurity ion

$$W'_{D.W.}(q) = \frac{\hbar q^2}{4M} \int_0^{\omega_D} d\omega \, \left(-\frac{6\omega}{\pi}\right) \mathrm{Im}\left[\frac{P(\omega)T'(\omega)}{\varepsilon\omega^2}\right] \times \frac{(2n(\omega) + 1)}{\omega} . \qquad (3.42)$$

In the limit T → 0, $W_{D.W.}(q)$ is not zero because of the zero point motion of the nuclei (43).

$$W_{D.W.}(q) \to \frac{3}{4} \left(\frac{\hbar^2 q^2}{2M}\right) \frac{1}{\hbar\omega_D} \quad : \quad T \to 0 \qquad (3.43)$$

while for high T

$$W_{D.W.}(q) \rightarrow 3 \left(\frac{\hbar^2 q^2}{2M}\right)\left(\frac{1}{\hbar\omega_D}\right)\left(\frac{T}{\theta_D}\right) \quad : \quad T >> \theta_D \qquad (3.44)$$

where θ_D is the Debye temperature, related to the maximum phonon energy $\hbar\omega_D$ by $k_B\theta_D = \hbar\omega_D$.

In their discussion of the phonon limited resistivity of pure sodium, Greene and Kohn $^{(32)}$ found that the correction due to the Debye-Waller factor is about 16% at the melting point, T = 98°C, while corrections due to other multiphonon processes, i.e., anharmonic processes, are of the same order of magnitude but of opposite sign, so that the net effect of such terms is small and was neglected. Kagan and Zhernov, however, point out that when the resistivity due to the impurities is considered, there is some cancellation between the various contributions. If the Debye-Waller factor is included then the scattering cross section for the host, $w_H(q)$, is replaced by $w_H(q)e^{-W_{D.W.}(q)}$, and similarly for the impurity. The residual resistivity, ρ_R, which is usually given by

$$\rho_R = \frac{3\pi m\Omega_0 c}{8\hbar e^2 E_F}\int_0^2 dx\, x^3 \,|\Delta w(x)|^2 \qquad (3.45).$$

where $x = q/k_F$ now becomes temperature dependent since $\Delta w(q)$ is replaced by $w_I(q)e^{-W'_{D.W.}(q)} - w_H(q)e^{-W_{D.W.}(q)}$. Since $W_{D.W.}(q) \sim q^2$ and it has been pointed out that large values of q, near $2k_F$, are expected to contribute most to the resistivity, this correction can be significant, particularly at high temperature where $W_{D.W.} \sim T$ from Eq. (3.44). If ρ_R' is defined to be the temperature dependent correction to ρ_R due to the Debye-Waller factor, then Kagan and Zhernov (40) have shown that, for $T \to 0$, $\rho_R' \to -\frac{1}{2}\rho_2$ while for $T >> \theta_D$, $\rho_R' + \rho_2 \to 0$. When the Debye-Waller factor is included in the theory but the impurity scattering cross sections are determined by fitting to the experimental value of ρ_R (this will be discussed later), the zero point motion part of $W_{D.W.}$ should not be included in calculating the temperature dependent corrections in ρ_R' and ρ_2.

The main advantage of defining effective frequency distributions like $\alpha_{TR}^2F(\omega)$ is that the resistivity can then be calculated trivially at any temperature by doing a simple integral over ω as in Eq. (3.13). If the scattering cross sections are allowed to be temperature dependent, then this advantage is lost and the amount of computation increases greatly. Even if it is assumed that the Debye-Waller factors are small so that the exponential $e^{-2W_{D.W.}}$ may be expanded to first order, this would require that additional effective frequency distributions be calculated which include the q^2 from $W_{D.W.}(q)$. These increases in the computation become particularly unmanageable when the effect of the anisotropy is to be considered as then the anisotropic $\alpha_{TR}^2F(\underline{k}\omega)$ given in Eq. (3.15) must be calculated for many points on the Fermi surface so that an accurate average of $\tau_0(\underline{k})$ as in

Eq. (3.21) may be obtained. Thus the Debye-Waller factor will be neglected in the calculation of ρ_0 and ρ_1. Since ρ_2 and ρ_R are incoherent scattering terms which contain the electron variable completely separate from the phonon variable ω, it is easily possible to include the Debye-Waller factor in the simple integrals of q as in Eqs. (3.33) and (3.45). This is very fortunate because it is just these two terms which are involved in the cancellation $^{(40)}$. It should also be mentioned that the detailed calculations of the pure metal resistivity usually give results which are low compared to experiment, especially at high temperature, and including the Debye-Waller factor without a systematic treatment of other multiphonon processes would make the agreement worse.

In the scattering time formalism, it will be assumed that one can define a total scattering time $\tau_a(\underline{k})$ for the alloy which depends on the state of the electron $\underline{k}$ considered, which is allowed to scatter to all other points $\underline{k}'$ on the Fermi surface. For the case of inelastic scattering involving the emission or absorption of a phonon the energy surface corresponding to the final electron state is actually displaced from the Fermi surface by an amount $\pm\omega(\underline{q}\lambda)$ $^{(33)}$ but this is typically only 0.1% of the Fermi energy so that to a good approximation the integrals are still just over the Fermi surface. The scattering time $\tau_0(\underline{k})$ will be found to be very anisotropic over the Fermi surface. The scattering times τ_i, i = 1, 2, 3 will be defined by

$$\tau_i = \frac{ne^2\rho_i V}{m} \tag{3.46}$$

and will all be considered isotropic so that there is no difference between the variational and scattering time formulae for the separate terms.

If the contributions to the scattering of an individual electron in state $\underline{k}$ are assumed additive then the total scattering time is given by (33)

$$\frac{1}{\tau_a(\underline{k})} = \frac{1}{\tau_0(\underline{k})} + \sum_{i=1}^{3}{}' \frac{1}{\tau_i} \tag{3.47}$$

To determine the resistivity the net effect of the scattering of all electrons on the Fermi surface must be considered. If this is done by making a Fermi surface average of Eq. (3.47), the result is equivalent to adding the resistivities of the individual electrons and gives the same result as obtained by the variational method using the lowest order trial wavefunction. If the suggestion of Robinson and Dow (37) is followed, i.e., that conductivities, not resistivities, should be averaged, then the total resistivity in the scattering time formalism will be determined by $\langle\tau_a(\underline{k})\rangle$ using

$$\rho_a^S(T) = \frac{m}{ne^2 \langle \tau_a(\underline{k}) \rangle} \tag{3.48}$$

which is the generalization of Eq. (3.21) if impurities are included.

For both methods of calculating the total resistivity, there will be D.M.R.. The nature of these D.M.R. will, however, be much dif[illegible]nt in the variational formulation if only the lowest order trial wavefunction is used. In that case, if the mass change is neglected, the $\tau_0(\underline{k})$ term will give the usual expression for the ideal resistivity and $\tau_3 = \tau_R$, will give the residual resistivity. Then, from Eq. (3.28), it is seen that only ρ_1^V and ρ_2^V contribute to the D.M.R.. If the mass change is included, then there is also a contribution to the D.M.R. from ρ_0^V (40). Calculations of these terms have in general led to results which are too small compared to the experimental data (39,40). The results are greatly improved in this formulation if higher trial wavefunctions are included (40). So far the calculations have been too model dependent (40) or they have just included the effect of ρ_0^V and ρ_R (41). In the latter work it was found that by a judicious choice of the higher trial wavefunctions and the pseudopotential, the D.M.R. in potassium at low temperature; e.g., T ≈ 4° - 20°K, could be adequately explained. The most important thing to note is that the inclusion of only the phonon scattering due to the pure lattice plus the residual scattering due to static impurities has lead to a substantial D.M.R., and also that it is very nonlinear in the concentration, especially for the very dilute alloys of potassium whose residual resistivity is of the order of 10^{-2} μΩ-cm (the residual resistivity of a typical alloy with 1% of impurities is ∿ 1 μΩ-cm). In this thesis it will be shown that the scattering time gives essentially the same results as those just mentioned when only the phonon scattering of the pure lattice plus the elastic scattering of the impurities is included but that the physics of the results is much more transparent. Also, the effects of the inelastic scattering off the impurities as well as the effect of the mass change will be investigated in detail.

3.2 Results in the Very Dilute Alkali Alloys

Recently there has been much experimental and theoretical interest in the low temperature resistivity of potassium (36,41,44,45,46). Of the theoretical papers only that of Ekin and Bringer (41) considers the important question of the D.M.R. in a serious manner. The same problem will now be discussed using the scattering time formalism. Most of the detailed results will be for potassium since that is where the best experimental data exists, but some typical results will also be presented for the other alkalis.

In discussing the effect of the anisotropy in the pure metal and how it is washed out by the addition of impurities into the metal, it is convenient to introduce a quantity closely related to the $\tau_0(\underline{k})$'s, namely the anisotropy in $1/\tau_0(\underline{k})$ which is denoted by $a(\underline{k})$ (note that the T dependence in $a(\underline{k})$ will be suppressed as it also is for the various scattering times)

$$\frac{1}{\tau_0(\underline{k})} = \left\langle\frac{1}{\tau_0(\underline{k})}\right\rangle (1 + a(\underline{k})) \tag{3.49}$$

where the brackets denote a Fermi surface average. The anisotropy parameter $a(\underline{k})$ is thus given by

$$a(\underline{k}) = \frac{\frac{1}{\tau_0(\underline{k})} - \left\langle\frac{1}{\tau_0(\underline{k})}\right\rangle}{\left\langle\frac{1}{\tau_0(\underline{k})}\right\rangle} \tag{3.50}$$

and averages to zero over the Fermi surface. In Fig. 2 the $a(\underline{k})$'s along 3 constant ϕ arcs versus θ on the irreducible part of the Fermi surface are shown for 3 different temperatures in potassium using the Bardeen pseudopotential (47). The intermediate temperature shown corresponds to the temperature at which the anisotropy is a maximum. The other 2 plots show how at very low T as well as at high T the anisotropy is reduced. In this, and all subsequent calculations for the alkalis, the pure metal $\tau_0(\underline{k})$'s calculated by Hayman and Carbotte (36) were used. They were calculated using realistic phonons taken from inelastic neutron scattering data and the electron ion scattering cross section was described by a pseudopotential which was screened in the Hartree approximation, i.e., f(q) in (2.42) was set equal to zero. This approximation will be used in all calculations. In the case of potassium, three different pseudopotentials were used: the Ashcroft, the lower Lee-Falicov and the Bardeen pseudopotential (a detailed discussion of these different pseudopotentials is given in the work of Rice and Sham (46)).

If the temperature is fairly low and the impurities are mainly substitutional, it is probably a good approximation to characterize the impurities only by their residual resistivity so that for the very dilute alloy

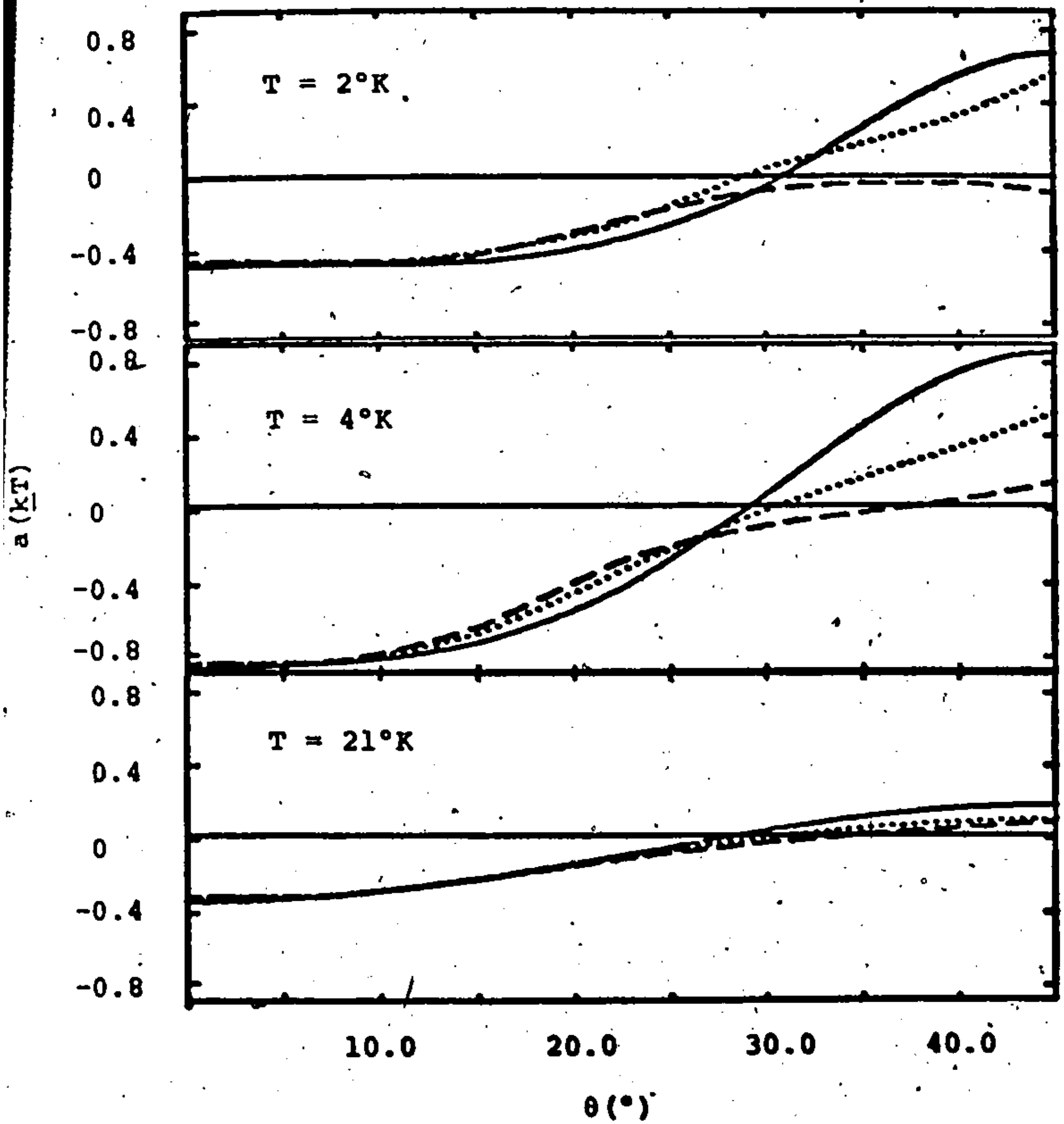


Fig. 2: The anisotropy parameter a(kT) for 3 constant φ arcs, φ = 0° (——), φ = 22½° (···) and φ = 45° (---) on the irreducible part of the Fermi surface, as a function of θ, for 3 different temperatures.

$$\frac{1}{\tau_a(\underline{k})} \approx \frac{1}{\tau_0(\underline{k})} + \frac{1}{\tau_R} . \tag{3.51}$$

For temperatures and concentrations such that $\tau_R >> \tau_0(\underline{k})$, $\tau_a(\underline{k})$ will reduce to the pure metal scattering time and will, therefore, have the same anisotropy. When $\tau_0(\underline{k}) >> \tau_R$, the impurities dominate the total scattering time and $\tau_a(\underline{k})$ becomes, approximately, equal to τ_R and is thus essentially isotropic. From the point of view of the D.M.R., the most interesting region occurs when $\tau_0(\underline{k}) \approx \tau_R$. This corresponds to the situation where the anisotropy in $\tau_a(\underline{k})$ is less than that in $\tau_0(\underline{k})$ because the impurities begin to wash it out. For a given residual resistivity there is always a temperature such that $\tau_0(\underline{k}) \approx \tau_R$. This has to happen since, as the temperature is raised from $T = 0$, $1/\tau_0(\underline{k})$ increases rapidly from zero, going through several orders of magnitude. Interesting effects will occur, of course, only for those samples where the temperature at which the equality occurs is sufficiently low that the $\tau_0(\underline{k})$'s are still anisotropic. In potassium this limits one to low temperature and to high purity samples of the kind studied recently by Ekin and Maxfield$^{(44)}$ and by Gugan$^{(45)}$.

The resistivity is now related to the scattering time $\tau_a(\underline{k})$ by

$$\rho_a^S(T) = \frac{m}{ne^2}\,\frac{1}{\langle\tau_a(\underline{k})\rangle} = \rho_R\,\frac{1}{\left\langle\dfrac{\tau_0(\underline{k})}{\tau_R + \tau_0(\underline{k})}\right\rangle} . \tag{3.52}$$

This quantity is easily evaluated for a given τ_R from a knowledge of $\tau_0(\underline{k})$ or equivalently, $a(\underline{k})$. This detailed calculation will be considered a bit later. It is possible to derive an approximate theory which although it would not be adequate for a detailed comparison with experimental data, will show clearly the effect of the washing out of the anisotropy and will also stress the great importance of the fact that even the purest experimental samples have impurities in them so that the anisotropy will have been partly washed out already. The scattering time $\tau_a(\underline{k})$ may be rewritten as

$$\tau_a(\underline{k}) = \tau_R[1 - A_R(T)][\frac{1}{1 + A_R(T)a(\underline{k})}] \tag{3.53}$$

where $A_R(T)$ is given by

$$A_R(T) = \frac{B_0(T)}{B_0(T) + \rho_R} . \tag{3.54a}$$

$B_0(T)$ is a parameter characterizing the pure metal

$$B_0(T) = \frac{m}{ne^2} \langle\frac{1}{\tau_0(\underline{k})}\rangle . \tag{3.54b}$$

The factor $A_R(T)$ depends on the temperature via $B_0(T)$ and on the sample purity via ρ_R. For the pure metal it takes on the value 1 and is constant. For an impure sample, however small the impurity concentration may be, it is quite different. $B_0(T)$ tends to zero as $T \to 0$ so that as long as $\rho_R \neq 0$, $A_R(T)$ will also tend to zero. As the temperature is increased, $B_0(T)$ increases rapidly and will eventually dominate over ρ_R in which case $A_R(T)$ will become one. The temperature at which $B_0(T) \gtrsim \rho_R$ gives a value of $A_R(T) \gtrsim \frac{1}{2}$ and can be taken as a measure of the temperature at which $A_R(T)$ ceases to be small.

For temperatures and impurity concentrations such that $A_R(T)$ is small, the denominator in Eq. (3.53) can be expanded in a Taylor series. Only the first few terms should be important and a considerable simplification will have been achieved. Alternatively, if the anisotropy function, $a(k)$, is small the same expansion should be valid. In any case, after expanding and averaging over the Fermi surface the following result is obtained

$$\langle\tau_a(\underline{k})\rangle = \tau_R[1 - A_R(T)][1 + \sum_{n=2}^{\infty} (-1)^n A_R^n(T)\langle a^n(k)\rangle] \tag{3.55}$$

where the sum extends only from n=2 because $\langle a(k)\rangle = 0$.

As it stands, Eq. (3.55) is an exact representation for the average of $\tau_a(\underline{k})$ in Eq. (3.51). It is most useful when it is valid to truncate the series at n=2. In that case, the resistivity reduces to

$$\rho_a^{(2)}(T) = (B_0(T) + \rho_R)[\frac{1}{1 + A_R^2(T)a^2(T)}] \tag{3.56}$$

where the notation, $a^n(T) = \langle a^n(k) \rangle$ is used and the superscript (2) denotes only terms up to and including n=2 have been retained. In the above approximation, the pure metal resistivity, denoted by $\rho_0^{(2)}(T)$ is given by the simple formula

$$\rho_0^{(2)}(T) = \frac{B_0(T)}{1 + a^2(T)} \quad . \tag{3.57}$$

If the sum of ρ_R and $\rho_0^{(2)}(T)$ is subtracted from $\rho_a^{(2)}(T)$ an approximate expression for the D.M.R. is obtained, namely

$$\begin{aligned}\Delta^{(2)}(T,c) &= \rho_a^{(2)}(T) - \rho_0^{(2)}(T) - \rho_R \\ &= \frac{a^2(T)[B_0(T)\{1-A_R^2(T)\}-\rho_R A_R^2(T)\{1+a^2(T)\}]}{[1+a^2(T)][1+a^2(T)A_R^2(T)]} \quad .\end{aligned} \tag{3.58}$$

While this formula is complicated, it shows that the D.M.R. is proportional to the mean square anisotropy function, $a^2(T)$. It will thus vanish at very low and very high T where the anisotropy vanishes.

It is of interest to simplify Eq. (3.58) further. So far it is valid provided the product $A_R(T)a(\underline{k})$ is small. If it is further assumed that the anisotropy is small so that $a^2(T) \ll 1$, then

$$\Delta^{(2)}(T,c) \approx a^2(T)\rho_R A_R(T)$$

$$= \frac{a^2(T)\rho_R B_0(T)}{\rho_R + B_0(T)} . \qquad (3.59)$$

For a given temperature, the factor $A_R(T)$ has a very nonlinear dependence on the impurity concentration c since $B_0(T)$ is independent of c while ρ_R goes linearly with c. In the region where $B_0(T) >> \rho_R$, then

$$\Delta^{(2)}(T,c) \approx a^2(T)\rho_R \qquad (3.60)$$

but this usually requires higher temperatures so that $a^2(T)$ is very small. For the opposite case, at very low T, where $\rho_R >> B_0(T)$, the result is

$$\Delta^{(2)}(T,c) \approx a^2(T)B_0(T) \qquad (3.61)$$

which is independent of c while Eq. (3.60) is linear in c. This means that the D.M.R. saturates with impurity content. Saturation is reached when the impurity residual resistivity is considerably greater than the pure metal ideal resistivity at that temperature. Similar results are also obtained in the two band model to be discussed later.

Now a more precise discussion is given of the conditions when this approximate theory is valid. Even in those situations where it is not quantitatively accurate, it is still useful because it allows one to see clearly, if somewhat approximately, how impurities affect the resistivity. It indicates the nature of its dependence on the anisotropy of the pure metal scattering times as well as its nonlinear dependence on the impurity concentration. In cases where the anisotropy is small, it could be used to deduce an experimental measure of the temperature dependence of the mean square anisotropy $a^2(T)$.

Consider the case of potassium. Figure 2 shows the variation of $a(\underline{k})$ with position on the Fermi surface for three different temperatures. The figure was computed using the Bardeen pseudopotential. For the temperature at which the anisotropy is largest, $a(\underline{k})$ can range roughly from −0.8 to 0.8 which is a considerable variation. For another choice of the pseudopotential, e.g., the Ashcroft or lower Lee-Falicov one, this variation would be greatly reduced. In any case, a simpler and very useful measure of the anisotropy is $a^2(T)$. In Fig. 3(a), $a^2(T)$ versus T for the Bardeen pseudopotential is shown while Figs. 3(b) and 3(c) give the same thing for the other two pseudopotentials. The Bardeen pseudopotential clearly tends to exaggerate the anisotropy as compared to the other two.

In all three cases considered in Fig. 3, the mean square anisotropy decreases rapidly with temperature so that the approximate theory should be applicable for those temperatures. It is of interest to compare the results

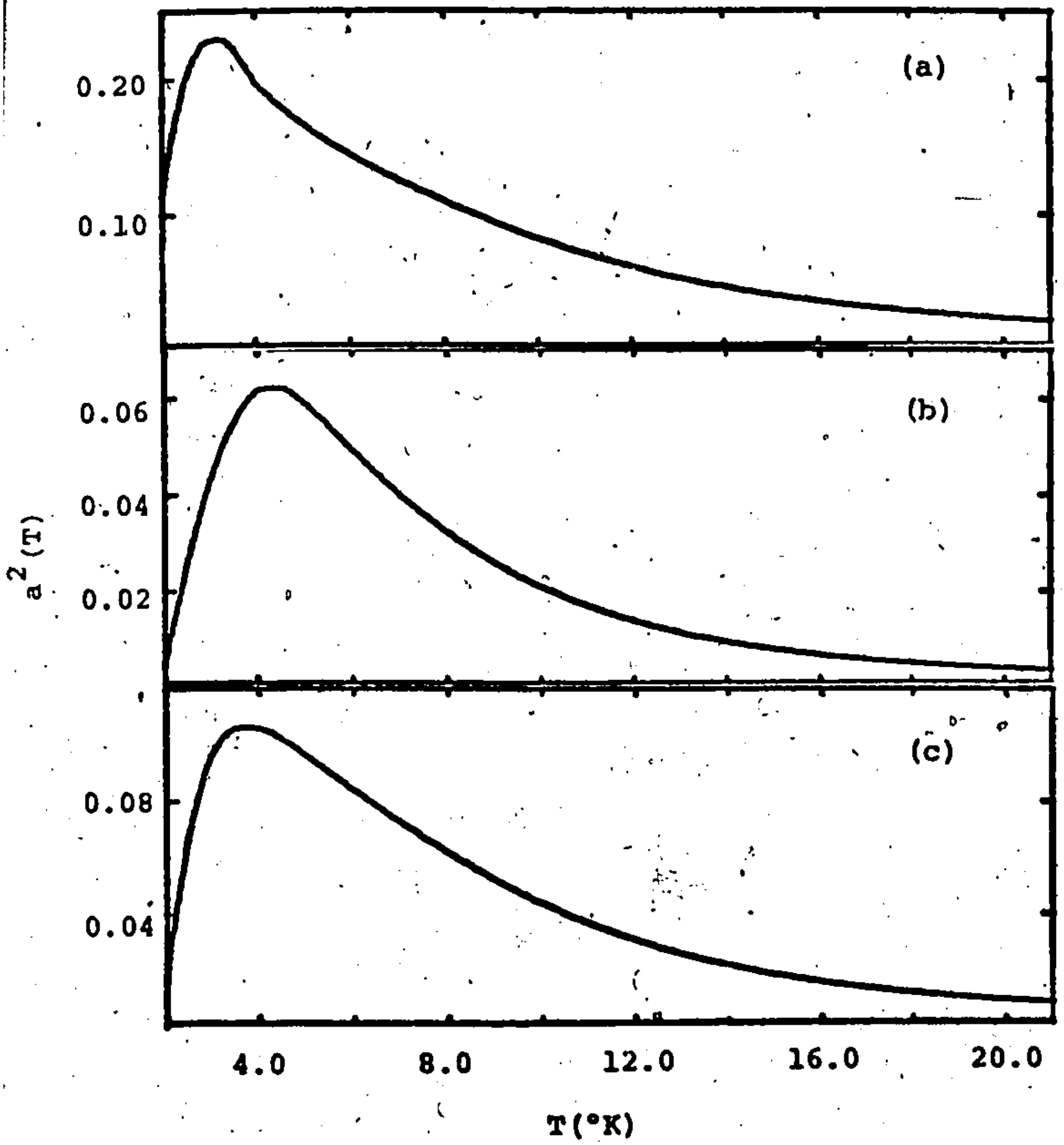


Fig. 3a: The mean square anisotropy parameter $a^2(T)$ versus T for the Bardeen form factor, in K.

3b: $a^2(T)$ versus T for the Ashcroft form factor, in K.

3c: $a^2(T)$ versus T for the lower Lee-Falicov form factor, in K.

obtained by evaluating Eq. (3.52) directly with those obtained from Eq. (3.56). For this purpose the Bardeen pseudopotential is particularly useful since $a^2(T)$ can be fairly large. In Fig. 4 the ratio $(\rho_a(T) - \rho_R)/T^5$ versus T is plotted for the case of the smallest ρ_R investigated by Ekin and Maxfield (44), $\rho_R = 9.02 \times 10^{-4}$ μΩ-cm. The result computed from Eq. (3.52) is given by the solid line which is to be compared with the dotted line representing the approximate results given by Eq. (3.56). The differences in the two curves can be fairly significant. This makes it interesting to compute a few higher moments in the expansion (3.55). In Fig. 5 the results for the third, fourth and fifth moments of $a(\underline{k})$ are shown as a function of temperature. As expected, the fourth moment, which must be positive definite, is smaller than $a^2(T)$. It has a similar temperature dependence to $a^2(T)$ with a maximum at about the same temperature. The third and fifth moments behave very differently from $a^2(T)$. They can be either positive or negative, but are however quite small and have about the same temperature dependence. In Fig. 6 it is shown how, for pure potassium, the approximate theory tends towards the exact theory as the number of moments included is increased. The convergence is not really very rapid but two points need to be kept in mind. First, a more realistic choice of the pseudopotential gives a smaller $a^2(T)$ than the Bardeen one; second, as previously discussed, the convergence will be

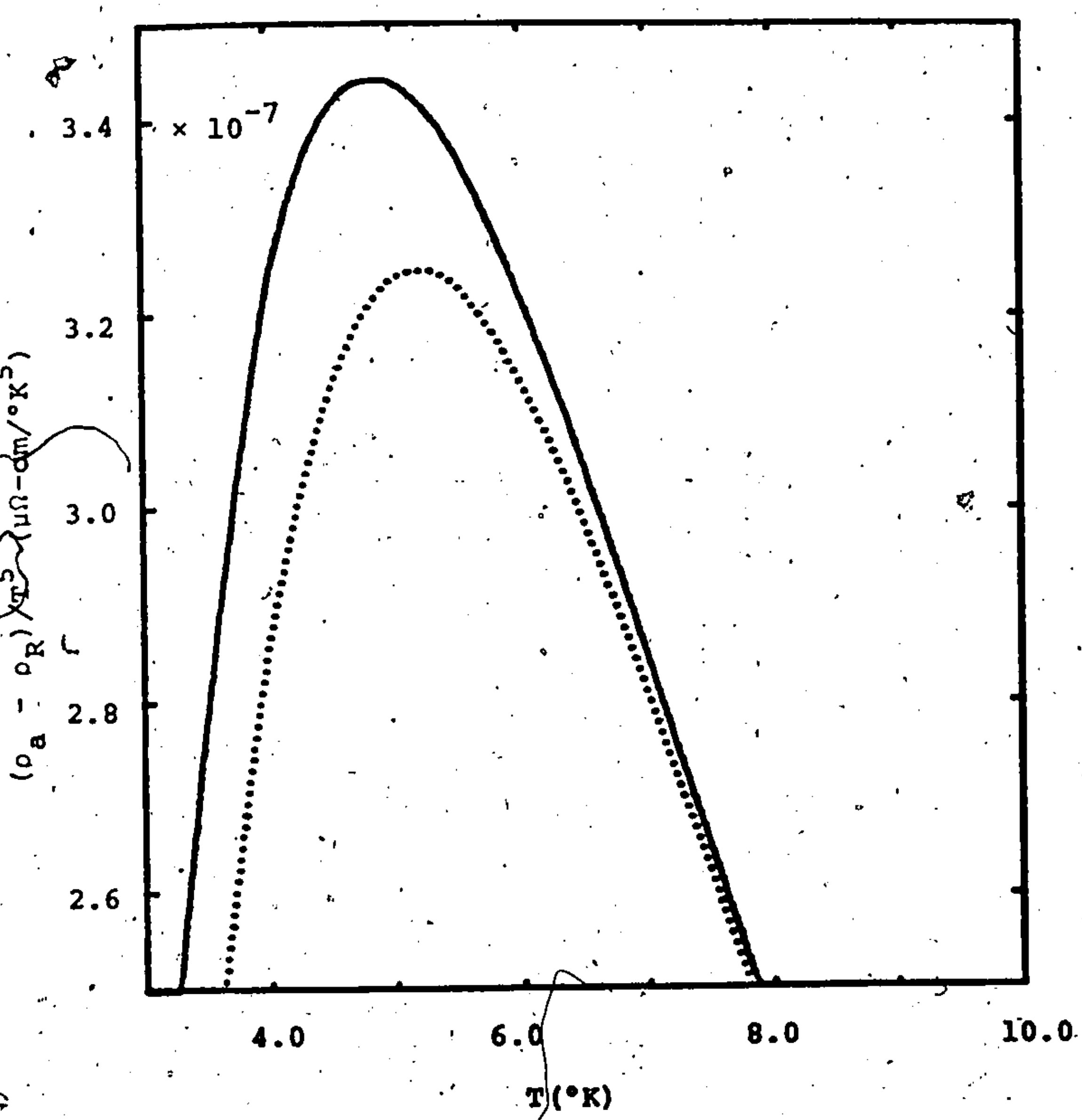


Fig. 4: $(\rho_a - \rho_R)/T^5$ versus T for the exact (——) and approximate $a^2(T)$ (•••) theory in K with $\rho_R = 9.02 \times 10^{-4}$ μΩ-cm using the Bardeen form factor.

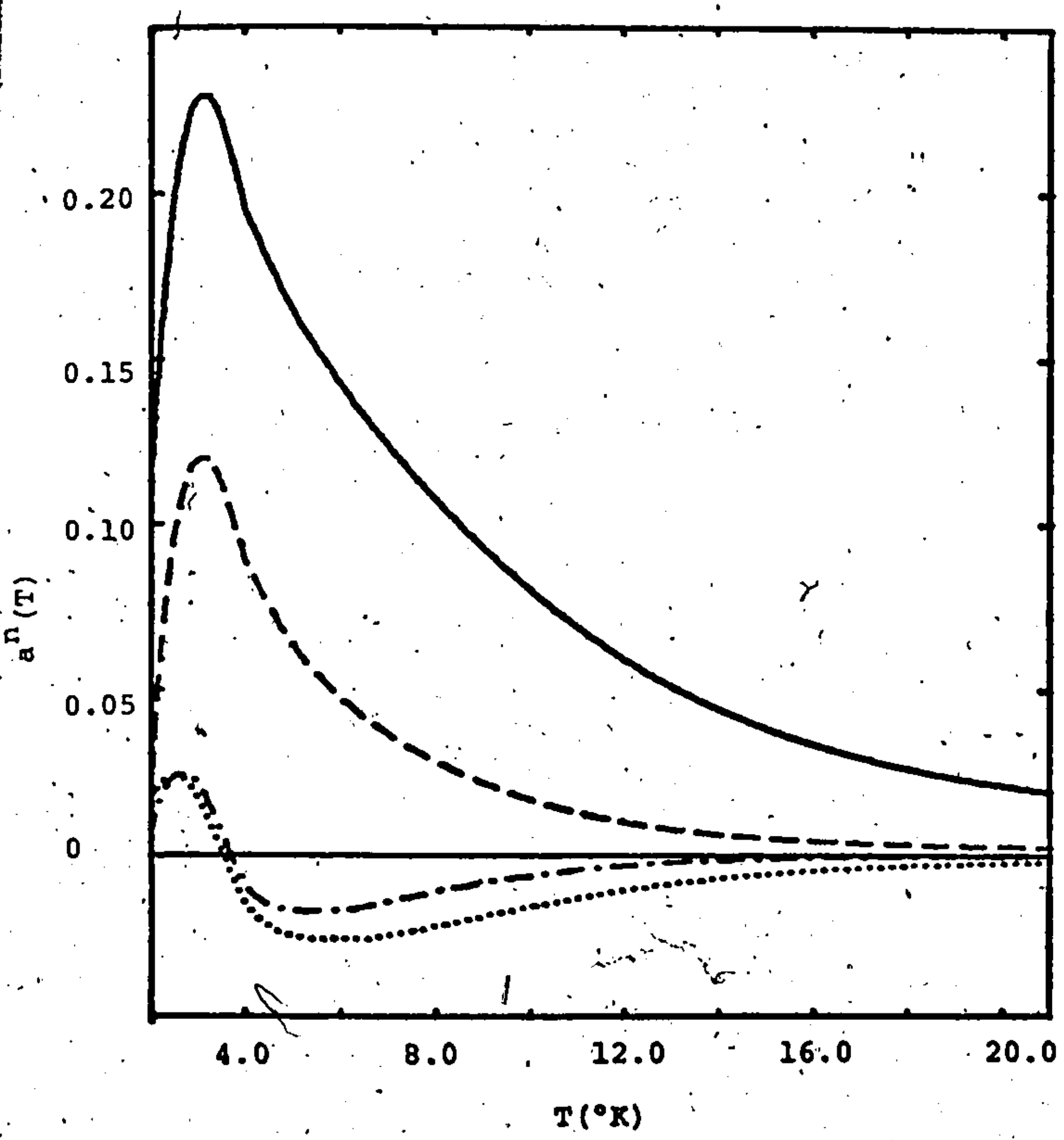


Fig. 5: Higher moments, $a^2(T)$ (——), $a^3(T)$ (···), $a^4(T)$ (---), and $a^5(T)$ (-·-·) versus T, in K using the Bardeen form factor.

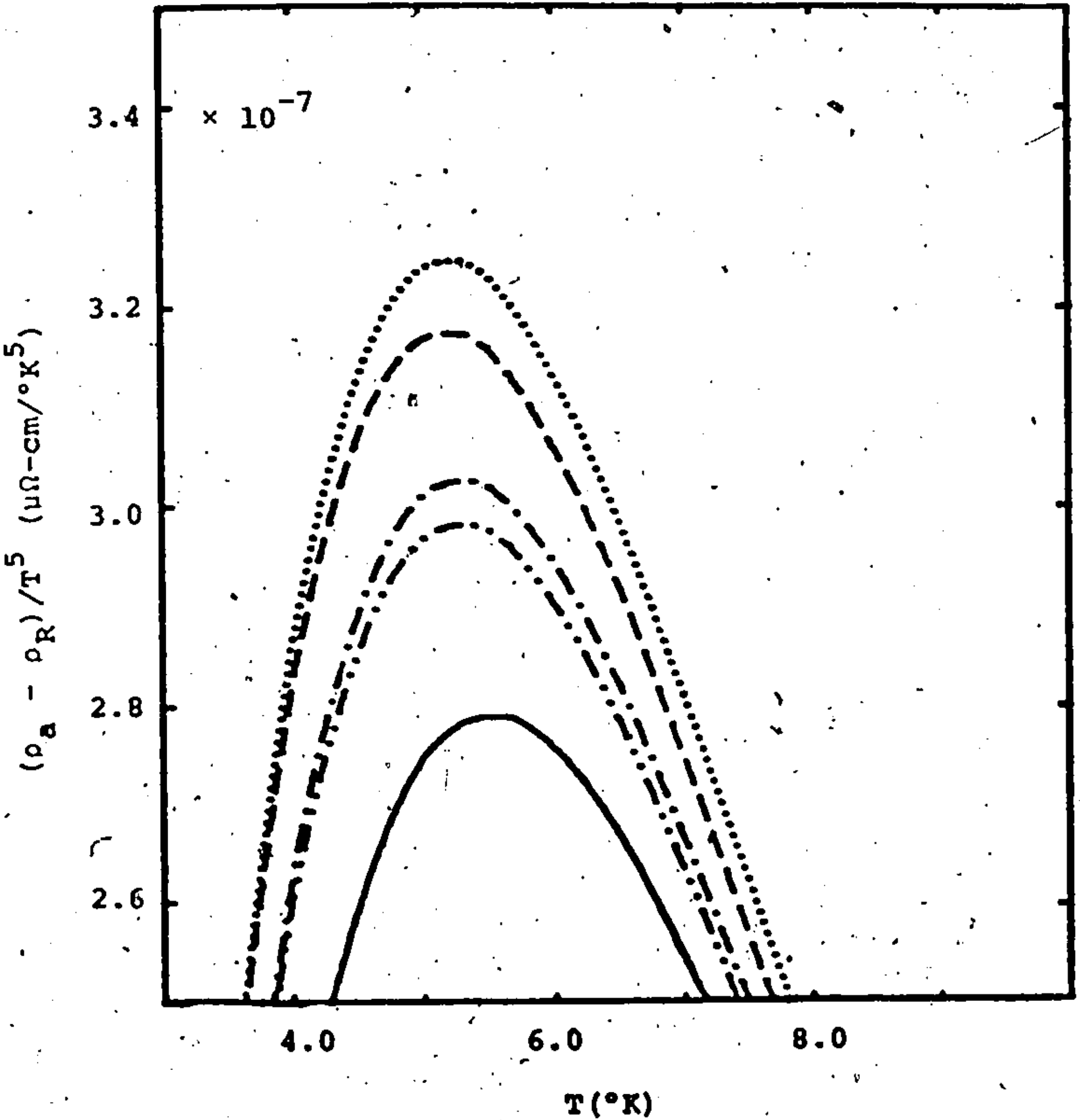


Fig. 6: $(\rho_a - \rho_R)/T^5$ versus T for the exact theory (——) and the approximate theory using moments up to $a^2(T)$ (···), $a^3(T)$ (---), $a^4(T)$ (-·-·) and $a^5(T)$ (-·····) in pure K using the Bardeen form factor.

more rapid for a real case when impurities are present, as in Fig. 4. It can be seen from Figs. 4 and 6 that the approximate theory is very much better for the case of even a very small amount of impurities giving $\rho_R = 9.02 \times 10^{-4}$ $\mu\Omega$-cm than for pure K. This is particularly so when one realizes that the figure applies to the Bardeen pseudopotential and, therefore, tends to exaggerate these differences. In what follows only the results using the exact expression will be presented.

In Fig. 7, a plot of $(\rho_a(T) - \rho_R)/T^5$ is given for the three different pseudopotentials for the various impurity concentrations considered by Ekin and Maxfield (44). These are compared with the results of the pure metal. The differences that exist between the pure metal and the purest real sample are quite substantial and should be noted. Also, the highest concentration corresponds to the case when the effect is fairly well saturated. Higher concentrations will not change the curves very much. Although it is not directly $\Delta(T,c)$ that has been plotted, the existence of a nonzero $\Delta(T,c)$ is obvious since otherwise the quantity $(\rho_a(T) - \rho_R)/T^5$ would be independent of concentration and only a single line representing the pure metal resistivity would be obtained. The reason $(\rho_a(T) - \rho_R)$ is divided by T^5 is to show that the simple Debye T^5 law (33) only holds at the lowest temperatures, e.g., below ∿ 2° in K. Detailed theoretical calculations also support this (48).

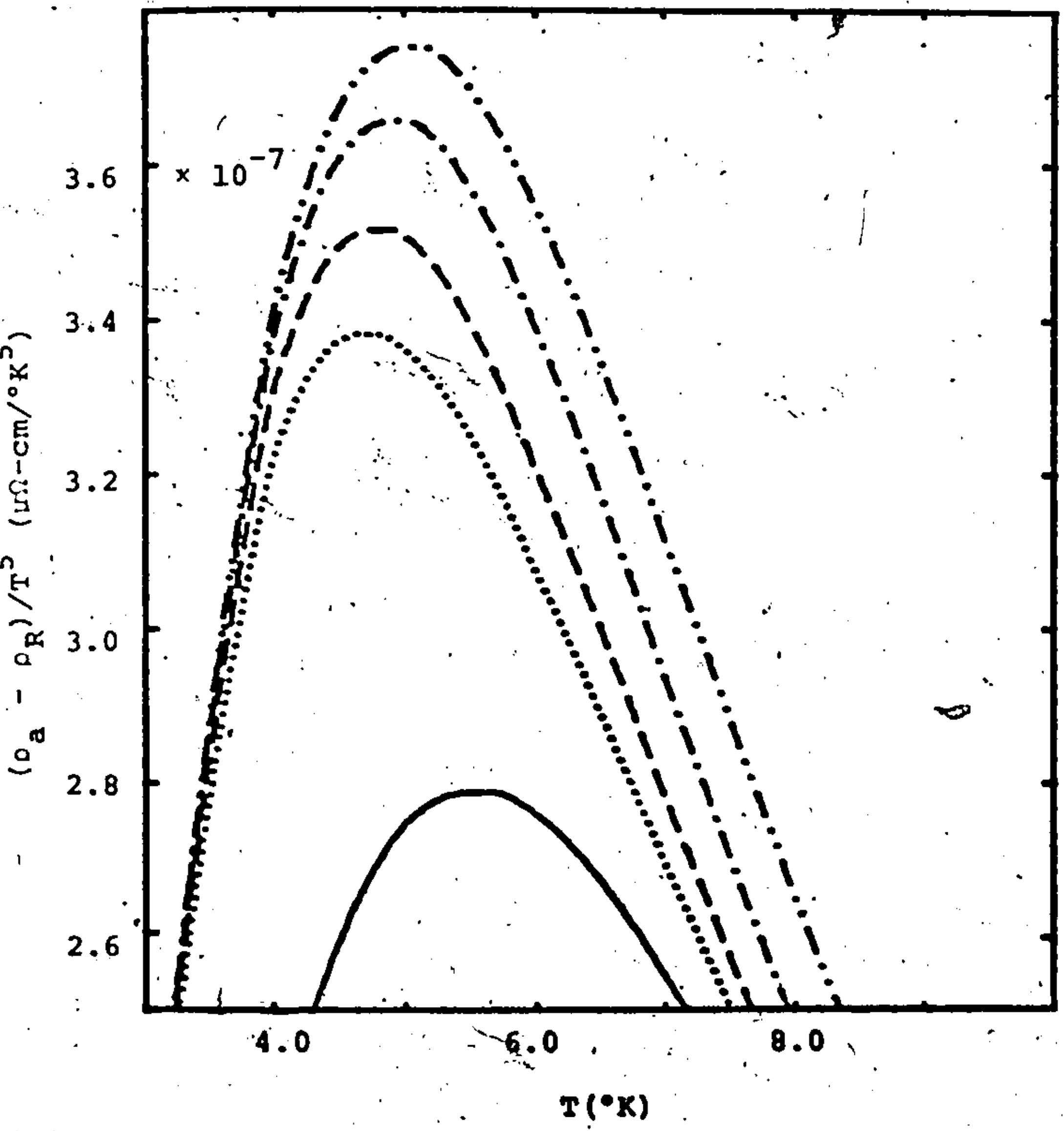


Fig. 7a: $(\rho_a - \rho_R)/T^5$ versus T for ρ_R = 0 (——), 9.02 × 10^{-4} μΩ-cm (···), 1.836 × 10^{-3} μΩ-cm (---), 5.53 × 10^{-3} μΩ-cm (-·--·), and 5.22 × 10^{-2} μΩ-cm (-·····) in K using the exact theory and the Bardeen form factor.

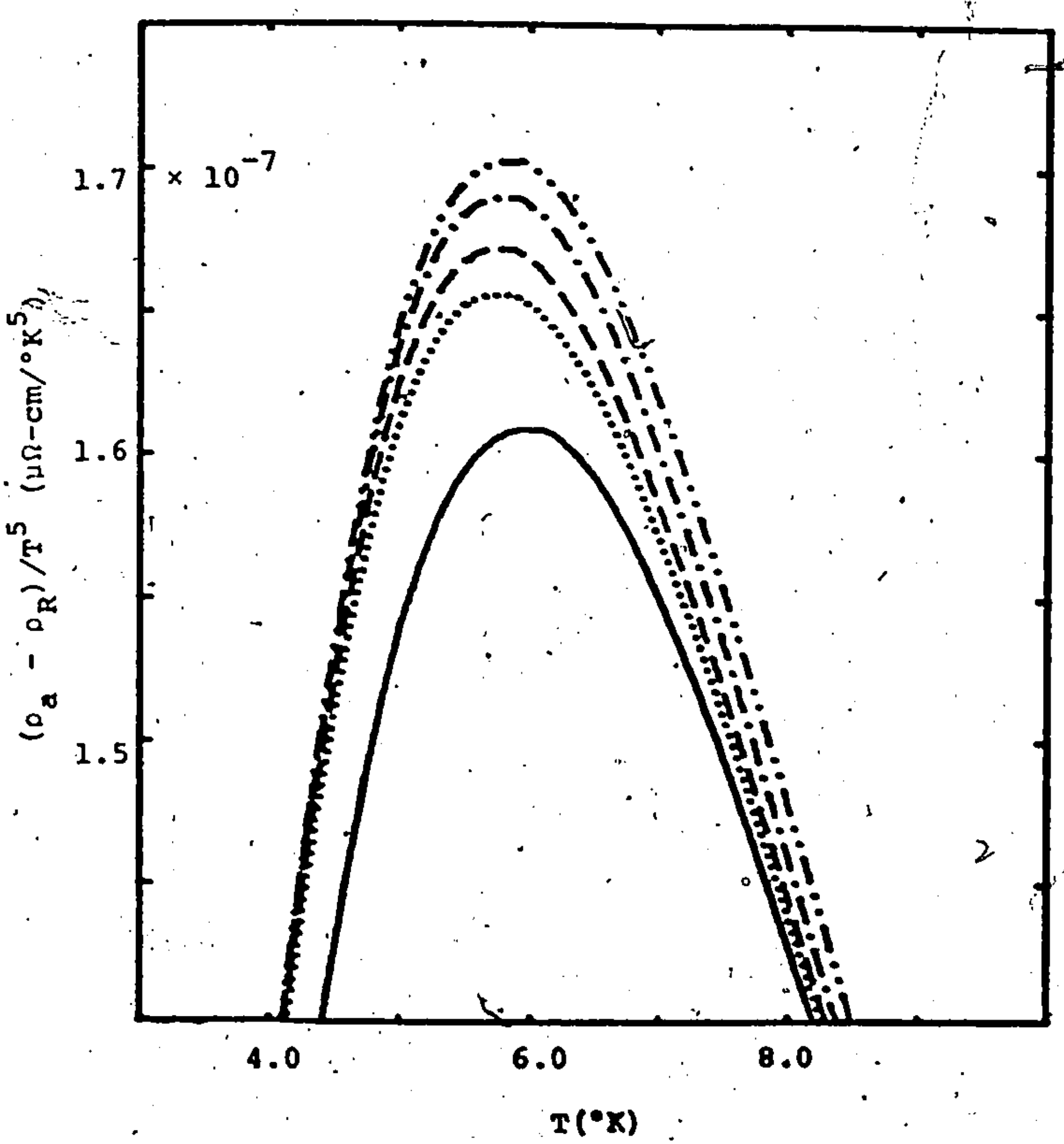


Fig. 7b: $(\rho_a - \rho_R)/T^5$ versus T for the Ashcroft form factor in K, for the same concentrations as in Fig. 7a.

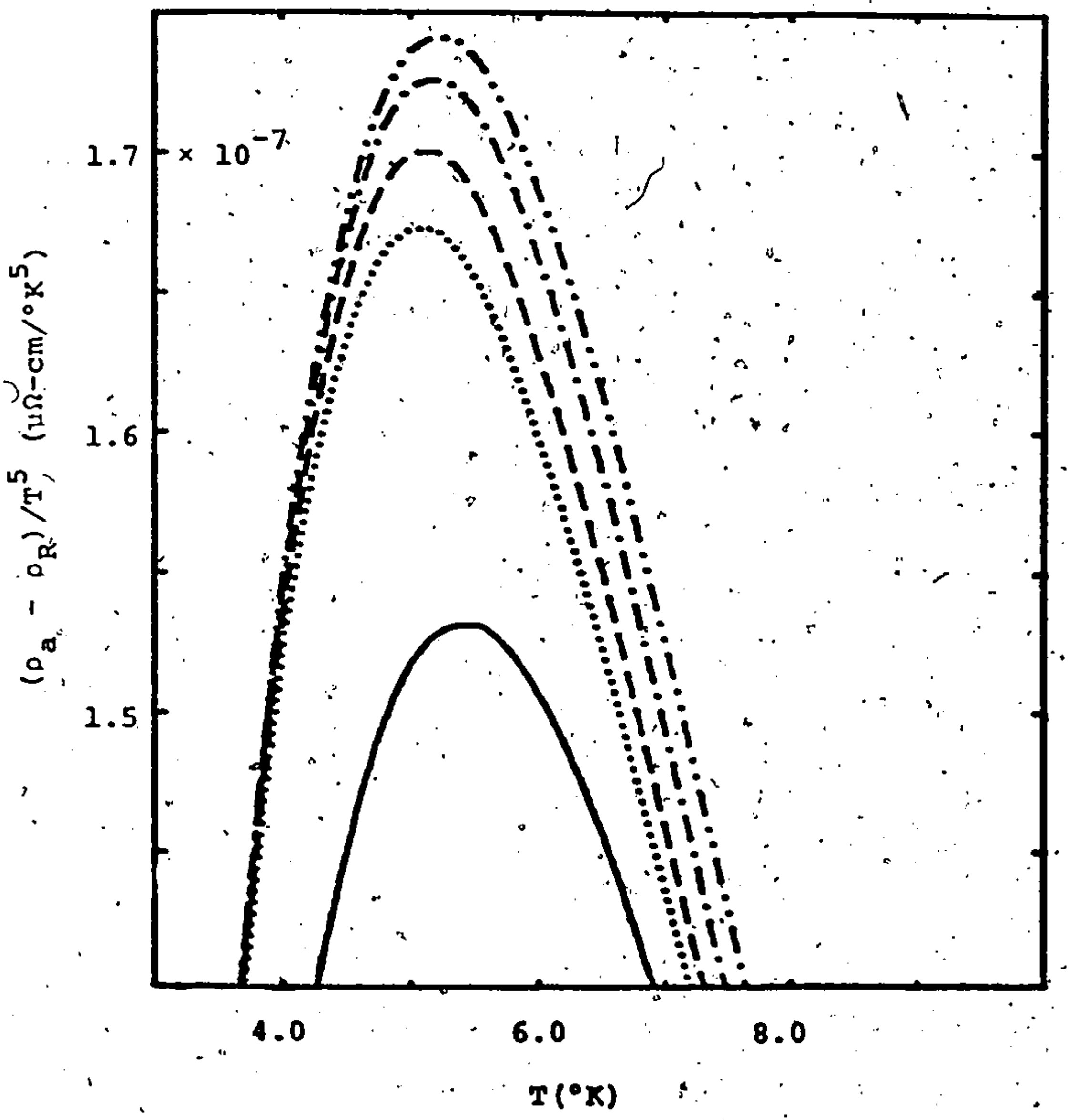
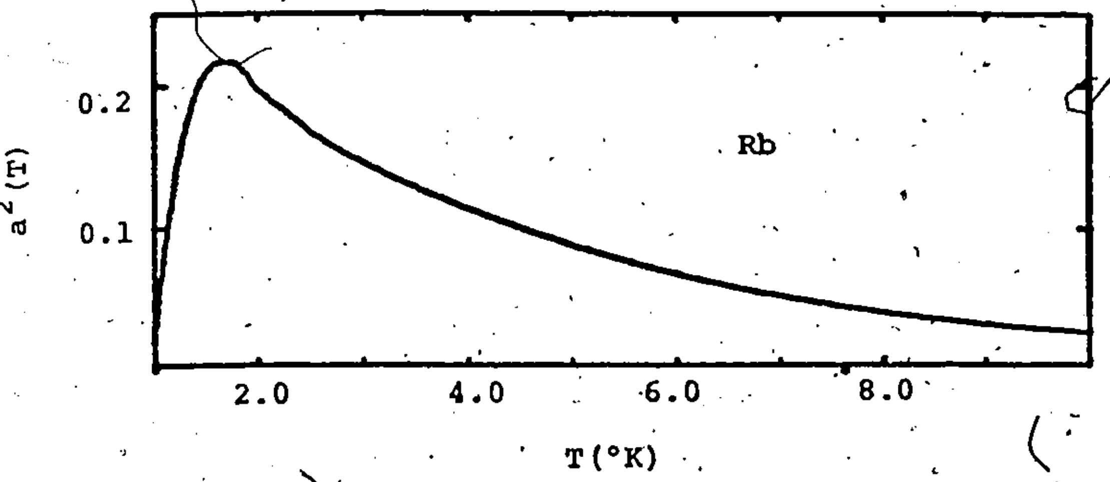


Fig. 7c: $(\rho_a - \rho_R)/T^5$ versus T for the lower Lee-Falicov form factor in K, for the same concentrations as in Fig. 7a.

Overall, the results are in qualitative agreement with the experimental data and are also in good agreement with the theoretical calculations of Ekin and Bringer (41) who used the variational solution for the resistivity. Since the theoretical predictions can vary substantially with the choice of pseudopotential, it would be of interest to attempt an interpretation of the data in terms of the approximate expressions so as to obtain an experimental measure of $a^2(T)$.

A brief discussion of sodium and rubidium is now given. Lithium will be considered in the next section where the effects of the inelastic scattering of the impurities and the effect of the mass change will be considered along with the effect of the residual resistivity on the anisotropy. In these calculations only the Ashcroft pseudopotential developed by Hayman and Carbotte (36) will be used.

The temperature dependence of the mean square anisotropy are shown in Fig. 8. In both Na and Rb the anisotropy is rather small. The low temperature resistivity of sodium is difficult to measure (49) because it undergoes a martensitic phase transformation at about 40°K, changing from the b.c.c. structure at high temperatures to a mixture of b.c.c. and h.c.p. below 40°K. Therefore, no more results will be presented for Na. Rubidium is of greater interest and in Fig. 9 the quantity $(\rho_a(T) - \rho_R)/T^5$ versus T for the



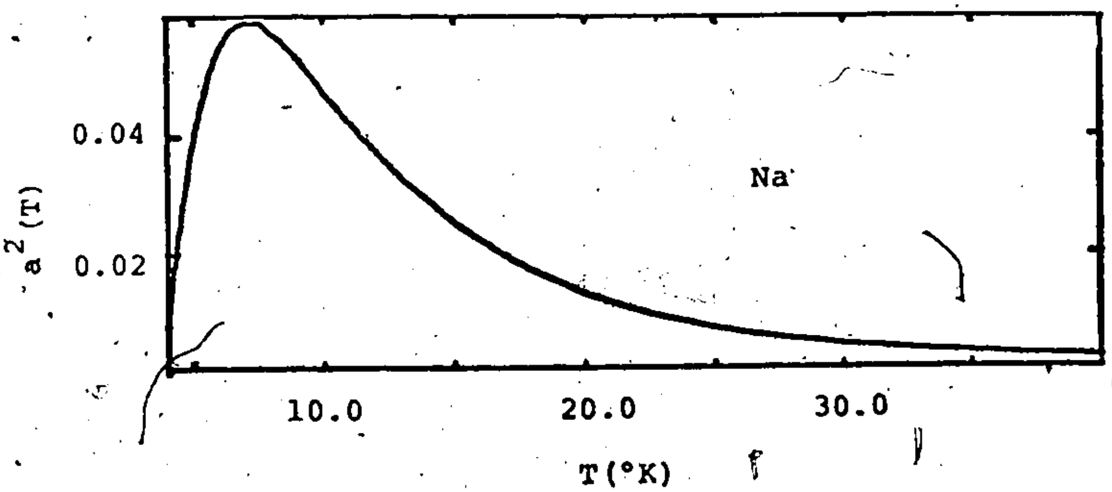


Fig. 8a: $a^2(T)$ versus T for Rb

8b: $a^2(T)$ versus T for Na

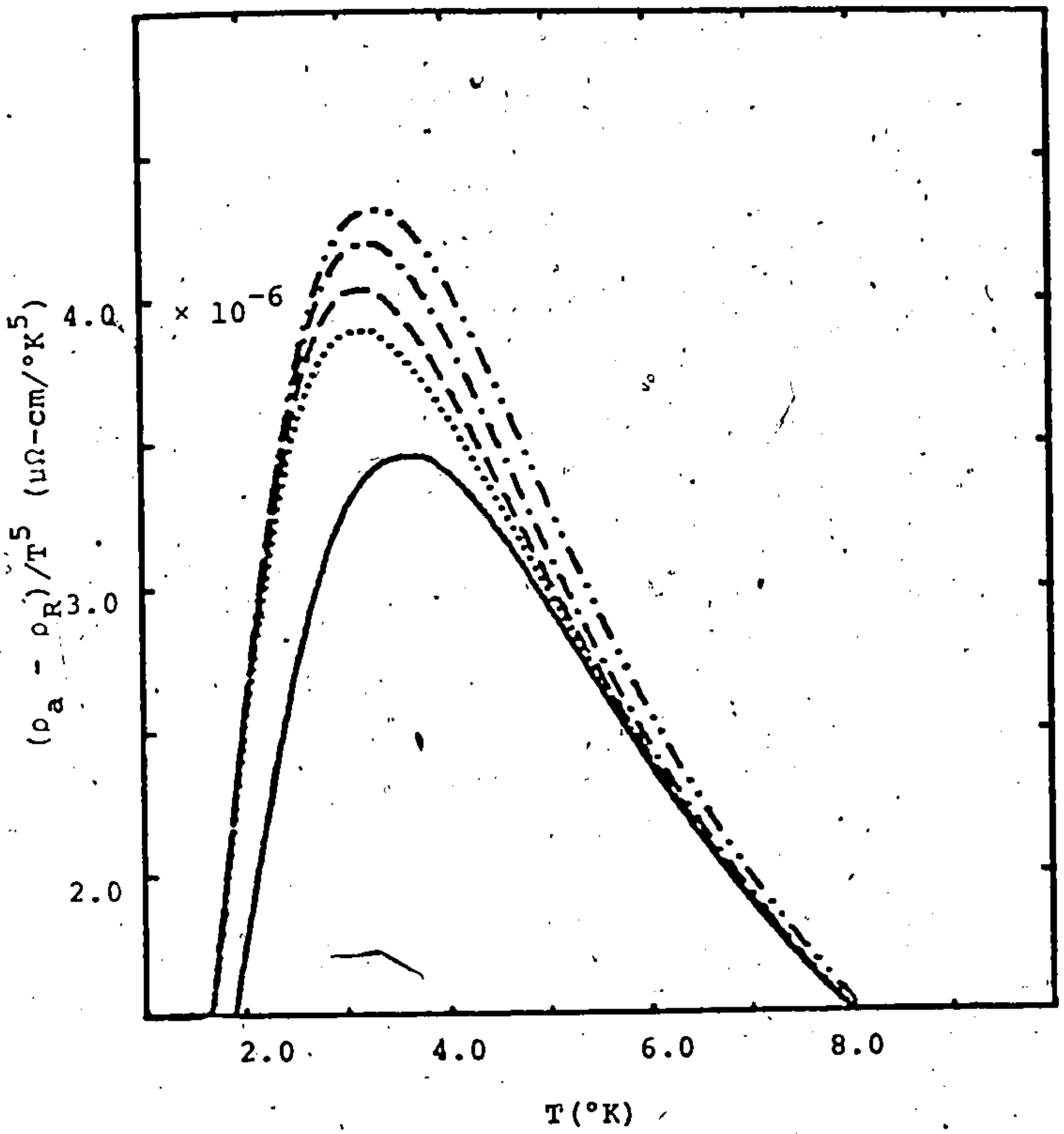


Fig. 9: $(\rho_a - \rho_R)/T^5$ versus T in Rb, for the same concentrations as in Fig. 7.

same impurity concentrations as in Fig. 7 is shown. The figure illustrates the nonlinear nature of the D.M.R. and shows the effect of the saturation with increasing ρ_R.

It has been mentioned that it would be interesting to make an experimental determination of $a^2(T)$. By considering formula (3.56) it is obvious that the experimental data for a dilute alloy may be fitted to this formula using the experimental values of $\rho_a(T)$ and ρ_R if $B_0(T)$ is known. $B_0(T)$ is a parameter characterizing the pure metal but it cannot be directly determined from experiments on very pure samples except at high temperatures such that $a^2(T) \approx 0$. Then (3.56) gives the direct relation between the experimental data and the $B_0(T)$. At low T, where the anisotropy which is to be determined is appreciable, one must rely on the theoretical calculations of $B_0(T)$. With this in mind and to facilitate the analysis, the values of $a^2(T)$, $B_0(T)$ as well as the results of the calculations of $(\rho_a(T) - \rho_R)/T^5$ using the exact expression (3.52) for two different impurity concentrations are presented in Tables 2 and 3 for two different pseudopotentials.

TABLE 2

BARDEEN PSEUDOPOTENTIAL

T(°K)	$a^2(T)$	$B_0(T)$ ($\mu\Omega$-cm)	$(\rho_a(T)-\rho_R)/T^5$ [a] ($\mu\Omega$-cm/°K^5)	$(\rho_a(T)-\rho_R)/T^5$ [b] ($\mu\Omega$-cm/°K^5)
2	0.113	2.28×10^{-6}	7.13×10^{-8}	7.13×10^{-8}
3	0.229	5.32×10^{-5}	2.16×10^{-7}	2.18×10^{-7}
4	0.194	3.49×10^{-4}	3.22×10^{-7}	3.37×10^{-7}
5	0.163	1.18×10^{-3}	3.35×10^{-7}	3.65×10^{-7}
6	0.141	2.77×10^{-3}	3.07×10^{-7}	3.38×10^{-7}
7	0.122	5.29×10^{-3}	2.69×10^{-7}	2.93×10^{-7}
8	0.106	8.82×10^{-3}	2.33×10^{-7}	2.48×10^{-7}
9	0.091	1.34×10^{-2}	2.00×10^{-7}	2.09×10^{-7}
10	0.079	1.91×10^{-2}	1.72×10^{-7}	1.77×10^{-7}
11	0.067	2.60×10^{-2}	1.47×10^{-7}	1.50×10^{-7}
12	0.058	3.41×10^{-2}	1.27×10^{-7}	1.28×10^{-7}
13	0.049	4.33×10^{-2}	1.09×10^{-7}	1.10×10^{-7}
14	0.043	5.38×10^{-2}	9.47×10^{-8}	9.52×10^{-8}
15	0.037	6.54×10^{-2}	8.22×10^{-8}	8.25×10^{-8}
16	0.032	7.81×10^{-2}	7.16×10^{-8}	7.18×10^{-8}
17	0.028	9.18×10^{-2}	6.25×10^{-8}	6.26×10^{-8}
18	0.025	1.07×10^{-1}	5.47×10^{-8}	5.48×10^{-8}
19	0.022	1.22×10^{-1}	4.81×10^{-8}	4.81×10^{-8}
20	0.020	1.39×10^{-1}	4.23×10^{-8}	4.23×10^{-8}

a : for $\rho_R = 9.02 \times 10^{-4}$ ($\mu\Omega$-cm) b : for $\rho_R = 5.53 \times 10^{-3}$ ($\mu\Omega$-cm)

TABLE 3

ASHCROFT PSEUDOPOTENTIAL

T (°K)	$a^2(T)$	$B_0(T)$ ($\mu\Omega$-cm)	$(\rho_a(T)-\rho_R)/T^5$ [a] ($\mu\Omega$-cm/°K^5)	$(\rho_a(T)-\rho_R)/T^5$ [b] ($\mu\Omega$-cm/°K^5)
2	0.004	1.42×10^{-6}	4.43×10^{-8}	4.43×10^{-8}
3	0.043	2.09×10^{-5}	8.60×10^{-8}	8.60×10^{-8}
4	0.062	1.40×10^{-4}	1.35×10^{-7}	1.36×10^{-7}
5	0.058	5.14×10^{-4}	1.61×10^{-7}	1.64×10^{-7}
6	0.048	1.32×10^{-3}	1.65×10^{-7}	1.69×10^{-7}
7	0.039	2.72×10^{-3}	1.57×10^{-7}	1.60×10^{-7}
8	0.031	4.85×10^{-3}	1.44×10^{-7}	1.46×10^{-7}
9	0.025	7.82×10^{-3}	1.29×10^{-7}	1.30×10^{-7}
10	0.020	1.18×10^{-2}	1.15×10^{-7}	1.16×10^{-7}
11	0.016	1.67×10^{-2}	1.02×10^{-7}	1.03×10^{-7}
12	0.013	2.29×10^{-2}	9.06×10^{-8}	9.09×10^{-8}
13	0.010	3.01×10^{-2}	8.04×10^{-8}	8.05×10^{-8}
14	0.008	3.87×10^{-2}	7.14×10^{-8}	7.15×10^{-8}
15	0.007	4.85×10^{-2}	6.34×10^{-8}	6.35×10^{-8}
16	0.006	5.95×10^{-2}	5.64×10^{-8}	5.65×10^{-8}
17	0.005	7.17×10^{-2}	5.02×10^{-8}	5.02×10^{-8}
18	0.004	8.49×10^{-2}	4.48×10^{-8}	4.48×10^{-8}
19	0.004	9.92×10^{-2}	3.99×10^{-8}	3.99×10^{-8}
20	0.003	1.14×10^{-1}	3.56×10^{-8}	3.56×10^{-8}

a : for $\rho_R = 9.02 \times 10^{-4}$ ($\mu\Omega$-cm) b : for $\rho_R = 5.53 \times 10^{-3}$ ($\mu\Omega$-cm)

3.3 Results for Lithium and Dilute Alloys of Lithium

Lithium is the most interesting of the alkali metals since more extensive and systematic data (49,50) exists for it than for the other alkalis, and from a theoretical point of view, the anisotropy is much greater and persists to a much higher temperature. Calculations of the pure metal anisotropic scattering times have been made by Hayman and Carbotte (36) and these will be used here also.

The first detailed study of D.M.R. in an alkali metal was made by Dugdale and Gugan (49) using dilute Li-Mg alloys. There are difficulties involved in the experiments and the interpretation of the data because Li, like Na, undergoes a martensitic transformation below ∿ 80°K, changing from the high temperature b.c.c. phase to a mixture of b.c.c. and h.c.p. below 80°K. All changes of the resistivity upon transformation were found to be small, e.g., ρ_R in the h.c.p. phase is 5-10% higher than in the b.c.c. phase. Upon cooling each sample they found that the apparent residual resistivity, i.e., the difference between the resistivity of the alloy and that of the pure comparison sample first increased slightly, and then below 90°K dropped off rapidly. The resultant D.M.R. were associated with the b.c.c. phase, and the observed values for $\Delta(T,c)$ represented a lower limit, in that to the extent that the alloy samples transformed during cooling, their resistances should increase.

Only the resistivity in the b.c.c. phase will be considered here since the detailed calculations require the results of inelastic neutron scattering to give the phonons, and a detailed consideration of the lattice structure in doing the various integrations. Other calculations of $\Delta(T,c)$ for the alkali metals $^{(39)}$, besides those mentioned with reference to potassium in the last section have yielded values considerably smaller than those observed by Dugdale and Gugan. Bross et al. $^{(51)}$ studied the low temperature resistivities of the alkali metals, using plane waves for the electrons in Na and K. $\Delta(T,c)$ was found to have the form of a hump with a maximum value of about 5% of $\rho_0(T)$ for both metals. For Li they decided that the electronic wavefunctions differed considerably from plane waves. Including this in their calculations gave larger values for $\Delta(T,c)$ but they were still much smaller than the experimental values. Fischer $^{(52)}$ considered the weak anisotropy of the Fermi surface of a monovalent cubic metal whose Fermi surface does not contact the Brillouin zone boundary and found $\Delta(T,c)$ to be only 2% of the total resistivity. In this thesis the effect of Fermi surface anisotropy will be neglected and the electron wavefunctions will be taken as a single plane wave but the full effect of the umklapp scattering and its effect on the anisotropy in the electron-phonon interaction will be included. That these are the essential effects is supported by the observation made by

Bass (39) in his review article on D.M.R.:

> "We see that the D.M.R. observed in these studies of alkali metals are similar in form and magnitude to those observed in most other metals, at least at intermediate and high temperatures. We conclude that the existence of an anisotropic Fermi surface is not a prerequisite for the existence of substantial D.M.R.."

Besides measuring the resistivities of Li-Mg alloys, Dugdale and Gugan (49) also measured the resistivity of several different very pure Li samples. By plotting the difference in resistivities, $\Delta\rho(T)$, of two such pure samples, they obtain a measure of the D.M.R.. Although the measurements are complicated by the transformation, they were able to tentatively assign values corresponding to the b.c.c. phase. The results, given in Fig. 7 of their paper (49), show a rapid increase in $\Delta\rho$ which reaches a maximum at about 50°K and then falls steadily, becoming essentially a constant above about 150°K.

The results of detailed calculation, including just the ideal scattering times $\tau_0(\underline{k})$ and the residual scattering times, are shown in Fig. 10 for several different values of the residual resistivity of both samples. These results show clearly that it is the washing out of the anisotropy which causes the hump at

Fig. 10: $\Delta\rho(T)$ versus T for some pure samples of Li. The curves represented by (···) and (---) are for the case of the more concentrated sample having $\rho_R = 3.0 \times 10^{-2}$ μΩ-cm and 2.56×10^{-2} μΩ-cm respectively while the purer sample in both cases had $\rho_R = 8.9 \times 10^{-3}$ μΩ-cm. If ρ_R for the purer sample is set equal to zero the curves become (-···-) and (-·-) respectively. The curve (——) was calculated for the more concentrated sample having $\rho_R = 3.0 \times 10^{-2}$ μΩ-cm while the purer sample has $\rho_R = 2.56 \times 10^{-2}$ μΩ-cm.

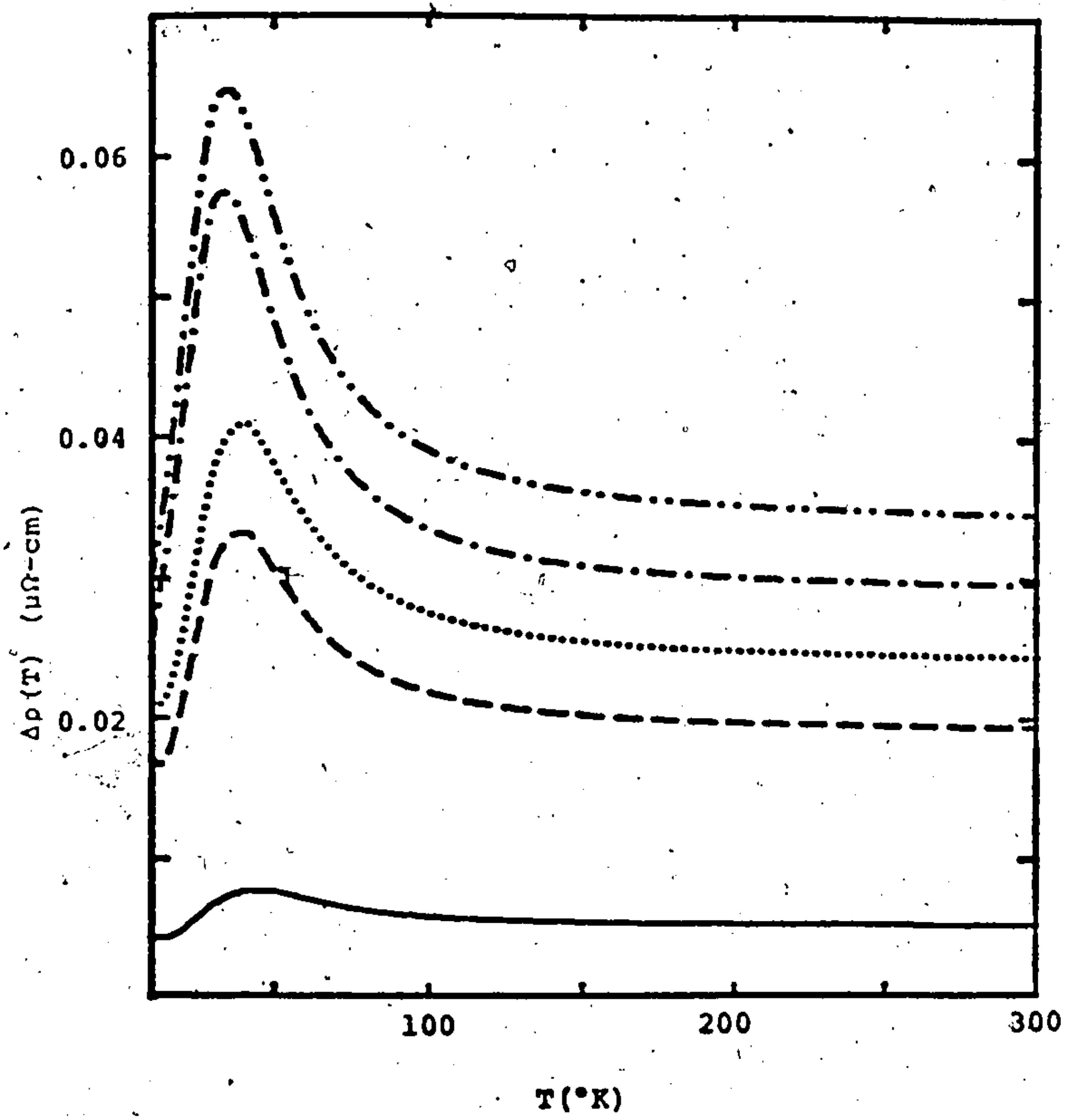


Fig. 10

about 50°K. The subsequent fall-off in the curve is due to the fact that the anisotropy in $\tau_0(\underline{k})$ is steadily decreasing with increasing temperature, so that relatively, the effect of the washing out of the anisotropy is decreasing. At the highest temperatures, when $\tau_0(\underline{k})$ has become nearly isotropic, then $\Delta\rho$ as plotted approaches the difference in the residual resistivities of the two samples, since the various scattering mechanisms, i.e., phonon and impurity, are then simply additive, so that the phonon contributions of the two samples will cancel. Figure 10 also provides strong evidence for the importance of explicitly including the concentration of impurities of both samples; thus $\Delta(T,c)$ should really be considered a function of c and c' where c' is the impurity concentration of the purer of the two samples being considered. These results should be compared with the top two curves which differ from the middle two curves only in that the ideally pure metal resistivity was subtracted. This causes a substantial increase in $\Delta\rho(T)$, making it much larger than the experimental results. The bottom curve corresponds to the $\Delta\rho(T)$ for two other very pure samples, and is included to show that even the very small differences in the two ρ_R values give a noticeable $\Delta\rho(T)$. It might be thought that if one is dealing with alloys whose impurity concentration is about 0.1% or more so that $c >> c'$, that it is sufficient to neglect the effect of the c' and just calculate the D.M.R.

assuming that the purer sample may be taken as ideally pure, i.e., having only phonon scattering. This could lead to qualitative as well as quantitative errors in the calculated D.M.R. since even the smallest value of c' introduces a substantial nonlinear behaviour into $\Delta(T,c)$, at least at those temperatures where the anisotropy is substantial. In fact it is one of the most interesting results of the calculations presented here that when $\Delta(T,c)/\rho_R(c)$ instead of $\Delta(T,c)$ is being considered, then the largest values are obtained for the smallest values of c, showing that $\Delta(T,c)$ depend on c more weakly than linearly. All the detailed calculations take this into account, and it is only for simplicity of notation that the c' dependence is dropped. Thus it is obvious that the approximate expression for $\Delta(T,c)$ given in Eq. (3.58) should be used with care, since not only does it assume that the anisotropy is small but it also assumes that the purer sample is ideally pure.

The dilute Li-Mg alloys investigated by Dugdale and Gugan $^{(49)}$ had the following concentrations of Mg: 0.21%, 0.47% and 0.95%. The experimental results obtained (see Fig. 6 of their paper $^{(49)}$) show that $\Delta\rho(T)$, the difference between the alloy resistivity and the resistivity of the purest Li sample, has a rapid decrease below 100°K with decreasing temperature. This decrease cannot be ascribed to the change in residual resistivity on transformation since they found that the transformation causes an increase in the resistivity at low temperature. There is also a small uncertainty in the resistivity of the purest Li sample because of the transformation but that was considered negligible $^{(49)}$. Since the mass ratio of Li-Mg is $\sim$ 7:24, there is the possibility of observing effects due to the extra scattering off the mass defect in addition to the usual scattering caused by the different scattering cross section of the impurity. To sort out the various effects of the different scattering mechanisms, results are presented where only some of the mechanisms were included in the calculation as well as where all of them were included. Because the q integral appearing in the expression for τ_2 is similar to the one in τ_R, i.e., it just has an extra factor of q^2, and because of the difficulty in calculating τ_2 or τ_R from first principles $^{(9,28)}$, the impurity pseudopotential was chosen to reproduce the experimental values of ρ_R. This is consistent with the use of the experimental values of ρ_R in the actual calculations. However, the q integral appearing in τ_2 is even more sensitive to the form of $\Delta w(q)$ for $q \gtrsim 2k_F$ so that this procedure sometimes, like in the case of Al-Mg to be discussed later, gave exaggerated values for τ_2. Fukai $^{(9)}$ has shown that the theoretical results for ρ_R may be put into better agreement for such alloys as Al-Mg by using multiple orthogonalized plane waves in representing the wavefunctions in Al. Since such effects have been generally neglected in the calculations of this thesis, the values of τ_2 calculated for such alloys were obtained using the same impurity pseudopotential parameter, R_c, usually used in theoretical calculations (9). The residual resistivity used, however, was always the experimental value. This is very important since the value of ρ_R is, at all but the highest temperatures considered, much larger than ρ_2, and a realistic value of ρ_R is vital to obtaining a proper representation of the washing out of the anisotropy which is the dominant effect leading to the D.M.R. of all the alloys considered.

In Fig. 11(a) the results including just $\tau_0(\underline{k})$ (or $\tau_0^{(M)}(\underline{k})$ for the two more concentrated alloys) and τ_R are shown for the three alloys; in Fig. 11(b) the effect of also including τ_1 and τ_2 as well is shown, while in Fig. 11(c) the Debye-Waller factor also has been included. In Fig. 11(d) the two more concentrated alloys alone are shown, once including $\tau_0(\underline{k})$, τ_1 and τ_R (with no mass change) and again with the additional effect of τ_2. Fig. 11(e) is the same as Fig. 11(d) except that the Debye-Waller factor is also included. By comparing the results in Figs. 11(b) and 11(d), particularly for Li-Mg 0.95%, the effect of the mass change is seen to be very small, contributing only a small decrease to the $\Delta\rho(T)$ plotted. The effect of a heavy

Fig. 11a: $\Delta\rho(T)$ versus T for the more concentrated Li-Mg alloys: $\Delta\rho(T)$ for c = 0.21% (——), $\Delta\rho^{(M)}(T)$ for c = 0.47% (···), and $\Delta\rho^{(M)}(T)$ for c = 0.95% (---) when only τ_0 (or $\tau_0^{(M)}$) and τ_R are included in the calculation.

11b: Same as Fig. 11a except that τ_1 and τ_2 (or $\tau_1^{(M)}$ and $\tau_2^{(M)}$ for the c = 0.47% and 0.95% alloys) also were included.

11c: Same as Fig. 11b but the Debye-Waller factor is also included.

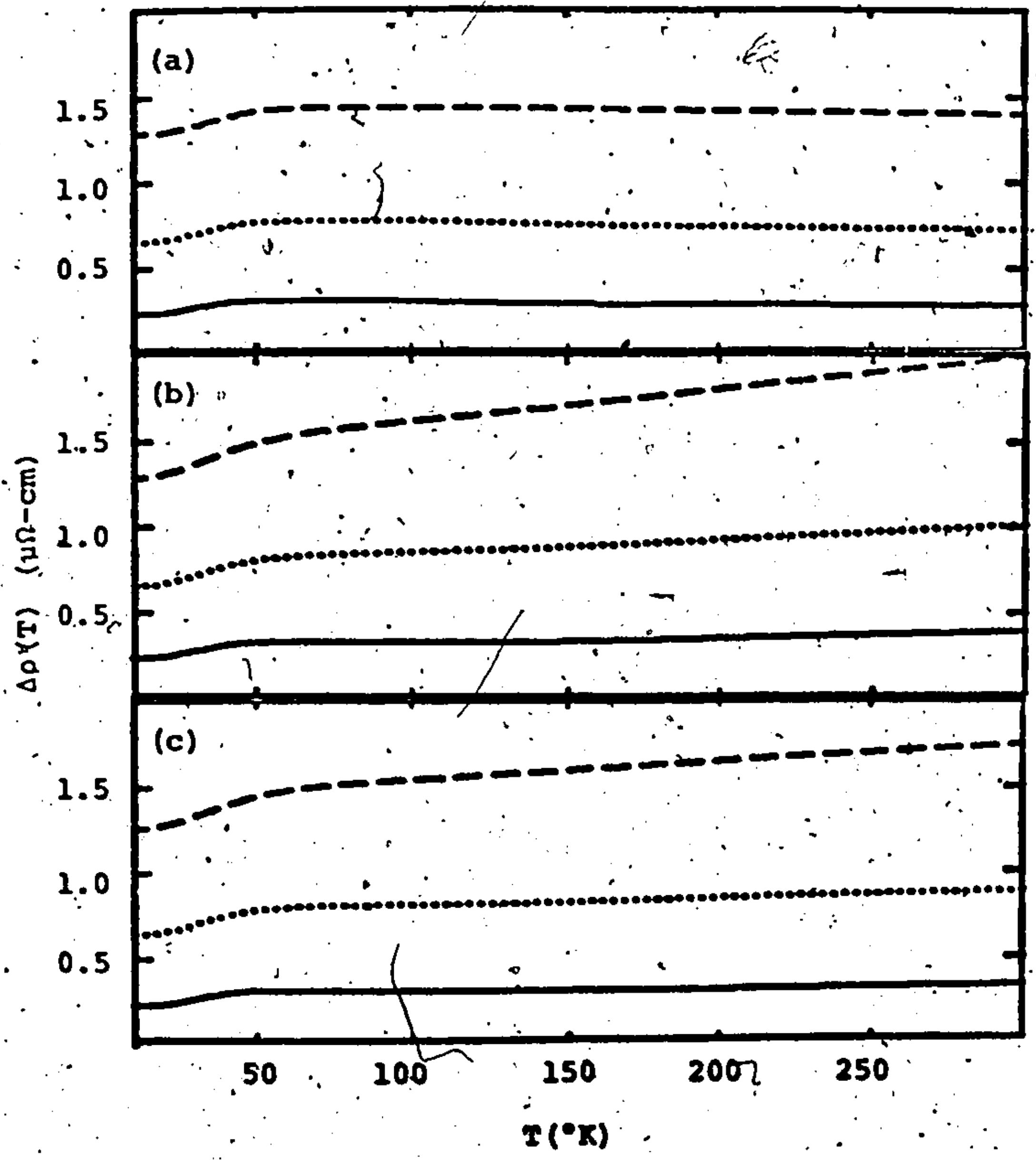


Fig. 11

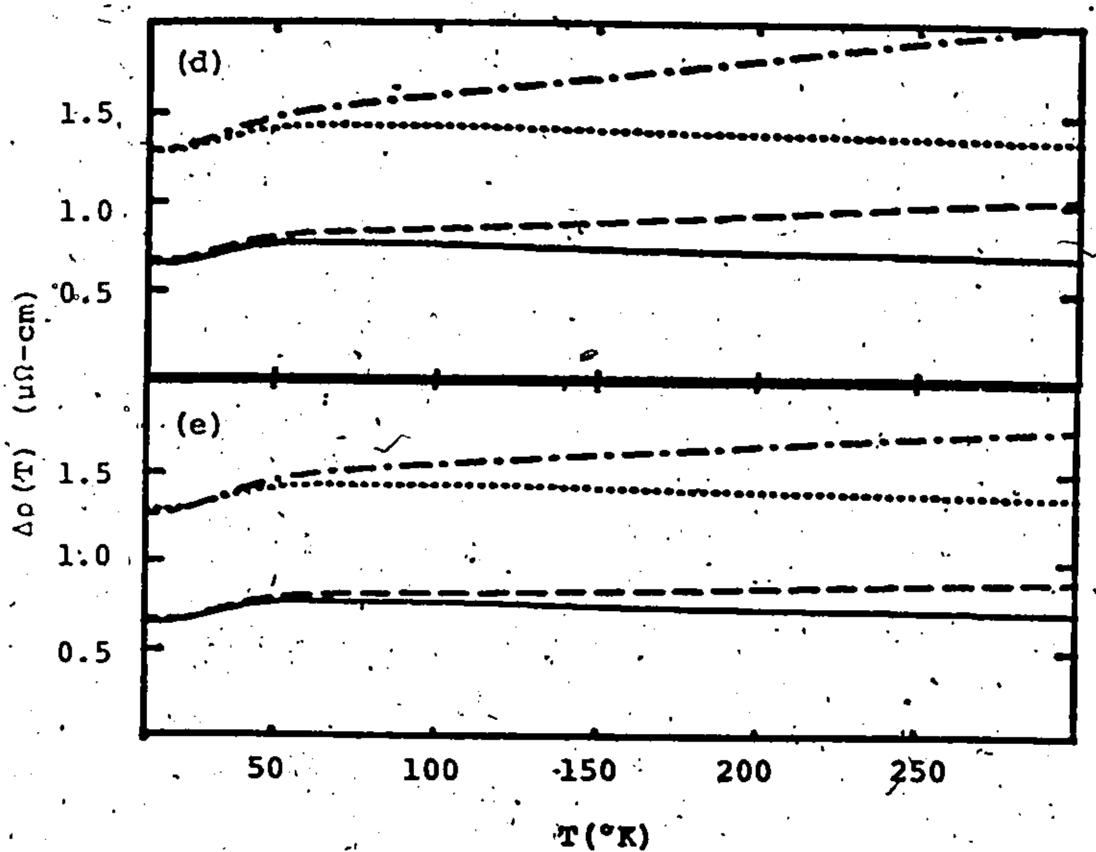


Fig. 11d: Δρ(T) versus T, with no mass change, for Li-Mg with c = 0.47% (——) and c = 0.95% (····) including τ_0, τ_1 and τ_R. The changes produced when τ_g is also included are given by (---) and (-·-) respectively.

11e: Same as Fig. 11d but with the Debye-Waller factor also included.

impurity in a light host is to increase the density of states in the low ω region, which is preferentially sampled in the ω integrals at low T. As the temperature is increased, more and more of the distribution is sampled so that the effect of having increased the density of states in the low ω region has progressively less and less effect until the classical region of temperature, above θ_D, is reached where the effect of the mass change essentially disappears. Some representative numbers illustrating the above point in more detail will be presented later in a table along with corresponding numbers for the case of an Li-Ag alloy.

The effect of including the τ_2 contribution, which contains the q integral with $q^5|\Delta w(q)|^2$, gives a linear component to the D.M.R. at high temperature which is, however, much too strong. In fact the experimental results for the three Li-Mg alloys show no sign of such a component. To account for this, Kagan and Zhernov (40) have suggested including the Debye-Waller factor which has the effect of reducing the strength of the scattering, particularly at high temperature. The results obtained when this is included are shown in Figs. 11(c) and 11(e). The agreement with experiment is definitely improved. Again, some detailed numbers showing the extra effect of the Debye-Waller factor will be presented later.

The D.M.R. in dilute Li-Ag alloys will now be considered. Krill and Lapierre (50) measured the resistivities of dilute (0.05% $\lesssim c \lesssim$ 0.6%) alloys of Ag in Li at temperatures from 4.2°K to 70°K. The behaviour of $\Delta(T,c)$ in the Li-Ag alloys is similar to that found by Dugdale and Gugan in Li-Mg alloys. $\Delta(T,c)$ increases rapidly between 4.2°K and 70°K, and $\Delta(T,c)/\rho_R$ at 70°K is about three times larger in the most dilute alloy than in the most concentrated alloy. The concentration of their most dilute alloy has only about twice the concentration of impurities as their nominally purest sample so that the c' dependence is critical in the calculation. The calculated D.M.R. for the various Li-Ag alloys are shown in Figs. 12(a) and 12(b), where Fig. 12(a) includes the impurities only via τ_R while Fig. 12(b) also includes τ_1 and τ_2. For the most concentrated alloy, the effect of the mass change is also shown separately.

The Debye-Waller factor was not included in the calculations of the D.M.R. presented in Fig. 12 because the temperature was not high enough for this to have an appreciable effect. Comparison of the experimental and theoretical curves shows that including just τ_R gives too low a D.M.R. for $T \gtrsim 70$°K, and the curve also is starting to bend over while the experimental curve (50) is still rising. The effect of the mass change can be definitely seen in Fig. 12(b). Krill and Lapierre analyse their results using the theory of Kagan and Zhernov (40) when the effect of the anisotropy is neglected. From Figs. 12(a) and

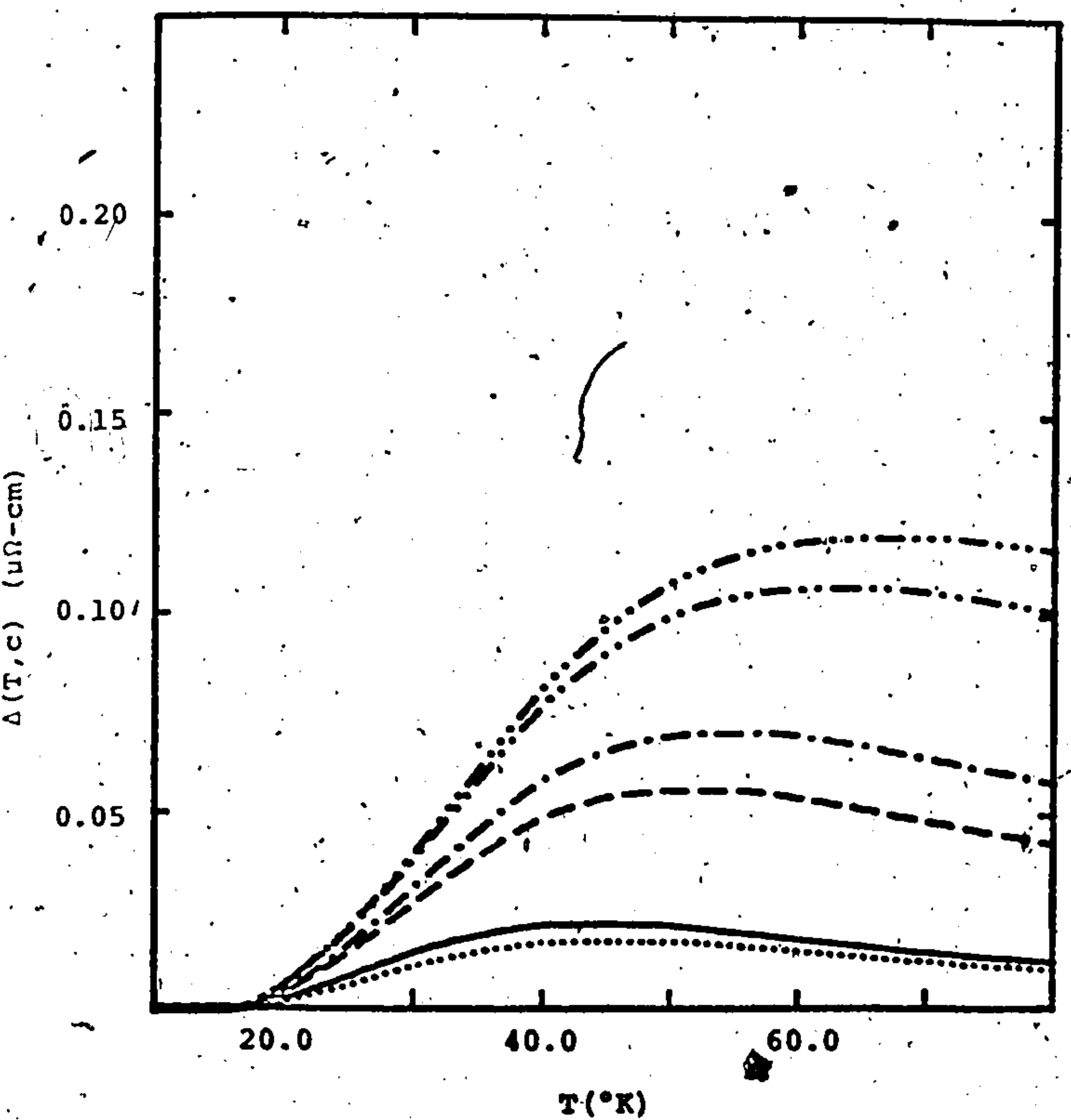


Fig. 12a: Δ(T,c) versus T for some Li-Ag alloys with $c = 0.043\%$ (···), 0.137% (---), 0.196% (-·-), 0.44% (-··-) and 0.59% (-···-) including just τ_0 and τ_R. The solid curve (——) is for the case where the purest Li sample was assumed ideally pure (in contrast to all the other calculations for which the impurity content was 0.02%) and the Li-Ag alloy had $c = 0.043\%$.

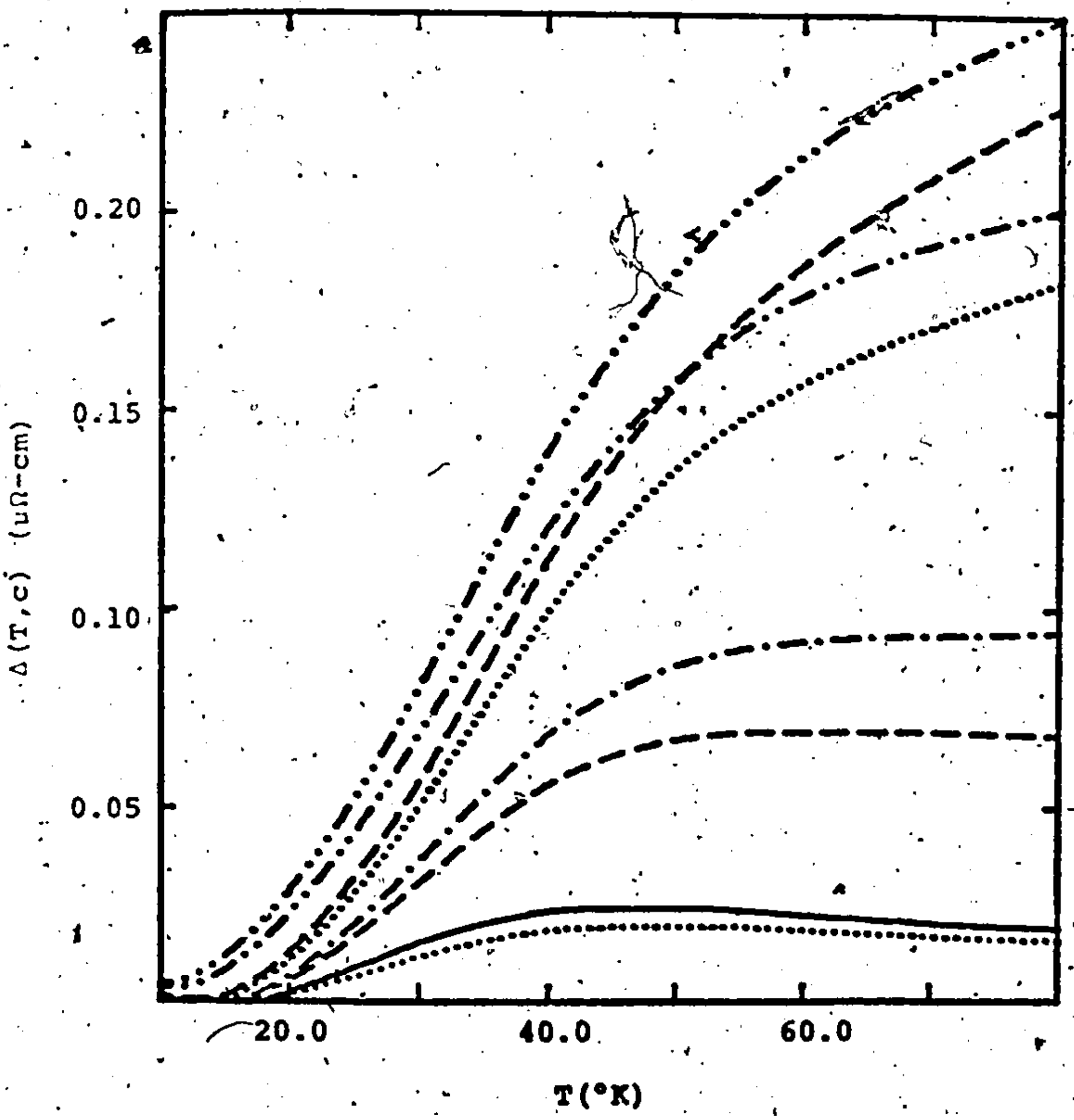


Fig. 12b: Same as Fig. 12a except that τ_1 and τ_2 were also included in the calculation. In addition, the effect of mass changes is included in (---) and (-·····-) for c = 0.44% and 0.59% respectively.

12(b) it is clearly seen that the fundamental effect leading to the D.M.R. is the washing out of the anisotropy in $\tau_0(\underline{k})$ by τ_R. To get the right qualitative and quantitative behaviour, τ_1 and τ_2 must also be included. The effect of the mass change should only be considered when all the other effects have been properly included. In contrast to this, Krill and Lapierre use a simple expression derived by Kagan and Zhernov (40) which gives

$$\Delta(T,c) = -2c\varepsilon(1 - \varepsilon\,\frac{9}{8}\,\frac{J_6}{J_5}\,\frac{T}{\theta_D})\,\rho_0(T)$$

where $\varepsilon = 1 - M'/M$ and $J_n = n!\zeta(n)$ with $\zeta(n)$ the Riemann zeta function. With this simple equation, they are able to get a reasonable fit to the data for the most concentrated Li-Ag sample considered up to about 35°K; above this the theoretical curve rises much too sharply.

Krill and Lapierre also made some measurements on the resistivity of dilute alloys of Li-Hg but the results obtained are very different from those of Li-Ag. All four concentrations of Hg in Li yielded results for $\Delta(T,c)$ which fell on the same curve, lying somewhat below the results for the most concentrated Li-Ag sample. The reason for this different behaviour is unknown (50,39). Hg produces a much stronger perturbation in Li than the Ag does, since it leads to a residual resistivity of about 3.63 μΩ-cm/at.% which is about three times as large as that produced by the same amount of

Ag in Li. The large value for the residual resistivity makes it very doubtful that the Born approximation could give a good representation for the scattering cross section, and the very large mass ratio, $M'/M \gtrsim 200/7$, and the different ionic radii probably mean that force constant changes are also important. It could also be that the large residual resistivity of Hg in Li has driven $\Delta(T,c)$ to its saturation limit even for the lowest concentration.

In order to give a better indication of the effect of the various terms contributing to $\Delta(T,c)$, Table 4 gives a breakdown of them for Li-Mg and Li-Ag, with $c = 1\%$. The superscript (M) on $\rho_0^{(M)}$, etc. denotes that the effect of mass change is included. Table 4 shows that at low temperature the total resistivity is dominated by the residual resistivity; this remains true even for very pure samples with $c \lesssim 10^{-4}\%$ but at progressively lower temperatures. Such concentrations are much less than those usually considered experimentally, e.g., the purest Li samples measured by Dugdale and Gugan had $\rho_R \gtrsim 10^{-2}$ $\mu\Omega$-cm or $c \gtrsim 10^{-2}\%$. Thus ρ_R in all their samples dominates the low temperature total resistivity. The pure metal resistivity, ρ_0, increases quickly with temperature so that, for fairly pure samples, it rapidly becomes larger than ρ_R. At room temperature, ρ_2 typically is within a factor of 2 of ρ_R. Such a strong ρ_2 term at high temperature is not observed

TABLE 4

Li-Mg : $\rho_R = 1.32$ (all resistivities are in μΩ-cm)

	T(°K)	ρ_0	ρ_2	$\rho_R'+\rho_2$	$\rho_2^{(M)}$	$\rho_R'^{(M)}+\rho_2^{(M)}$
WITHOUT	10	9.2×10^{-5}	2.4×10^{-3}		2.7×10^{-3}	
DEBYE-WALLER	50	3.1×10^{-1}	6.3×10^{-2}		8.5×10^{-2}	
FACTOR	300	5.9	6.6×10^{-1}		6.6×10^{-1}	
WITH	10		2.4×10^{-3}	2.1×10^{-3}	2.7×10^{-3}	2.4×10^{-2}
DEBYE-WALLER	50		6.2×10^{-2}	5.5×10^{-2}	8.5×10^{-2}	7.4×10^{-2}
FACTOR	300		5.8×10^{-1}	4.6×10^{-1}	5.8×10^{-1}	4.6×10^{-1}

Li-Ag : $\rho_R = 1.17$

	T(°K)	ρ_0	ρ_2	$\rho_R'+\rho_2$	$\rho_2^{(M)}$	$\rho_R'^{(M)}+\rho_2^{(M)}$
WITHOUT	10	9.2×10^{-5}	2.8×10^{-3}		7.6×10^{-3}	
DEBYE-WALLER	50	3.1×10^{-1}	7.2×10^{-2}		1.2×10^{-1}	
FACTOR	300	5.9	8.0×10^{-1}		8.0×10^{-1}	

continued...

TABLE 4 - continued

Li-Ag : $\rho_R = 1.17$

	$T(^\circ K)$	ρ_0	ρ_2	$\rho_R'+\rho_2$	$\rho_2^{(M)}$	$\rho_R'^{(M)}+\rho_2^{(M)}$
WITH	10		2.8×10^{-3}	2.5×10^{-3}	7.6×10^{-3}	6.9×10^{-3}
DEBYE-WALLER	50		7.5×10^{-2}	6.6×10^{-2}	1.2×10^{-1}	9.8×10^{-2}
FACTOR	300		6.9×10^{-1}	5.5×10^{-1}	6.7×10^{-1}	5.0×10^{-1}

experimentally. Making reasonable changes in the relevant scattering cross section, $\Delta w(q)$, can help a bit but this does not solve the problem. A more plausible solution seems to be the inclusion of the Debye-Waller factor in ρ_R and ρ_2 as suggested by Kagan and Zhernov$^{(40)}$. Then in the calculations ρ_2 should be replaced by $\rho_R' + \rho_2$ where ρ_R' is the temperature dependent part of ρ_R. ρ_R' will always be negative since the Debye-Waller factor always decreases the value of any expression. At low temperatures this produces a decrease in the value of $\rho_R' + \rho_2$ compared to ρ_2 calculated without the Debye-Waller factor but the absolute value of this term is very small compared to ρ_R. At room temperature, however, the value of ρ_2 has been decreased by about 15% by the Debye-Waller factor, and the value of ρ_R' has increased in absolute value, so that a substantial decrease of $\rho_R' + \rho_2$ is obtained with respect to ρ_2 calculated without the Debye-Waller factor, e.g., 4.6×10^{-1} compared to 6.6×10^{-1} $\mu\Omega$-cm for Li-Mg at 300°K. At very high temperature, $T \gtrsim 2000$°K, the value of $\rho_R' + \rho_2$ approaches zero fairly rapidly. At such temperatures, however, the solids would have long melted. Thus it is important to retain the ρ_2 term, along with ρ_R', and not to drop this term altogether as did Bhatia and Gupta$^{(53)}$ in their calculations of D.M.R. for Al-Mg alloys. This will be discussed in more detail when the calculations for the Al alloys are presented.

Since $W_{D.W.} \sim q^2T$ at high temperature, one would expect that it would cause a fairly rapid decrease in $\rho_R' + \rho_2$. However, the relevant scattering cross section which appears in these terms, $\Delta w(q)$, is such that $|\Delta w(q)|^2$ for an alloy like Li-Ag where there is no valence change, in fact reaches its maximum value at $q \stackrel{\sim}{>} 1.2\ k_F$ and then rapidly decreases when q increases to $2k_F$. If there is a valence change, as in Li-Mg, then $|\Delta w(q)|^2$ decreases steadily from its largest value at $q = 0$ so that it has a relatively small value at $q \stackrel{\sim}{>} 2k_F$, although there can be a slight upturn in $|\Delta w(q)|^2$ near $2k_F$ from some impurities. Since it is expected physically that the large angle scattering, or $q \stackrel{\sim}{>} 2k_F$, should contribute most to the resistivity, this may be taken as evidence that the functional form of the scattering cross section is not properly given by the Born approximation, especially if there is a valence difference. A more rigorous phase shift calculation would give more weight to the large q values so that the effect of $W_{D.W.} \sim q^2T$ would be much greater.

The relative effect of including mass changes is seen to be greater at low temperatures than high temperatures. The changes produced are much greater for Ag in Li than Mg in Li since Ag is about four times as heavy as Mg. This also has the effect of producing the greatest change in ρ_2, for example, at a lower temperature since more of the density of states has been shifted to lower frequencies for Ag than for Mg.

Including the mass change in the calculation of ρ_0 causes a small decrease in its value at high temperature, while at low temperature, it is increased. For Li-Ag with $c = 1\%$, ρ_0 is increased by a maximum of about 50% at $T \approx 10°K$, while at temperatures above $T \approx 50°K$, it is decreased by a small amount, about 1%. In comparison, ρ_2 is increased by a factor of almost three at $T \approx 10°K$ while at $T = 300°K$, this increase has dropped to about 5%. But, even though the effect of the mass change is much less in ρ_0 than in ρ_2, ρ_0 is over an order of magnitude larger than ρ_2 at $T = 300°K$, and the small decrease of about 1% in ρ_0 is actually equal to about 10% of the actual value of ρ_2, with or without the mass change included in ρ_2.

The reason that the mass change produces a much stronger effect in ρ_2 than in ρ_0 is that ρ_2 contains the t-matrix directly as a factor while ρ_0 contains it in the combination $(\omega^2 - \omega'^2 - cT'(\omega))^{-1}$. Thus the effect of the $T'(\omega)$ on the value of ρ_0 is greatly decreased by the factor c. The detailed behaviour of ρ_0 when the $T'(\omega)$ is included is also more complicated by its appearance in the denominator. If c and/or ε are small, it would be possible to make a binomial expansion, the first term of which would give just the ordinary expression for the resistivity of a pure metal while the second term would give a term proportional to $cT'(\omega)$. In order to really study the effect of the mass change on the resistivity, larger concentration, i.e., $c \sim 5\%$, should be studied. In the section on D.M.R. for Al alloys results will be presented for Al-Zn with $c = 2.1\%$ but there the mass ratio is less than 3 to 1.

To see the effect of the mass change in detail, it is convenient to consider the following effective frequency distribution.

$$\alpha^{2(M)}_{TR}F(\underline{k}\ \omega) = -\frac{2}{\pi}\,\mathrm{Im}\int d\omega'\omega'\,\frac{\alpha^{2}_{TR}F(\underline{k}\omega')}{\omega^{2}-\omega'^{2}-cT'(\omega)} \, .$$

As $c \to 0$ this reduces to just $\alpha^{2}_{TR}F(\underline{k}\omega)$. The values of $\alpha^{2(M)}_{TR}F(\underline{k}\omega)$ versus ω for two values of $\underline{k}$ are shown in Figs. 13 and 14 for $c = 0$, $c = 0.5\%$ and $c = 1\%$. Also shown in these graphs are the thermal factors $\hbar(\omega)(n(\omega)+1)$. The first and most important thing to notice is the very large amount of anisotropy in the $\alpha^{2}_{TR}F(\underline{k}\omega)$ for Li. Some more graphs of $\alpha^{2}_{TR}F(\underline{k}\omega)$ for Li as well as for K and Rb covering the whole frequency range are given by Hayman and Carbotte (36). The curves for $\alpha^{2(M)}_{TR}F(\underline{k}\omega)$, which include only the low frequency portions of the spectrum, show that there is a general shift to lower values of ω, as well as the buildup of a resonance peak due to the increased density of states arising from the lower frequency of vibration of the heavy impurity ions. By doing an average

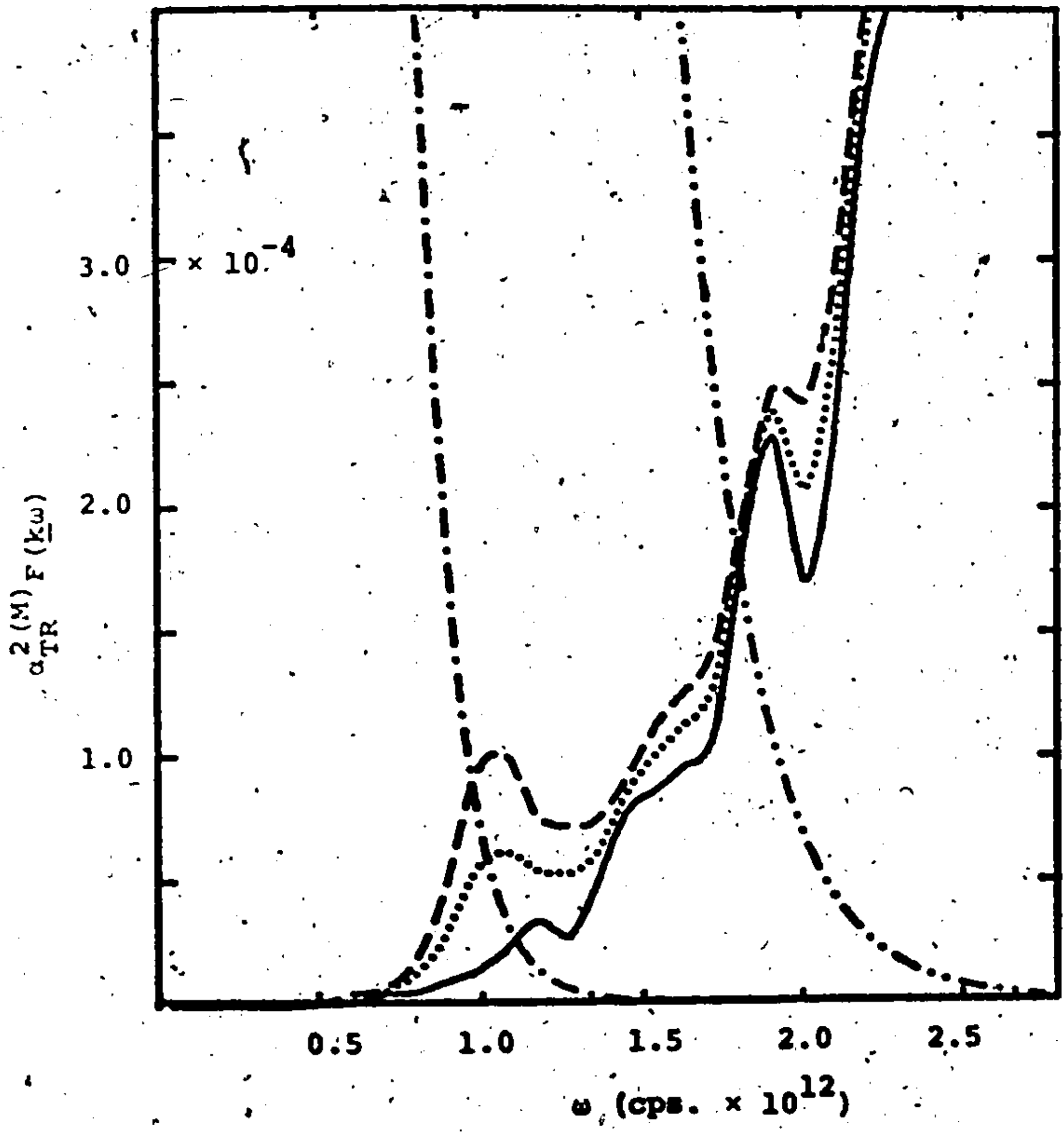


Fig. 13a: The effective frequency distributions $\alpha^{2(M)}_{TR}F(\underline{k}\omega)$ including the mass effect for alloys of Li-Ag with c = 0% (——), 0.5% (···) and c = 1.0% (---) in the low ω region. The thermal factors, n(ω)(n(ω)+1) for T = 5°K (-·-) and T = 10°K (-··-) are also shown. The value of $\underline{k}$ = (k_F,0°,0°).

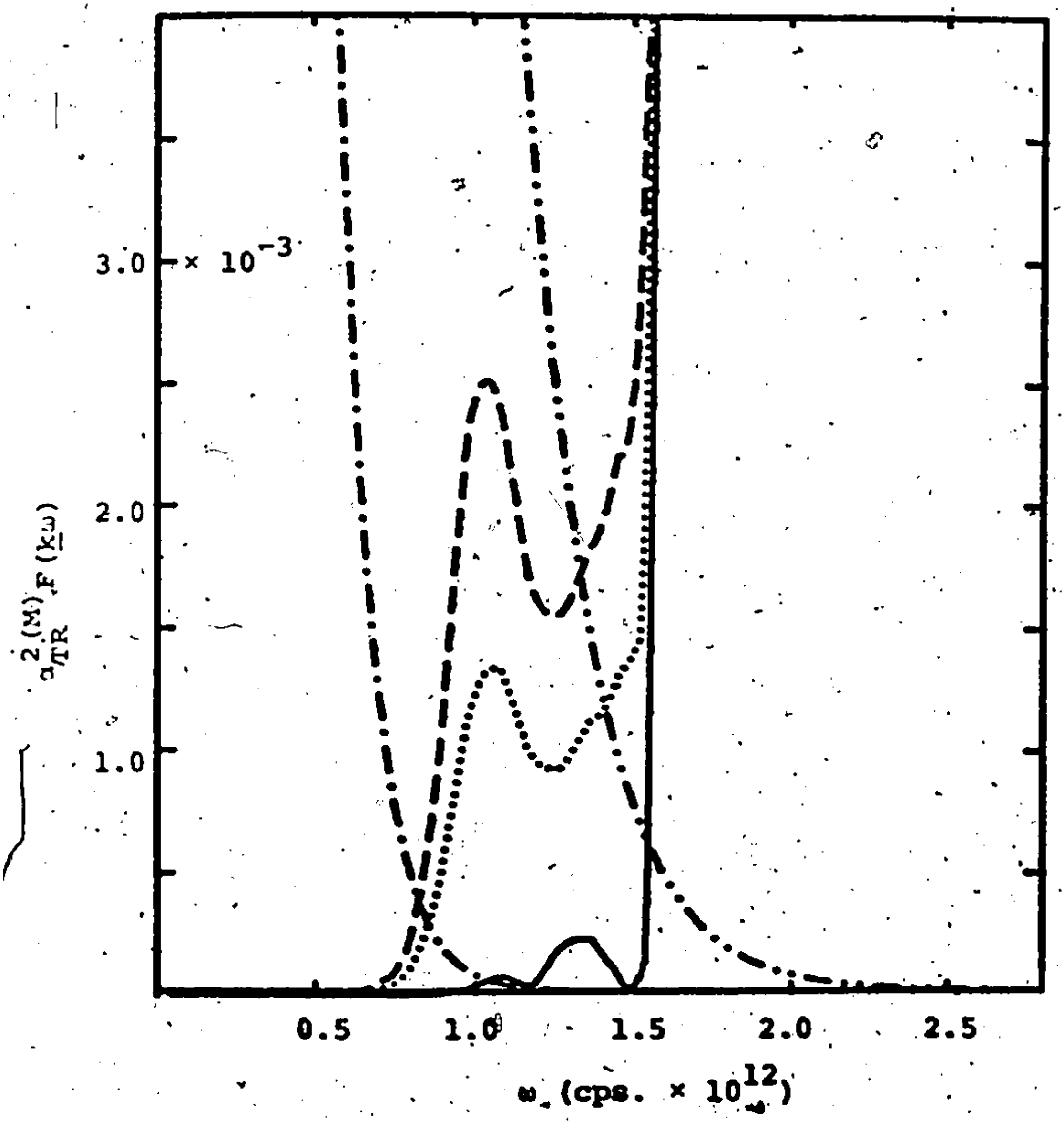


Fig. 13b: Same as Fig. 13a except that $\underline{k}$ = (k_P,30°,0°).

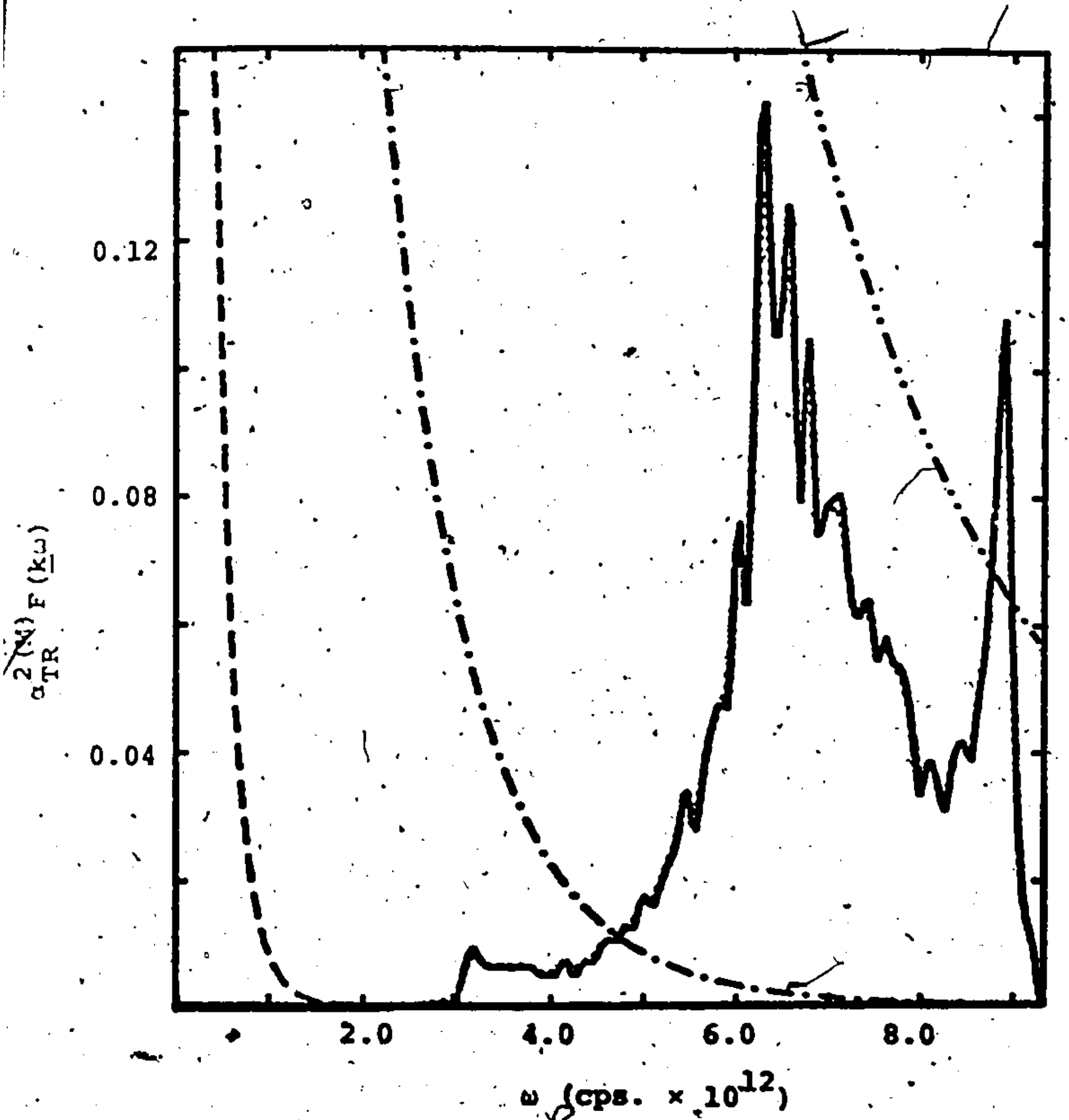


Fig. 14a: $\alpha^{2(M)}_{TR}F(\underline{k}\omega)$, with $\underline{k} = (k_F,0,0)$ for the Li-Ag alloy with c = 0% (——) and 1% (···) for the complete frequency range. The thermal factors $n(\omega)(n(\omega)+1)$ for T = 10°K (---), 50°K (-·-) and 150°K (-···-) are also shown.

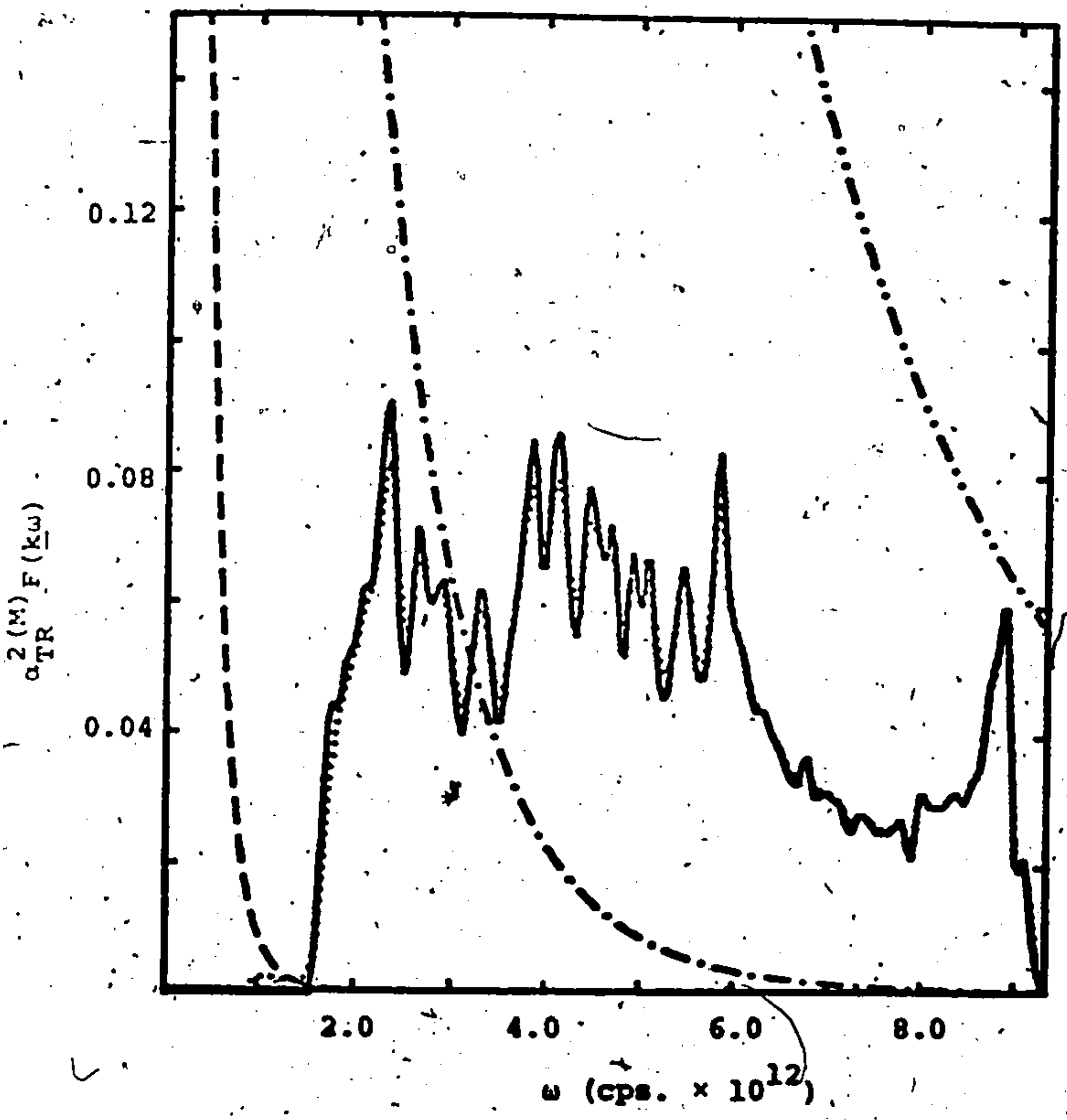


Fig. 14b: Same as Fig. 14a except that $\underline{k} = (k_F, 30°, 0°)$.

of $\alpha_{TR}^{2(M)}F(\underline{k}\omega)$ over all directions on the Fermi surface, it is possible to just focus the attention on the effect of the resonance peak created by the mass change. This is shown in Fig. 15 for c = 0 and 1%. Similar results for just the density of states exist in the literature; see, for example, Maradudin et al. (54).

The contribution to the resistivity from $\tau_0(\underline{k})$ essentially involves an overlap integral of the thermal factors and $\alpha_{TR}^{2(M)}F(\underline{k}\omega)$. In Fig. 16 the ratio $\tau_0^{(M)}(\underline{k})/\tau_0(\underline{k})$ is plotted for $\phi = 0$, as a function of θ for three values of the temperature; the other values of ϕ give similar results. By noting the way the thermal factors overlap with the $\alpha_{TR}^{2(M)}F(\underline{k}\omega)$ in the different directions, especially how much of the resonance hump they include, the large deviation of $\tau_0^{(M)}(\underline{k})/\tau_0(\underline{k})$ from 1 can be explained. At T = 40°K the thermal factors are already completely off the scale of the graphs, and so the extra resonance hump contributes relatively little to the integral, leading to a ratio of about 1. When $\rho_0^V(T)$ and $\rho_0^{(M)}(T)$ are calculated all the directions contribute, and the net effect is quite substantial, e.g., $\rho_0^V(T) = 6.1 \times 10^{-3}$ while $\rho_0^{V(M)}(T) = 9.9 \times 10^{-3}$ μΩ-cm at T = 10°K, but at T = 40°K, this is reduced to 2.84×10^{-3} and 2.81×10^{-3} μΩ-cm. This small relative decrease of $\rho_0^{(M)}(T)$ compared to $\rho_0(T)$ persists generally at the higher temperatures. The increase in $\rho_0^{(M)}(T)$ compared to $\rho_0(T)$ at T = 10°K is much smaller than

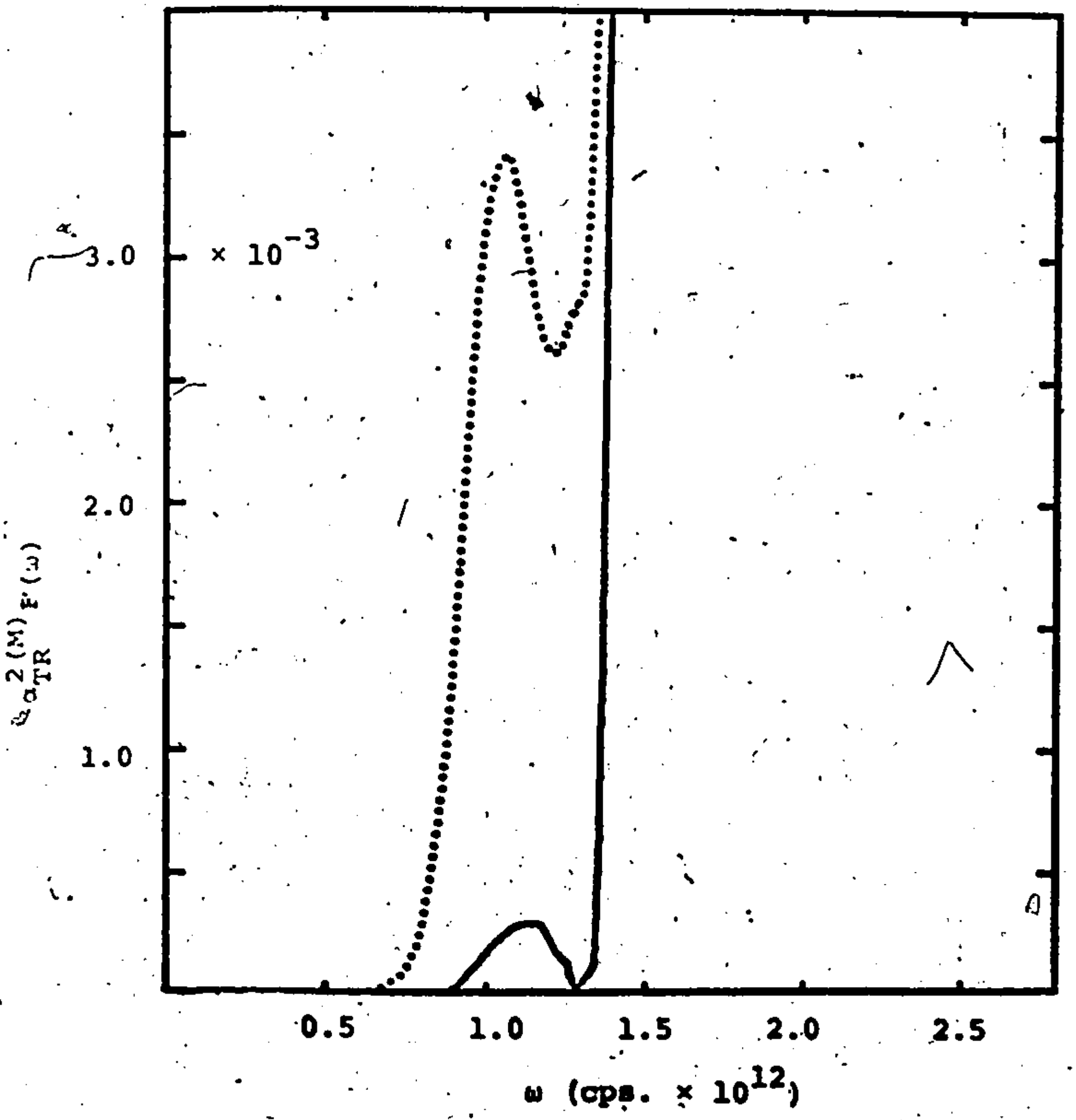


Fig. 15: The isotropic effective frequency distribution $\alpha^{2(M)}_{TR}F(\omega)$, including the mass effect, for the alloy Li-Ag with c = 0% (——) and 1% (···).

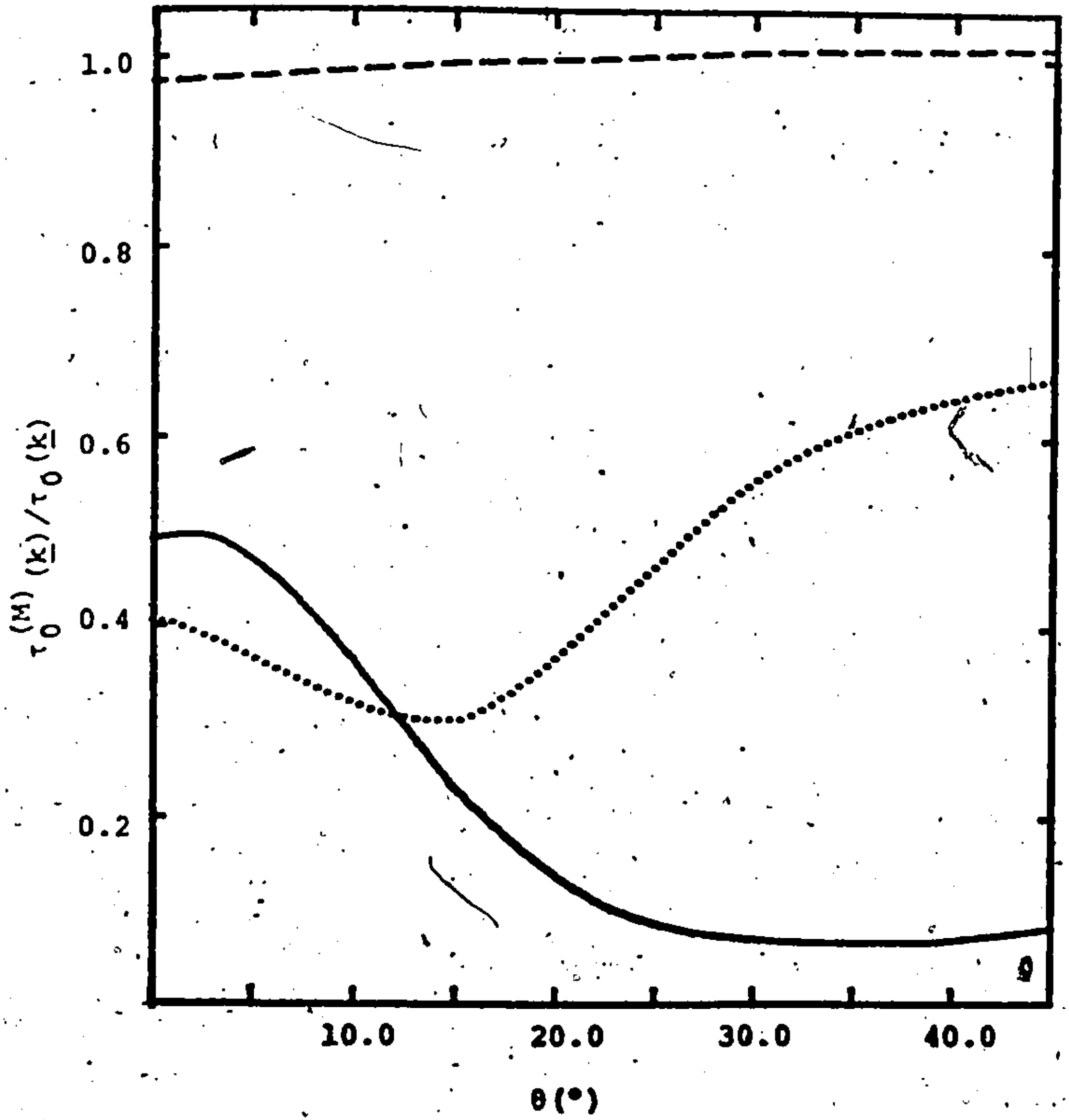


Fig. 16a: The ratio $\tau_0^{(M)}(\underline{k})/\tau_0(\underline{k})$ for an Li-Ag alloy with c = 1% for $\phi = 0°$ as a function of θ on the irreducible part of the Fermi surface. The curves correspond to the ratio at T = 5°K (——), 10°K (···) and 40°K (---).

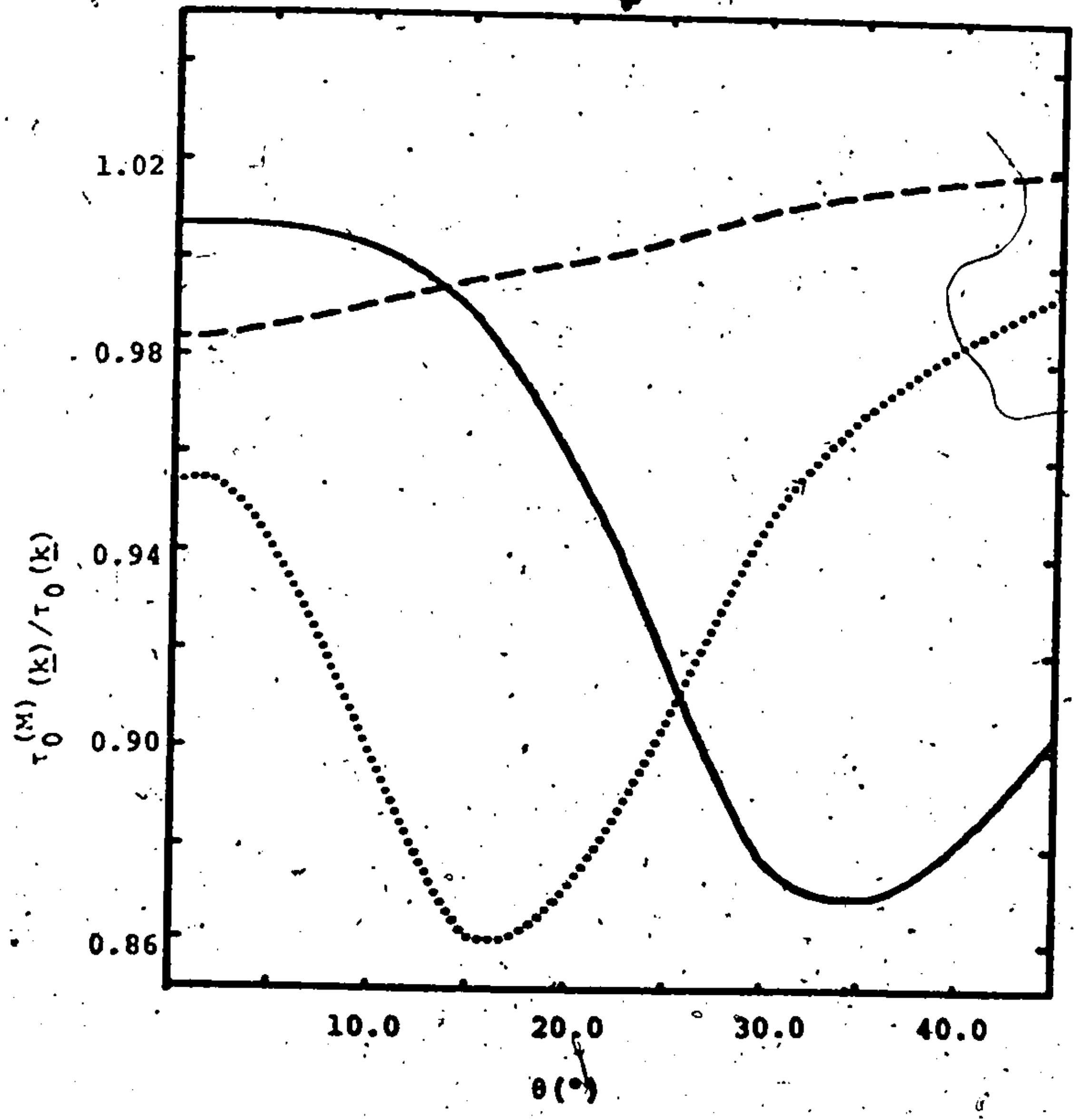


Fig. 16b: Same as Fig. 16a except the results are for an Li-Mg alloy.

the increase in $\rho_2^{(M)}(T)$ compared with $\rho_2(T)$. If one went to very large concentrations, like $c \gtrsim 10\%$, then the ratio of $\rho_0^{(M)}/\rho_0$ would be greatly increased from its value for $c = 1\%$ while $\rho_2^{(M)}/\rho_2$ would stay essentially the same. Unfortunately, ρ_2 dominates ρ_0 at $T \gtrsim 10°K$ at such concentrations so that it is not possible to study the changes in $\rho_0^{(M)}$. However, the substantial increase in $\rho_2^{(M)}$ compared to ρ_2 at any given concentration introduces a hump into $\Delta(T,c)$ at low temperatures which should be directly observable at $c \gtrsim 5\%$ such that the hump due to washing out of the anisotropy has essentially disappeared. In such cases, $\Delta(T,c)$ is given approximately by $\rho_1 + \rho_2 + \rho_R'$ if $\rho_0^{(M)}(T)$ has not changed very much from $\rho_0(T)$. An estimate for results may be obtained by suitably scaling the results for $\rho_2^{(M)}$, etc. given in Table 4 to allow for the higher concentration.

3.4 D.M.R. in Al Alloys

There has been a great deal of interest recently in the D.M.R. in dilute Al alloys (see the review article by Bass (39) for a detailed account of all the experiments and their theoretical interpretations). The most recent, systematic experiments which cover the whole temperature range from 4.2°K to 300°K are those of Seth and Woods (55) and Carter (56). Seth and Woods obtained results for Al-Mg, c = 0.13, 0.61 and 1.75% and Al-Ag, c = 0.06 and 0.18%, while Carter obtained results for Al-Mg, c = 0.03, 0.1, 0.5 and 1.5%; Al-Cu, c = 0.09, 0.52 and 1.03%; Al-Zn, c = 0.1 and c = 2.1%; and Al-Ga, c = 0.035, 0.108, 0.198 and 0.664%. There are also results for Al-Ag obtained by Panova et al. (57) which are similar to those of Seth and Woods in their major features although there are some discrepancies in detail. The data for the most concentrated alloys of Al-Mg are in agreement between Seth and Woods and Carter; however, the data for the more dilute alloys are not.

Seth and Woods state that they confined their attention to alloys in which the impurity content is less than 2% because there is reason to believe from Mössbauer experiments (58,59), for example, that in general, the phonon spectrum is little changed from that of a pure metal, and from de Haas-van Alphen measurements (60), that the electronic structure of a metal is not greatly changed by the impurities. Under these circumstances, they expected that contributions to $\Delta(T,c)$ that might arise from a deformed phonon spectrum as calculated by Kagan and Zhernov (40), or from changes in the Fermi surface, would be negligible. They considered that D.M.R. could arise from three different mechanisms: (i) Inelastic scattering of the electrons by the excess potential of the vibrating impurity ions, i.e., ρ_2 (61,62). The thermal vibrations of the impurity may also modify the form of the impurity potential (63). (ii) An interference term between the scattering by the vibrating impurities and the host ion, i.e., ρ_1 (40,53). (iii) Different anisotropies of the phonon and impurity scattering over the Fermi surface (54) will give rise to positive values of $\Delta(T,c)$. This contribution is usually discussed in terms of the two band model (65,66).

The two band model is really a simplified model for the anisotropy in the scattering and it is appropriate to give a short discussion of it (see Bass (39) for more details of the model and its application to experimental data). Sondheimer and Wilson (67) made the first study of D.M.R. arising from anisotropic scattering. They studied the transport properties of a metal containing two parabolic bands of electrons and assumed that the resistivities due to each band would separately obey Matthiessen's rule. If the two bands do not interact with each other, their conductivities will add, yielding a net D.M.R.. Using the variational principle, Kohler (66) investigated the nature of $\Delta(T,c)$ when the scattering probability for electrons in the alloy is the sum of the probabilities for the scattering by phonons and by impurities. By noting that the trial function, $\phi_{\underline{k}}^{a}$, should be the one appropriate to the alloy, while the ideal phonon and the residual resistivity are calculated separately using trial functions appropriate to each of these two cases, i.e., $\phi_{\underline{k}}^{0}$ and $\phi_{\underline{k}}^{R}$ respectively, Kohler showed that Matthiessen's rule was only obeyed if $\phi_{\underline{k}}^{0} = \phi_{\underline{k}}^{R}$. This is certainly true if the Fermi surface of the metal and all scattering processes are isotropic or if both $\phi_{\underline{k}}^{0}$ and $\phi_{\underline{k}}^{R}$ have exactly the same anisotropy. D.M.R. will exist whenever $\phi_{\underline{k}}^{0}$ is not identical to $\phi_{\underline{k}}^{R}$. In that case a linear combination of $\phi_{\underline{k}}^{0}$ and $\phi_{\underline{k}}^{R}$ may be used to represent $\phi_{\underline{k}}^{a}$ in the variational calculation.

MacDonald (68) generalized this procedure by defining a relaxation time, $\tau_0(\underline{k})$, for the scattering of electrons by phonons which was allowed to be an arbitrary function of $\underline{k}$. If τ_R, the relaxation time for scattering by impurities, is isotropic and the total scattering time can be written as

$$\frac{1}{\tau_a(\underline{k})} = \frac{1}{\tau_0(\underline{k})} + \frac{1}{\tau_R} ,$$

MacDonald obtained for the conductivity of the alloy

$$\sigma = \frac{ne^2}{m} \sum_{\underline{k}} \left[\frac{1}{\tau_0(\underline{k})} + \frac{1}{\tau_R}\right]^{-1} .$$

If $\tau_0(\underline{k})$ is independent of $\underline{k}$, this would yield $\Delta(T,c) = 0$. More generally, $\tau_0(\underline{k}) = \tau_0 + \delta(\underline{k})$ where τ_0 is the average of $\tau_0(\underline{k})$. For $\delta(\underline{k})/\tau_0$ small, the limit $\tau_0 << \tau_R$ gives

$$\rho_a(T) = \rho_0(T) + \rho_R[1 + \frac{<(\delta(\underline{k}))^2>}{\tau_0^2}] .$$

Since the second term in the brackets is in general a function of temperature, $\Delta(T,c)$ will be given by $\rho_R<(\delta(\underline{k}))^2>/\tau_0^2$ in this limit. In the opposite limit, when $\tau_0 >> \tau_R$

$$\rho_a(T) = \rho_R + \rho_0(T)[1 + \frac{<(\delta(\underline{k}))^2>}{\tau_0^2}]$$

so that $\Delta(T,c)$ is proportional now to $\rho_0(T)$ instead of ρ_R. These approximate equations are unable to explain the nonlinear concentration dependence and the variation from impurity to impurity which is often observed in $\Delta(T,c)/\rho_R$.

It is apparent that the two band model, as generalized by MacDonald, is very similar in spirit if not in detail to the theory presented earlier in this thesis, particularly the approximate theory given in Eqs. (3.56) to (3.61). In fact, Eq. (3.60) is essentially the same as the result $\Delta(T,c) = \rho_R<(\delta(\underline{k}))^2>/\tau_0^2$ when $a^2(T)$ is identified with $<(\delta(\underline{k}))^2>/\tau_0^2$ in the limit $\tau_R >> \tau_0$, or, what is equivalent,

$B_0(T) >> \rho_R$. The result in Eq. (3.61) for the other limit of $\tau_0 >> \tau_R$ or $\rho_R >> B_0(T)$ is analogous to $\Delta(T,c) = \rho_0(T)\langle(\delta(\underline{k}))^2\rangle/\tau_0^2$. The use of $\delta(\underline{k})$ to define the anisotropy in $\tau_0(\underline{k})$ while $a(\underline{k})$ defines the anisotropy in $1/\tau_0(\underline{k})$ is mainly one of convenience, but the use of $\delta(\underline{k}) << 1$ means that it is subject to the same criticisms already mentioned for the $a^2(T)$ which is really not small at some temperatures. In practise, the two band model finds its most useful application in the noble metals (65) where the anisotropy in the Fermi surface is used to define different scattering times for phonons and impurities, for the neck and belly orbits. However, Gugan (45) has also discussed his low temperature resistivity data in potassium in terms of this model, as has Carter (56) in his study of Al alloys.

In their study of D.M.R., Seth and Woods considered, as well as Al-Ag where the impurity is heavier than the host ion, dilute alloys such as Ag-Al, Ag-Mg and Cd-Mg where the impurity is lighter and may thus have a local mode associated with it. By comparing these results with the results of other alloys they studied where there is essentially no mass change, e.g., Al-Mg, they found no difference in the $\Delta(T,c)$ obtained which they could ascribe to the effect of mass changes. Thus they concluded that modifications of the phonon spectrum in the dilute alloys considered are not large enough to produce substantial D.M.R. This is consistent with the conclusion reached by Damon and Klemens (69) after a study of gold alloys. On the other hand, Panova et al. (57) report an effect in Mg-Pb alloys from the quasilocal resonant mode. Independent evidence for the existence of such modes has been provided by measurements of the specific heat (70) and inelastic neutron scattering (71).

Seth and Woods (55) attributed the observed D.M.R. to the three effects listed earlier but stated that it was not possible to entirely separate out contributions to the observed values through their temperature dependence. However, they did conclude that at low temperature only the D.M.R. due to inelastic scattering from impurities and the two band effect are expected to be important. Damon et al. (72) measured $\Delta(T,c)$ in some dilute gold alloys and were able to separate out the various contributions and their temperature dependence.

The D.M.R. arising from ρ_1, the interference between the scattering by impurities and by the phonon spectrum of the host lattice, is small if only small angle scattering is included in the calculation (40,53). Bhatia and Gupta (53) included scattering at all angles and found that this produced a contribution to D.M.R. which was a few per cent of ρ_R at $T \gtrsim \theta_D$. This contribution can be either positive or negative, depending on the sign of $\Delta w(q)$; this is in contrast to the other contributions to the D.M.R. which are positive. For complementary pairs of alloys, for which the role of host and impurity are interchanged, the sign of the interference contribution should change but its magnitude remains proportional to T at high temperature. This will result in a change in the sign of the slope of this contribution versus T, and it may be possible to experimentally determine its presence. Seth and Woods find qualitative agreement with this difference in the sign of the slope of $\Delta(T,c)$ for the complementary pairs: Al-Mg and Mg-Al; Ag-Cd and Cd-Ag; Ag-Mg and Mg-Ag and Al-Ag and Ag-Al. They concluded that not only does the interference term explain the change in the sign of the slope of $\Delta(T,c)$ but it must be included if the origin of the negative values of $\Delta(T,c)$ itself, which were observed for Cd-Ag, Cd-Mg and Mg-Al at high temperature, is to be understood (55).

In his study of dilute Al alloys, Carter (56) examined the applicability to his data of three models for D.M.R.: (i) The two band model. (ii) A relationship for $\Delta(T,c)$, having the form $\Delta(T,c) \sim T^3 \ln\rho_R$, which was suggested by Campbell et al. (73) on the basis of their experiments on dilute Al alloys between 1.5 and 40°K. They attributed such a dependence to the loss of translation symmetry in the lattice upon introduction of a substantial amount of impurities. (iii) A model proposed by Ehrlich (74) which estimated the effect of thermal umklapp scattering upon the temperature dependence of the resistivity of dilute, noble metal based alloys. Ehrlich extended a theory developed by

Klemens and Jackson (75) to include impurity scattering. The Fermi surface of the noble metals was constructed by truncating a sphere by means of planes corresponding to the Brillouin zone boundaries. By assuming that the electron-phonon interaction moves an electron over the spherical portions of the Fermi sphere in small random steps, so that the process can be regarded as taking place by diffusion, the Boltzmann equation could be converted into a two-dimensional diffusion equation. Describing the impurity scattering by an isotropic relaxation time so that in the absence of thermal umklapp scattering there would be no D.M.R., Ehrlich obtained for the alloy resistivity (74)

$$\rho_a(T,c) - \rho_R = \rho_0'(T) + \Delta(T,c),$$

$$= \rho_0'(T)F(2\rho_R/\rho_0'(T),\eta),$$

where $\rho_0'(T)$ is the phonon limited resistivity in the absence of umklapp scattering, and η is a measure of the amount of contact between the Fermi surface and the Brillouin zone boundaries. The D.M.R. are produced by the factor F, which is a function of temperature and concentration. The form of F was found to be nearly the same for all values of η and all three cubic crystal structures.

Carter also compared his data to a theory by Mills (76) which considered higher order processes in which an electron was scattered first by a phonon and then by an impurity. He found this theory successful in predicting the concentration and temperature dependence of the D.M.R. in Al alloys at low T, but unsuccessful at high T since the observed temperature dependence is not consistent with the theory. Mills' calculation has recently been criticized by Dworin (77), Smith (78), and Sherrington (79), all of whom claim that Mills made an improper use of the Boltzmann equation in including higher order scattering processes in the manner he did. Since Mills' calculation claimed to support the heuristic arguments by Campbell et al. (73) for $\Delta(T,c) \sim T^3 \ln\rho_R$, their physical explanation of this form as arising from the loss of translational symmetry is also in doubt.

In comparing his data with Ehrlich's theory (74), Carter assumed that the model predicted that $\Delta(T,c)$ has the form

$$\rho_a(T) = \rho_R + AT^2 + BT^5$$

where A/B should vary as $\rho_R^{3/5}$. He found, however, that A/B varied more nearly as $\rho_R^{2/5}$. He took this as evidence against the applicability of Ehrlich's model, but Ehrlich stressed that his model did not generally yield the simple form for $\rho_a(T)$ assumed by Carter. This was also confirmed by Schotte and Schotte (80) who used a simplified model for the Fermi surface of Al and showed that $\rho_a(T)$ could vary as any power of T between $T^{2.5}$ and T^5, depending on the various assumptions made in the calculation. Thus Carter's arguments do not really invalidate Ehrlich's theory.

Carter found that he could fit his data to the two band model, although the variation of the parameters in this model with temperature was not completely as predicted. He concluded that the two band approximation may not fully represent the relaxation time anisotropy or that additional mechanisms not considered in that model may give a temperature dependent impurity resistivity. A more serious flaw occurred in some of his data at about 90°K where the fitted parameters were such as to imply $\Delta(T,c) = 0$, while the experimental data gave a non-zero $\Delta(T,c)$. However, in this temperature region the thermal expansion begins to be important, and the error bars on his data made a choice of parameters giving a non-zero $\Delta(T,c)$ possible at all temperatures.

In comparing the experimental data and the theoretical calculations for $\Delta(T,c)$, it is very important to consider the problem of volume changes. All the calculations in this thesis were made assuming the same volume, appropriate to the host material at low temperature, throughout. Volume changes are due to thermal expansion and, for an alloy, changes in sample volume arising from the addition of impurities. These effects are usually neglected by the experimenters. Dugdale and Basinski (65) suggested that it is very important to correct for these changes, using available experimental data, before comparing experiment with theory. To lowest order the resulting corrections to $\Delta(T,c)$ have the form (81)

$$\Delta_1'(T,c) = \frac{d\rho_R}{d\Omega}\,[\Omega(T) - \Omega(0)]$$

$$\Delta_2'(T,c) = c\,\left.\frac{d\rho_0(T)}{d\Omega}\right|_T \frac{d\Omega}{dc} \;.$$

Δ_1' is the correction for thermal expansion and Δ_2' is the correction for changes in average atomic volume upon alloying. For dilute alloys both are proportional to c and very nearly proportional to T. Δ_1' and Δ_2' must be obtained from independent experiments, and then subtracted from the experimental values of $\Delta(T,c)$. The correction for thermal expansion was found by Dugdale and Basinski (65) to give a 10 to 20% correction to $\Delta(T,c)$ at T = 300°K. The form of $\Delta_2'(T,c)$ is more questionable since microscopic volume changes produced by alloying are not spread uniformly throughout the crystal lattice. This is basically a similar problem to the one dealt with in the correction to the Friedel Sum Rule due to displacement of the host ions around an impurity. The resulting change in the resistivity could, therefore, be different from that produced by a uniform dilitation of the pure lattice, as Δ_2' assumes. The changes in resistance produced by this correction can be quite large - at 300°K

Dugdale and Basinski (65) found values as large as 50% of $\Delta(T,c)$. Seth and Woods (55) have not applied these corrections to their data but Carter (56) did. He found the following values for the total relative change, $\delta\Delta/\Delta$, in the D.M.R.: -0.73 for Al-Cu, $c = 1.03\%$; $+0.06$ for Al-Ga, $c = 0.66\%$; $+0.84$ for Al-Mg, $c = 1.5\%$; and -0.34 for Al-Zn, $c = 2.1\%$. This correction can have an important effect on the comparison of theory with experiment at high temperature if the linear term in $\Delta(T,c)$ due to the interference between phonon and impurity scattering is small. In that case it is possible that applying the volume correction could change the sign, leading to disagreement with theory.

3.5 Results of Calculations of the D.M.R. in Aluminum Alloys

The ideal resistivity was calculated using an Ashcroft pseudopotential with $R_c = 0.628$ Å. This value was chosen so that the calculated values of the pure metal resistivity were in good agreement with the data of Seth and Woods (55) at a temperature where the effects of the anisotropy and thermal expansion are not too large. The theoretical values of $\rho_0(T)$ in general lie below the experimental values for T greater than the value at which it is decided to fit theory to experiment. Below this temperature the theoretical values are in general higher. Since the anisotropy is largest below 100°K and the thermal expansion introduces corrections to the experimental data which increase with increasing temperature, the value is fitted between 100°K and 150°K, i.e., using the variational formula with the lowest trial wavefunction for the resistivity, the choice of $R_c = 0.628$ Å gives a value of $\rho_0(T = 140°K) = 0.896$ μΩ-cm while the experimental value is 0.893 μΩ-cm. The scattering time formula gives lower values for $\rho_0(T)$ than the lowest order variational formula, the difference being more pronounced at lower temperatures. Thus if theory and experiment were chosen to agree at a given value of T, the value at which agreement is obtained when the scattering time formula for $\rho_0(T)$ is used instead of the variational one, will be at some lower temperature. The value thus obtained using $R_c = 0.628$ agrees with experiment at about 120°K. Below 120°K the calculated values are consistently higher than the experimental values, sometimes by as much as a factor of two while above 120°K the values are all below the experimental ones, by about 15-20% at room temperature. This latter comparison does not include the effect of the thermal expansion. The low temperature values of the resistivity are not expected to be quantitatively correct since the effect of the nonspherical Fermi surface was not included. This gives rise to an artificial divergence in $\alpha_{TR}^2F(\underline{k}\omega)$ and $\alpha_{TR}^2F(\omega)$. Allen and Cohen (82) have suggested a simple procedure to, approximately, remove this difficulty. The lowest $\frac{1}{5}$ of the frequency distributions, where the divergence occurs, is renormalized by multiplying by ω/ω_D. It is hoped that it will eventually be possible to put the details of the Fermi surface into these calculations so that the low temperature D.M.R. in dilute alloys of Al as well as the pure metal resistivity may be more reliably calculated. In an analysis of the resistivity of the polyvalent metals, Lawrence and Wilkins (83) came to the conclusion that the distortion of the Fermi surface should have its most important effect below about 40°K.

Since the values of $\Delta(T,c)$ are typically of the order of 0.05 μΩ-cm, the relatively large discrepancies between the theoretical and experimental values of $\rho_0(T)$, which are of the order of 0.4 μΩ-cm at room temperature, would seem to make the calculations of $\Delta(T,c)$ rather dubious. However, in calculating $\Delta(T,c)$, one must calculate both the alloy resistivity, $\rho_a(T)$, as well as $\rho_0(T)$. Since $\rho_a(T)$ is calculated by adding the various inverse scattering times for the different processes, including the one for the pure metal phonon scattering, the effect of the large error in $\rho_0(T)$ will largely cancel out when $\Delta(T,c) = \rho_a(T) - \rho_0(T) - \rho_R$ is calculated. At high T, where the anisotropy is essentially gone, this cancellation will be essentially exact, and at such temperatures the D.M.R. are mainly given by the impurity resistivities ρ_1 and ρ_2 which vary linearly with concentration and temperature for high T. At low T, the averaging of the total $\tau_a(k)$ causes the $\tau_0(k)$ and the various other τ's to be mixed in a complicated, nonlinear fashion so that it would not be expected that the errors in $\rho_0(T)$ cancel when $\Delta(T,c)$ is calculated. Since the residual scattering time dominates at low T for all but the purest samples, and it is of the order of $\tau_0(\underline{k})$ for $T \sim 100°K$ (e.g., Seth and Woods (55) give the temperature at which $\rho_0(T) \gtrsim \rho_R$ as 50°K for c = 0.13%, T = 80°K for c = 0.61, and T = 120°K for c = 1.75% in Al-Mg alloys) it is expected that such errors, as well as errors arising from the neglect of the Fermi surface distortions, will lead to the "hump" that is observed in $\Delta(T,c)$ coming at the wrong temperature and with the wrong magnitude. This can be seen by looking at the approximate expressions for $\Delta(T,c)$ given in the section on the D.M.R. in the alkali metals where it was shown that the most interesting, non-linear effects occur when $\tau_0(k) \gtrsim \tau_R$, and changing one of these quantities will lead to this equality occurring at a temperature where the anisotropy in $\tau_0(k)$ is different.

The results for the various alloys of Al are presented in the form of two graphs for each impurity. In the first graph, only $\tau_0(\underline{k})$ and τ_R have been included in the calculation, while in the second one the other scattering mechanisms have been included as well as the Debye-Waller factor. The effect of the mass change is only included for those alloys where the mass ratio is at least 2:1 and only for the largest concentrations. As before, a superscript M will be used to denote the fact that the mass effect has been included, i.e., $\rho_a^{(M)}(T)$. For some alloys a third graph is also given which includes all the scattering mechanisms except the Debye-Waller factor.

In Fig. 17, the results for $\Delta(T,c)$ in Al-Ag for the various concentrations studied by Seth and Woods$^{(55)}$ are given. Figure 17(a) was calculated including just $\tau_0(k)$ and τ_R but to show the influence of the mass change on $\tau_0(\underline{k})$, the third curve, for c = 0.18%, was calculated with $\tau_0^{(M)}(\underline{k})$ instead of $\tau_0(\underline{k})$. The effect is to cause a slight decrease in $\Delta(T,c)$ particularly at high T, but it must be remembered that only one of the terms containing mass changes has been included. Figure 17(b) was calculated

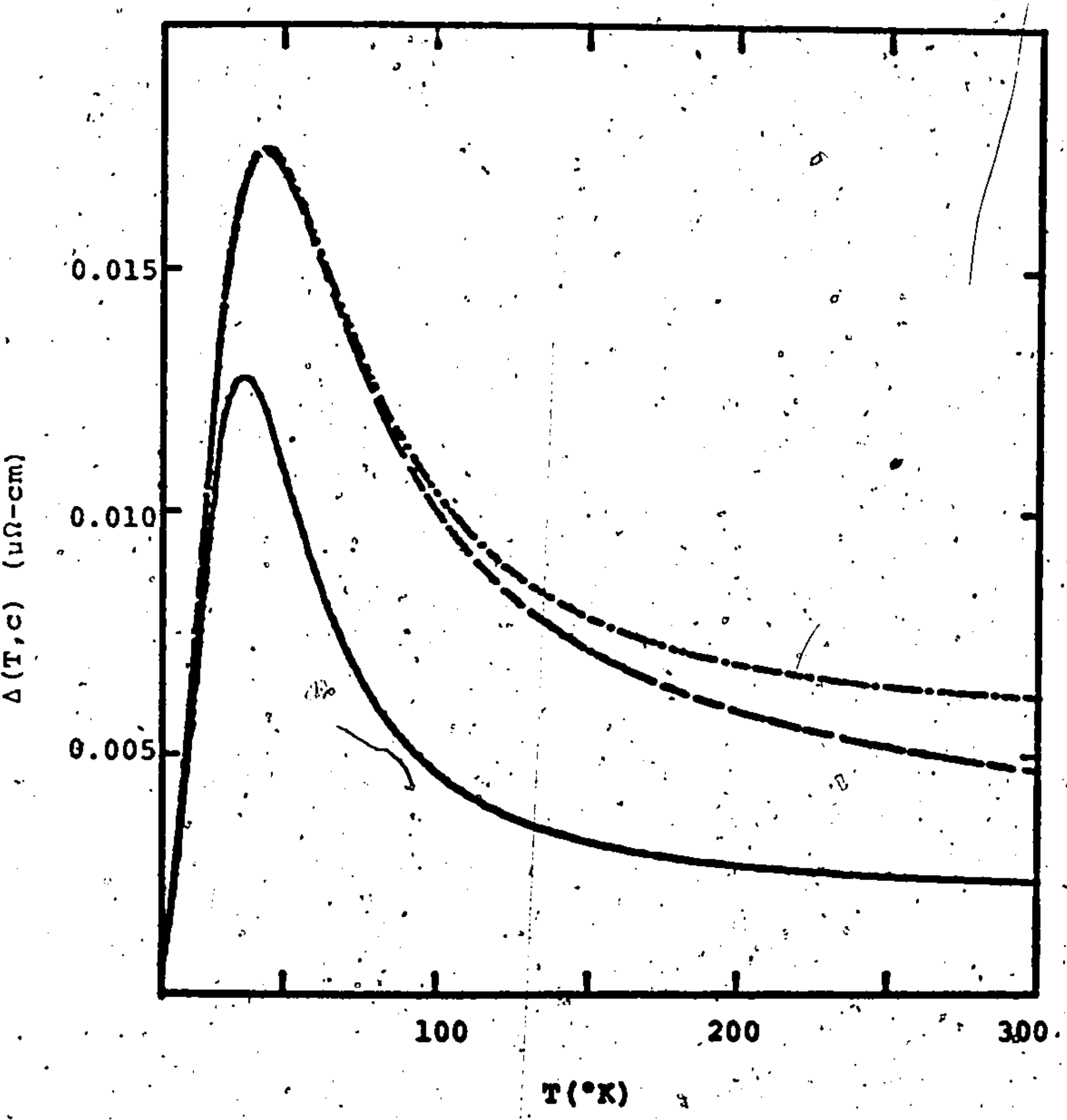


Fig. 17a: Δ(T,c) versus T for Al-Ag with c = 0.06% (——), c = 0.18% (---) and (-·-) including $\tau_0(\underline{k})$ and τ_R in the calculation. For the curve represented by (---) the effect of the mass change was included in $\tau_0^{(M)}(\underline{k})$.

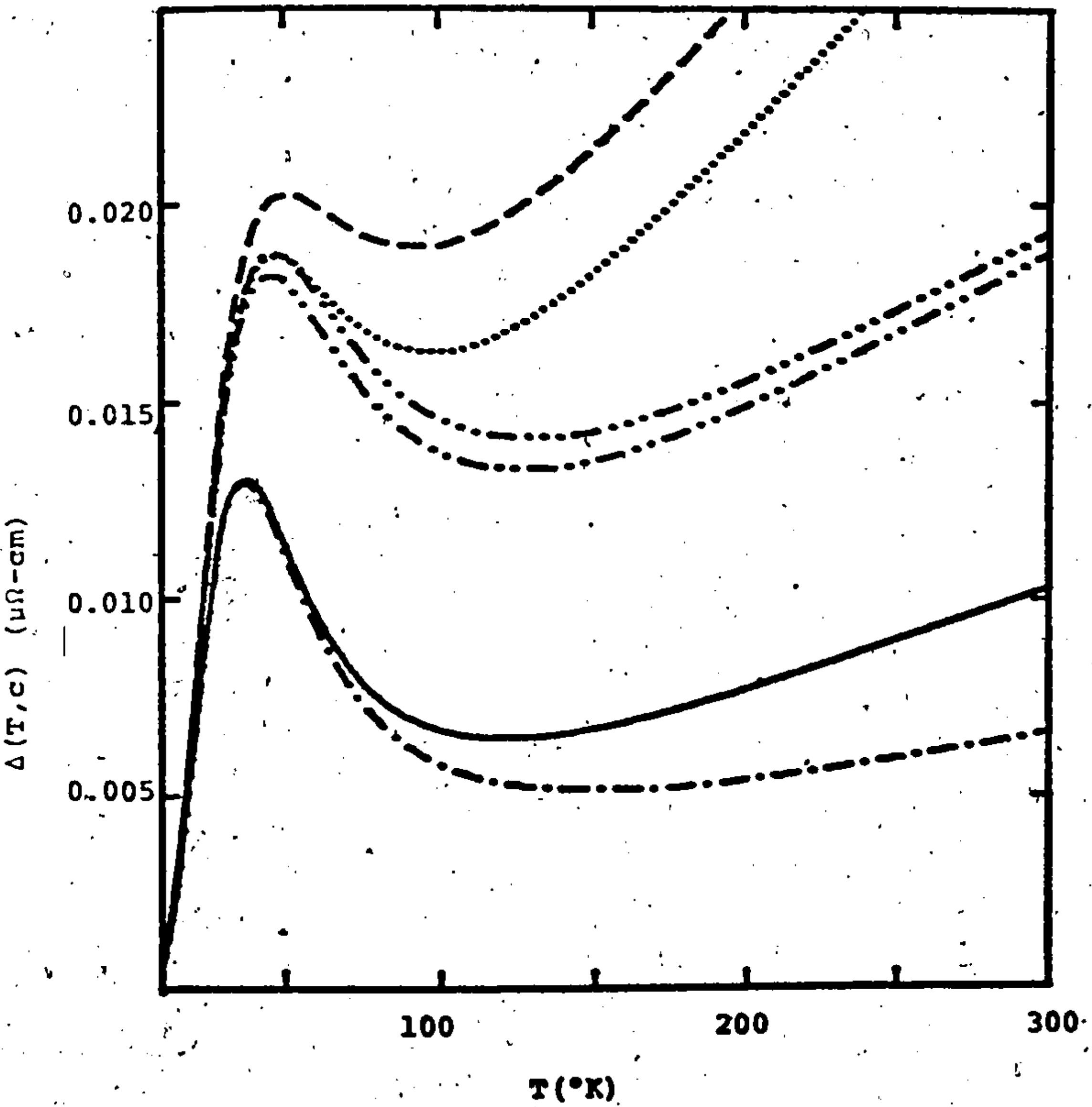


Fig. 17b: Δ(T,c) versus T for Al-Ag including τ_1 and τ_2 as well as $\tau_0(\underline{k})$ and τ_R in the calculation. The results are for c = 0.06% (——) and 0.18% (···) using a value of R_c = 0.359 Å for the silver impurity. The result when the mass changes are included is given by (– – –) for c = 0.18%. The corresponding results using R_c = 1.109 Å for the silver impurity are given by (–·–), (–··–) and (–····–) respectively.

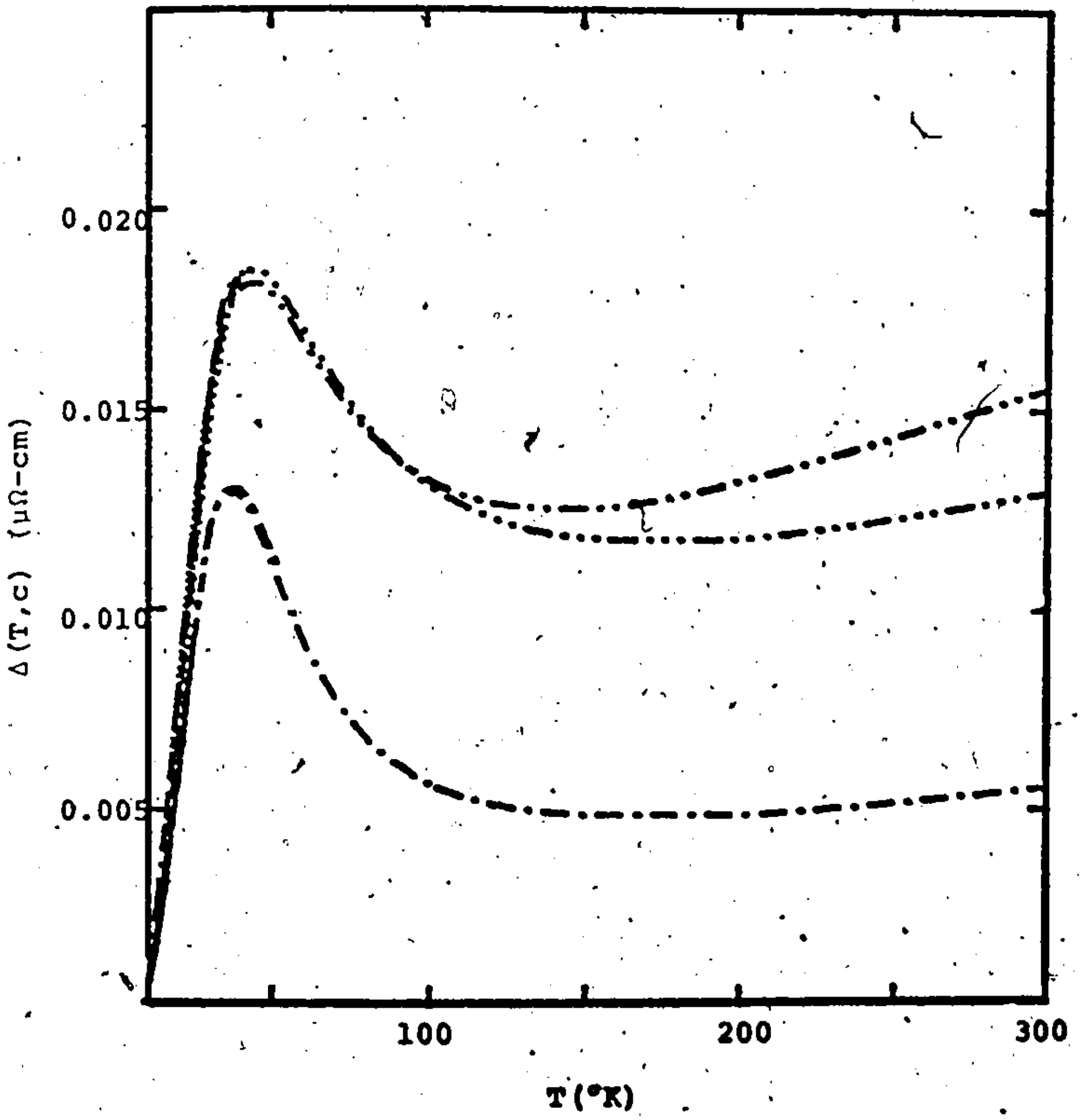


Fig. 17c: Δ(T,c) versus T for Al-Ag using R_c = 1.109 Å for the silver impurity and also including the Debye-Waller factor in the calculation. The results are for c = 0.06% (-·-), 0.18% (-···-), and 0.18% (-··-) when the mass changes are included.

including τ_1 and τ_2 as well, using two different values of the Ashcroft parameter R_c for the impurity, both of which give the same τ_R but which give very different values for τ_1 and τ_2. The value $R_c = 0.359$ Å gives larger values for $\Delta(T,c)$ especially at high T where it causes a very rapid rise in $\Delta(T,c)$. Comparison with experiment shows that in general there is not such a rapid rise, and so in all other calculations, the value of R_c for the impurity producing the smaller $\Delta(T,c)$ was used. Including the mass effect in all relevant terms is now seen to produce a small increase in $\Delta(T,c)$. Figure 17(c) shows the effect of including the Debye-Waller factor as well in ρ_R' and ρ_2. This causes a decrease in $\Delta(T,c)$, particularly at high T leading to better agreement with experiment.

Detailed comparison with the experimental results shows that the size of the hump is a bit too small and that its peak is at a slightly lower temperature. There is more disagreement at high T, particularly when τ_1 and τ_2 are included, giving rise to a linear component in $\Delta(T,c)$ with a positive slope while the experimental $\Delta(T,c)$ has a negative slope above ~ 100°K. Nevertheless, the results in Fig. 17(a), where just $\tau_0(k)$ and τ_R are included, show that the qualitative behaviour of $\Delta(T,c)$ is well understood. These results also show that a negative slope in $\Delta(T,c)$ at high temperature is not necessarily the result of τ_1 giving a negative contribution to $\Delta(T,c)$. In fact, the contribution of τ_1 to $\Delta(T,c)$ calculated in this thesis is always smaller than that of τ_2, which is always positive. Thus the change in the sign of the slope of $\Delta(T,c)$ at high T for complementary alloys mentioned earlier will probably not arise as stated by Bhatia and Gupta (53). However, since none of the calculations here could be done for both members of a pair as this, in general, would involve a noble metal host, i.e., Ag, or a hexagonal closed packed structure for the host material, i.e., Mg, this is not conclusive proof against such a mechanism for explaining the change in sign. Also, the use of better impurity potentials and not restricting the calculation to the Born approximation, might alter the relative importance of τ[illegible] and τ_2.

In Fig. 18 the results for $\Delta(T,c)$ for the Al-Mg alloys considered by Seth and Woods (55) are given. In this case, the results including just $\tau_0(k)$ and τ_R give values that are much too small compared to the experimental ones, while the results when τ_1 and τ_2 are also included are in much better qualitative agreement. The size of the hump, especially for the more concentrated alloys, is about a factor of 2 too small, but the strong linear rise at high T for c = 1.75% is in fair agreement. The linear component for c = 0.61% is, however, too strong. The value of $R_c = 0.772$ Å for the Mg impurity was chosen to give ρ_R in agreement with the usual theoretical values (9). As mentioned by Fukai (9), including the effect of the distorted

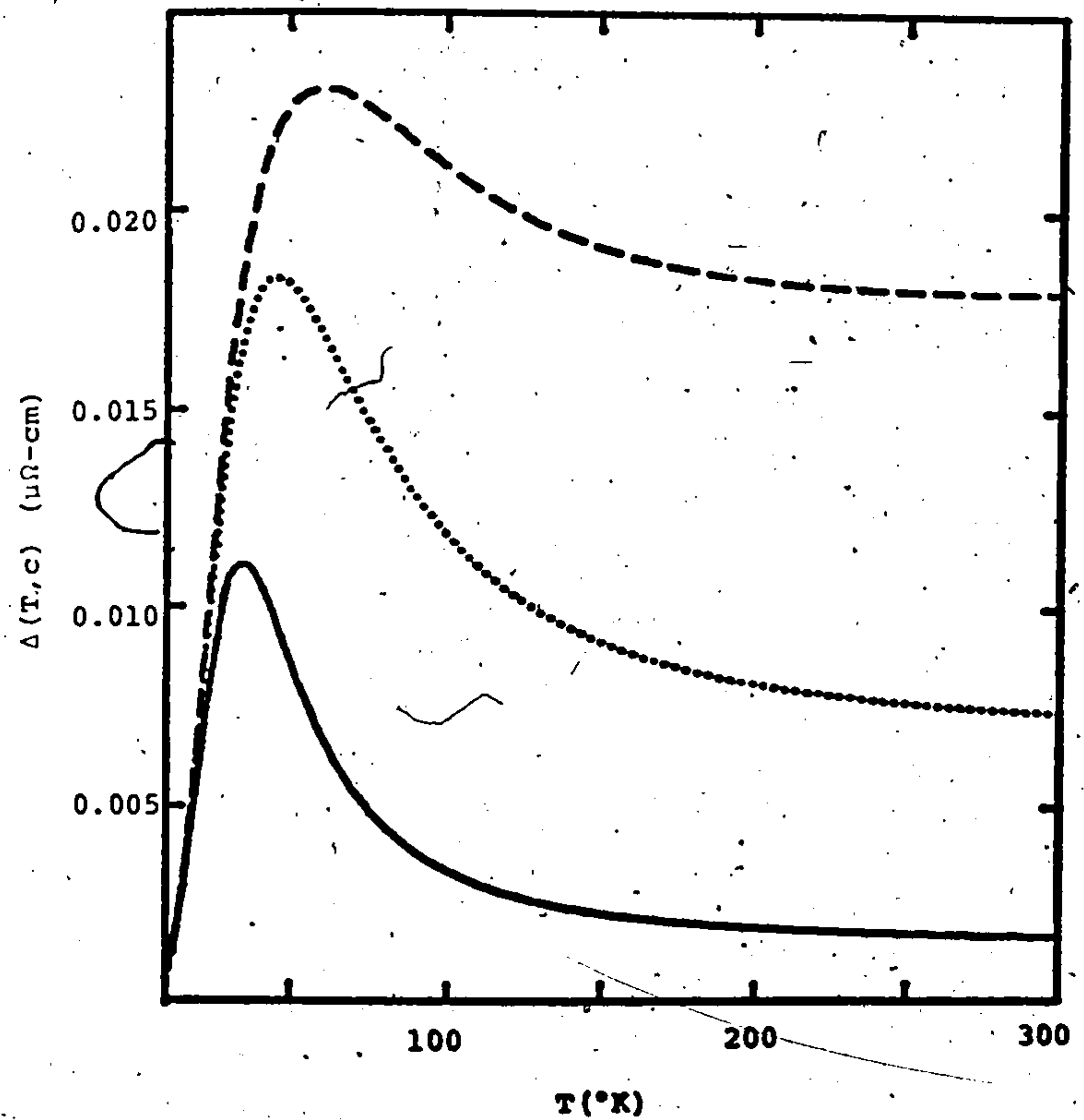


Fig. 18a: Δ(T,c) versus T for the Al-Mg alloys studied by Seth and Woods, with c = 0.13% (——), 0.61% (···) and 1.75% (---). Only $\tau_0(\underline{k})$ and τ_R were included in the calculation.

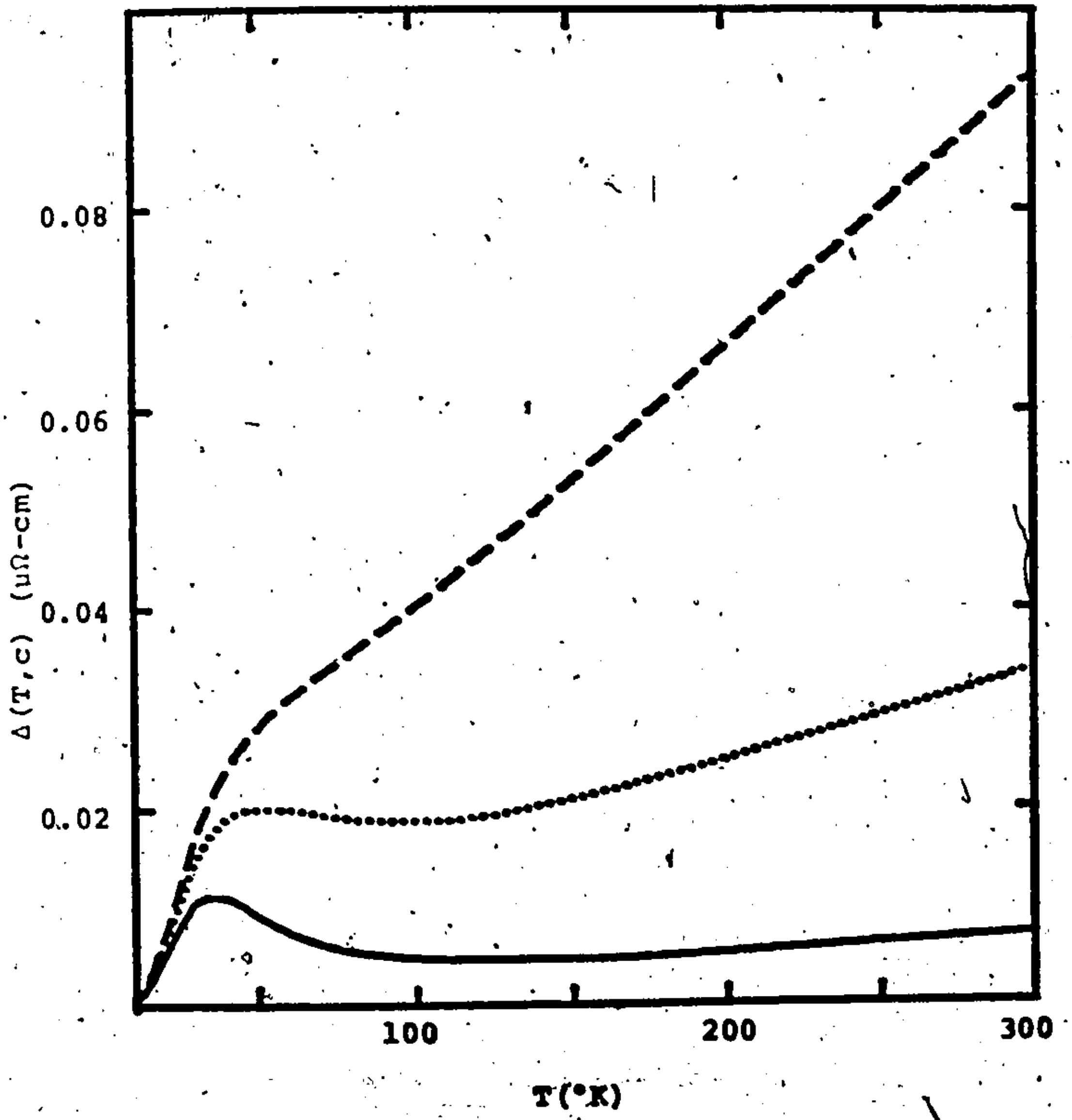


Fig. 18b: Same as Fig. 18a except that τ_1 and τ_2 were also included in the calculation.

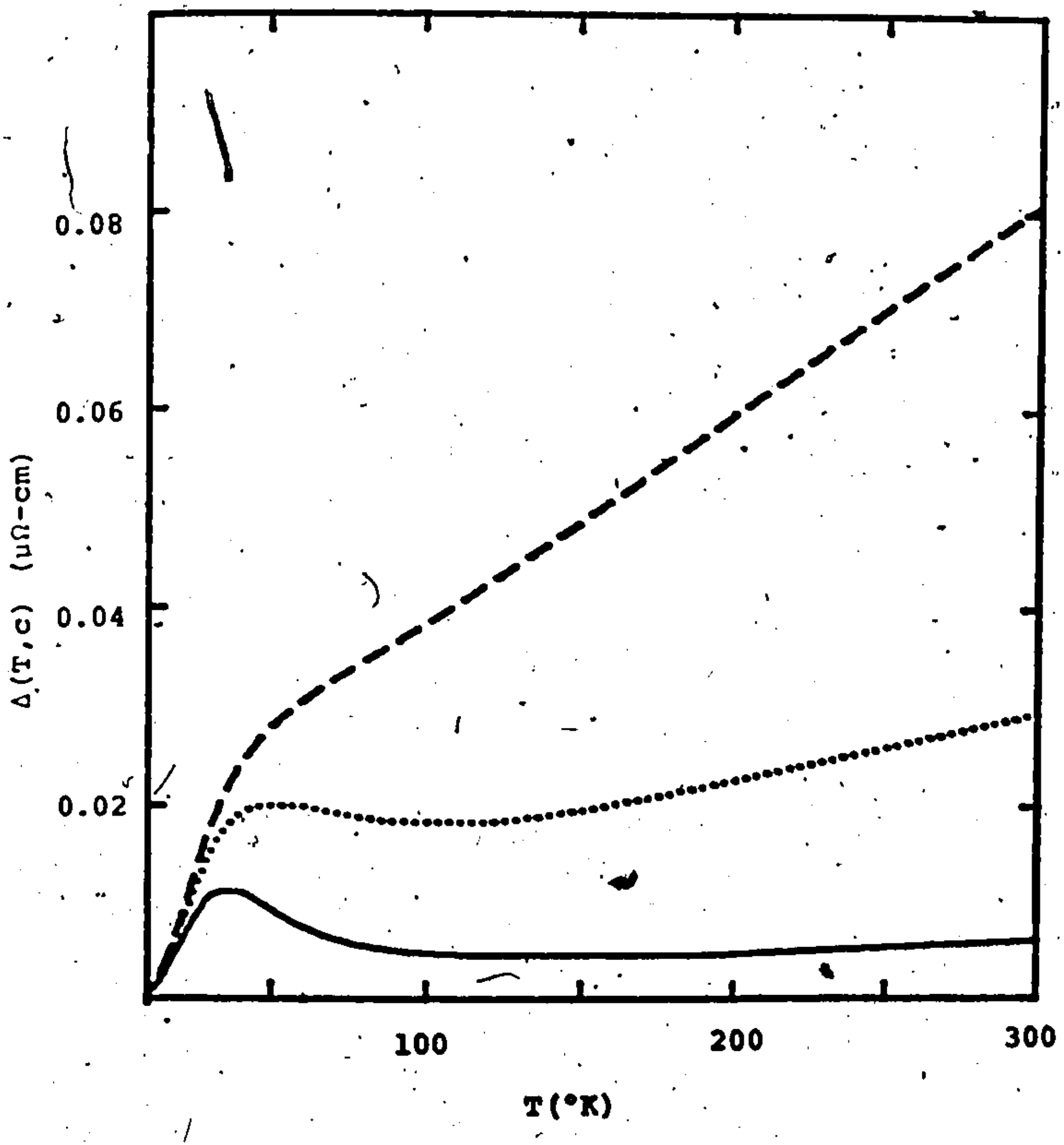


Fig. 18c: Same as Fig. 18b except that the Debye-Waller factor was included.

Fermi surface in calculating ρ_R gives much better agreement with experiment. Such effects would also influence ρ_2 as well as ρ_0 and ρ_1.

Next, in Fig. 19 the results for $\Delta(T,c)/\rho_R$ for the Al-Mg alloys considered by Carter (56) are presented. The most noticeable result of plotting $\Delta(T,c)/\rho_R$ instead of $\Delta(T,c)$ is that in the former case the largest values are obtained for the smallest ρ_R while in the latter case, the opposite is true. This provides strong evidence that it is a fundamental property of the pure metal, i.e., the anisotropy, which is very sensitive to a small amount of impurities, that gives the major contribution to the D.M.R.. Also, it shows that $\Delta(T,c)$ has a concentration dependence which is weaker than linear at low T. Detailed comparison with the experimental data shows that the hump is of the right magnitude and occurs at almost the correct temperature; but that the subsequent decrease in $\Delta(T,c)/\rho_R$ is much too large. For the more concentrated samples, there is again a too large linear component at high T. Also, the experimental data shows a significant linear rise in $\Delta(T,c)/\rho_R$ for the 2 most dilute alloys, in direct contrast to the theoretical results in Fig. 19 which are essentially flat at high T. This is also in disagreement with the data of Seth and Woods, as has been pointed out by Bass (39). Carter (56) has included corrections for volume changes to his data while Seth and Woods have not. If Carter's data is indeed correct

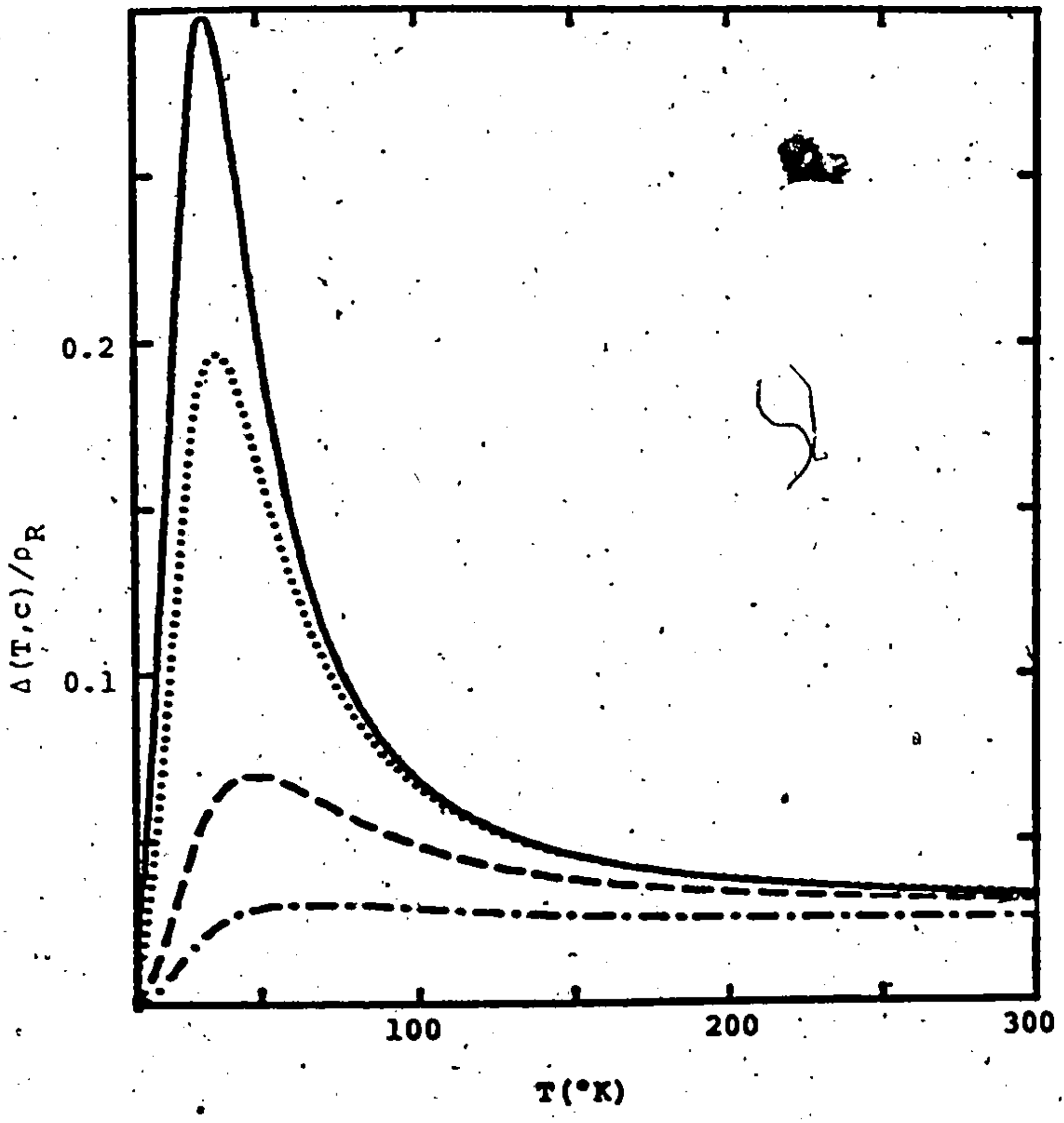


Fig. 19a: $\Delta(T,c)/\rho_R$ versus T for the Al-Mg alloys studied by Carter, with c = 0.03% (——), 0.1% (···), 0.5% (----) and 1.5% (-·-). Only $\tau_0(\underline{k})$ and τ_R were included in the calculation.

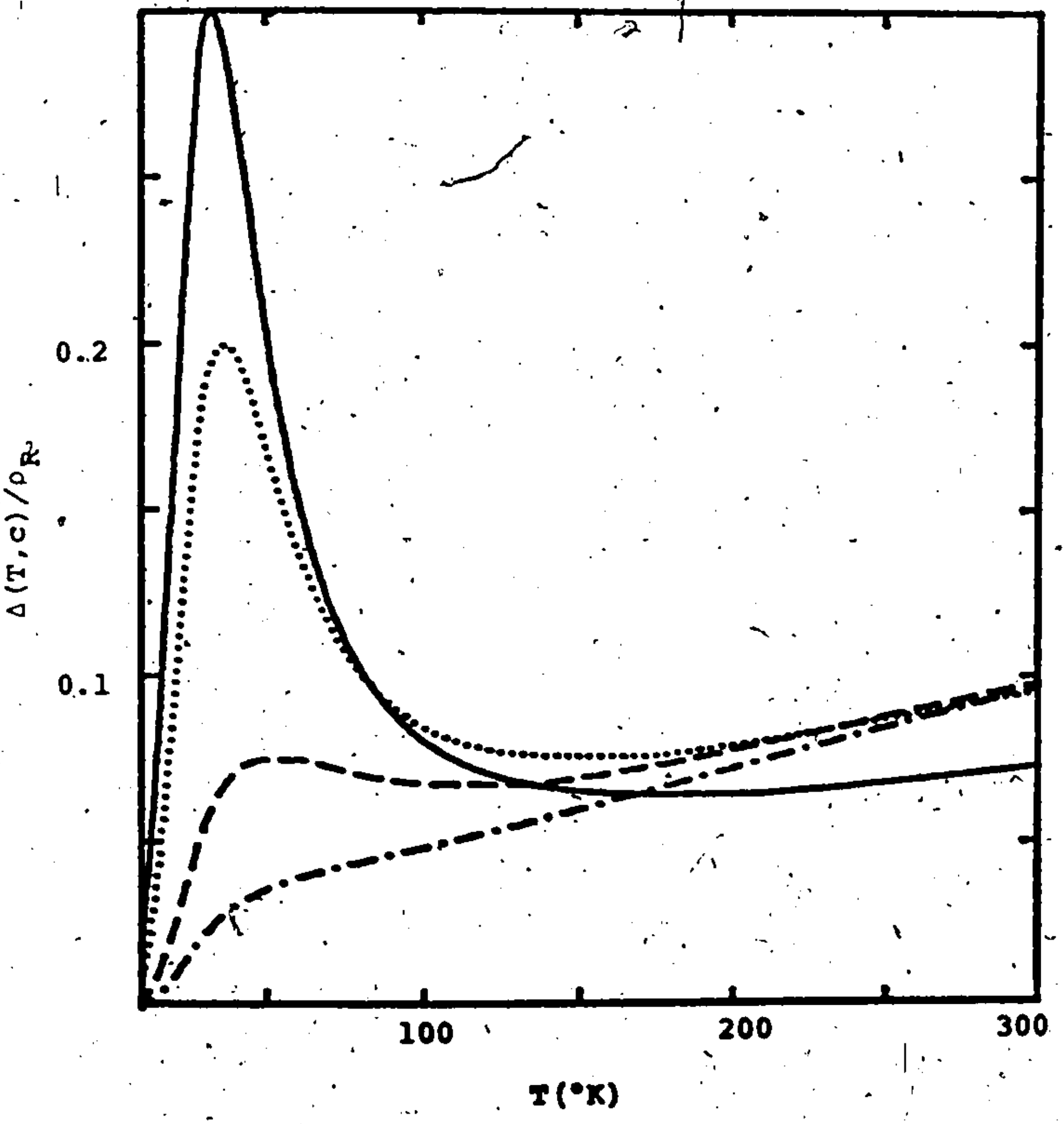


Fig. 19b: Same as Fig. 19a except that τ_1 and τ_2 as well as the Debye-Waller factor were included in the calculation.

so that a strong linear component exists in $\Delta(T,c)/\rho_R$ for small ρ_R and a weaker component for larger ρ_R, then it would be in very strong disagreement with the basic mechanisms contributing to the D.M.R. presented here since it is difficult to imagine that the use of better treatments of the Fermi surface anisotropy and the impurity potential could ever give a result for $\Delta(T,c)/\rho_R$ which has a stronger linear component for the smaller values of ρ_R. This is simply due to the fact that it is τ_1 and τ_2 which give this linear component and they are both proportional to the concentration while Carter's results give larger values for $\Delta(T,c)/\rho_R$ for the more dilute samples at room temperature.

The results corresponding to Carter's data for Al-Cu, Al-Ga and Al-Zn alloys are shown in Figs. 20 to 22 respectively. The agreement between theory for the size and location of the hump in $\Delta(T,c)/\rho_R$ is in general fair but the rapid decrease in $\Delta(T,c)/\rho_R$ past the peak is a general feature of the calculations which is not observed experimentally. For the more concentrated samples, the qualitative behaviour of $\Delta(T,c)/\rho_R$ is better given when only $\tau_0(k)$ and τ_R are included but the magnitude is usually only about one half the experimental value. Similarly, the strong linear rise in $\Delta(T,c)/\rho_R$ present for the more dilute alloys but essentially absent for the concentrated ones is in sharp contrast to the theoretical results, but as mentioned above, there is disagreement between the experimentalists on this

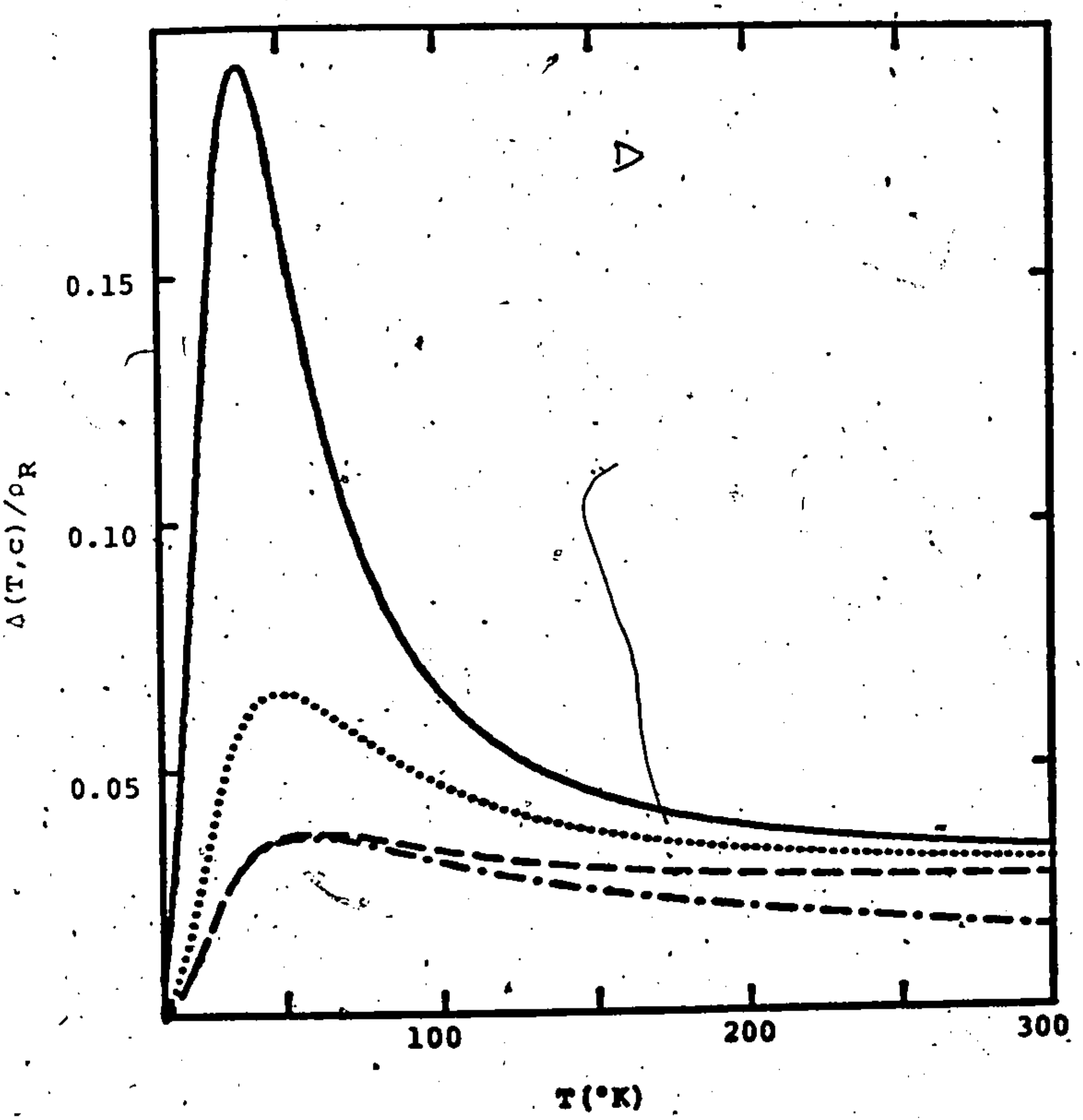


Fig. 20a: $\Delta(T,c)/\rho_R$ for the Al-Cu alloys studied by Carter, with c = 0.09% (——), 0.52% (···), 1.03% (---) and 1.03% (-·-) (including the mass change). Only $\tau_0(\underline{k})$ and τ_R were included in the calculation.

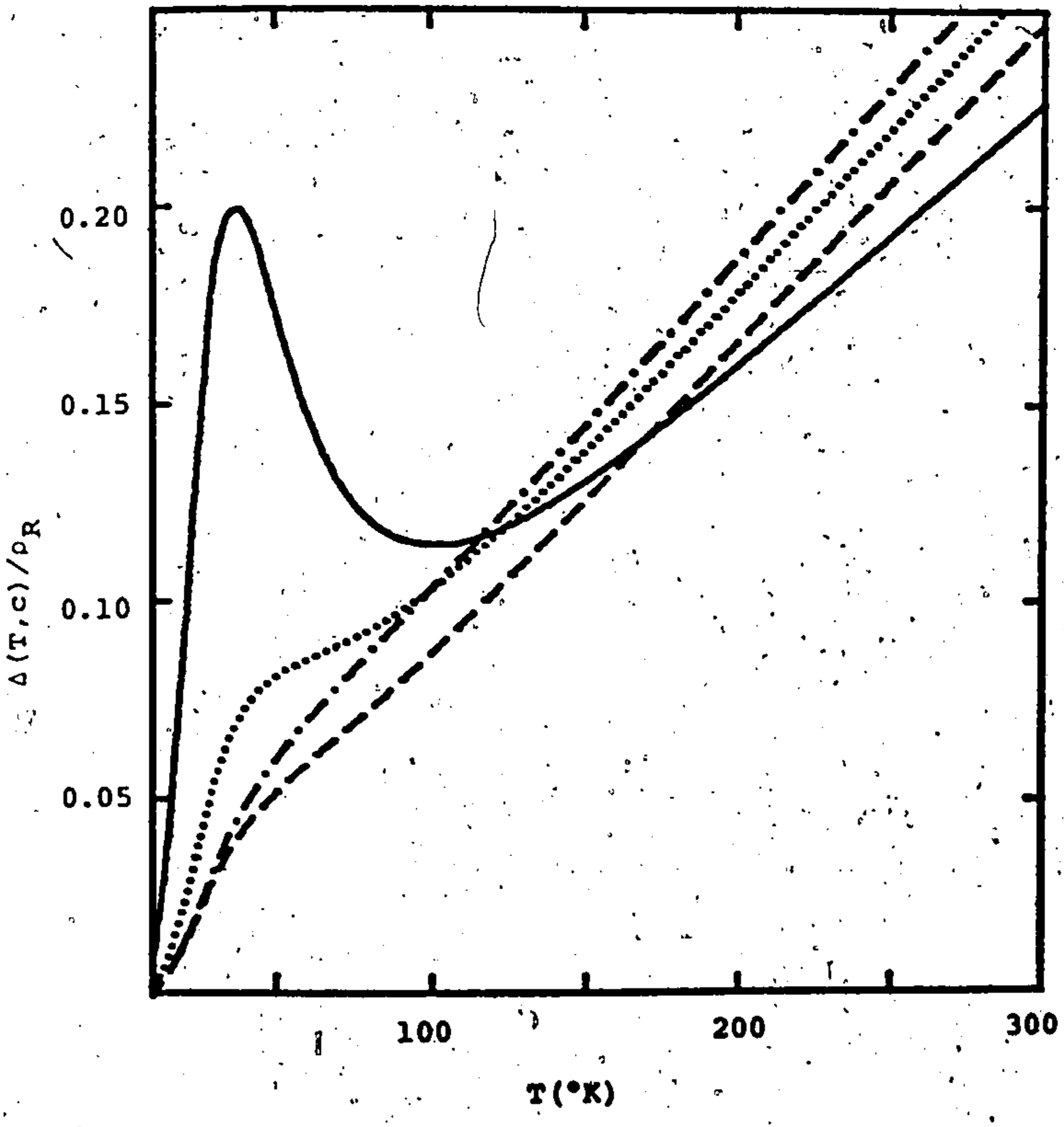


Fig. 20b: Same as Fig. 20a except that τ_1 and τ_2 were included in the calculation.

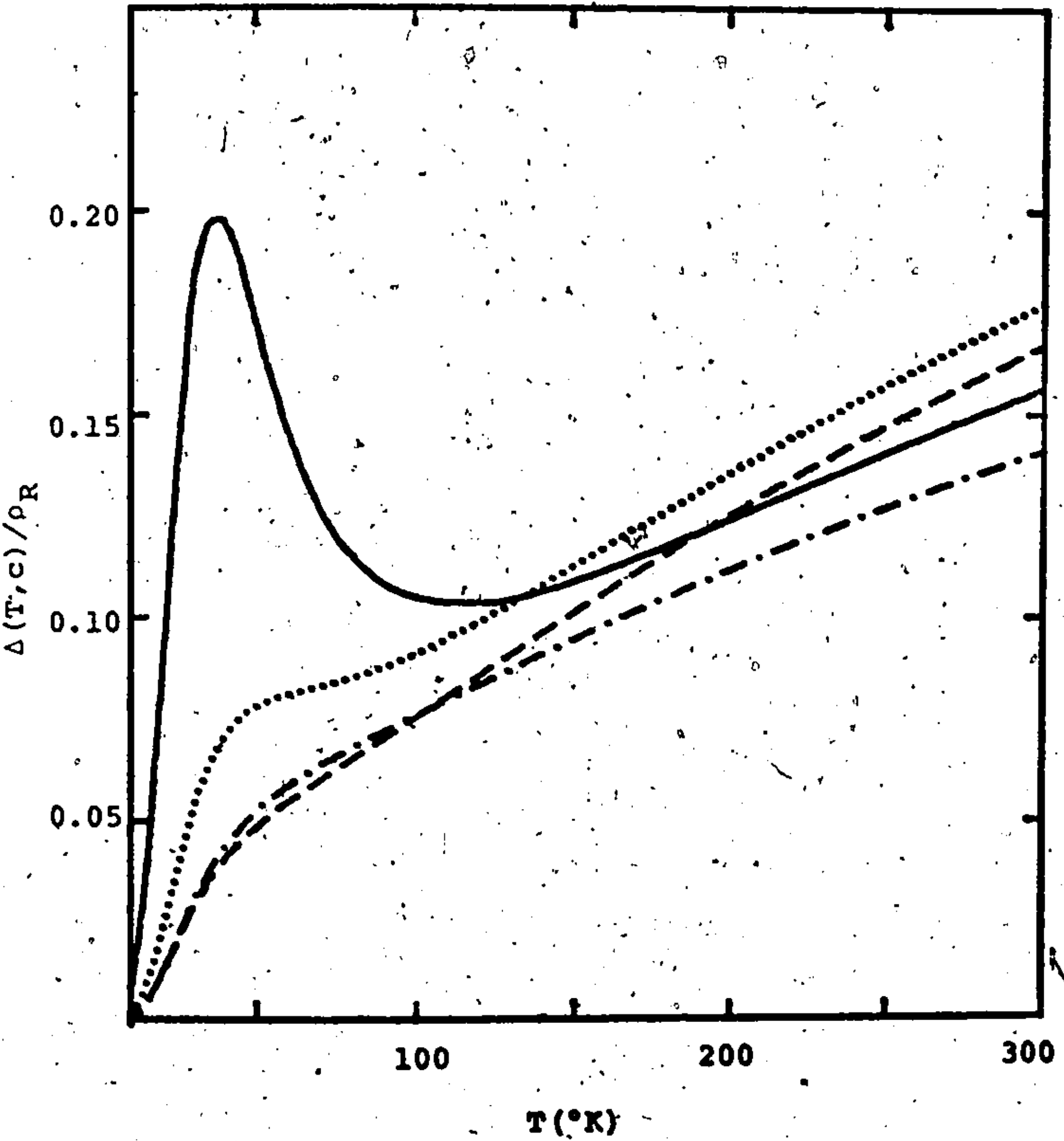


Fig. 20c: Same as Fig. 20b except that the Debye-Waller factor was also included in the calculation.

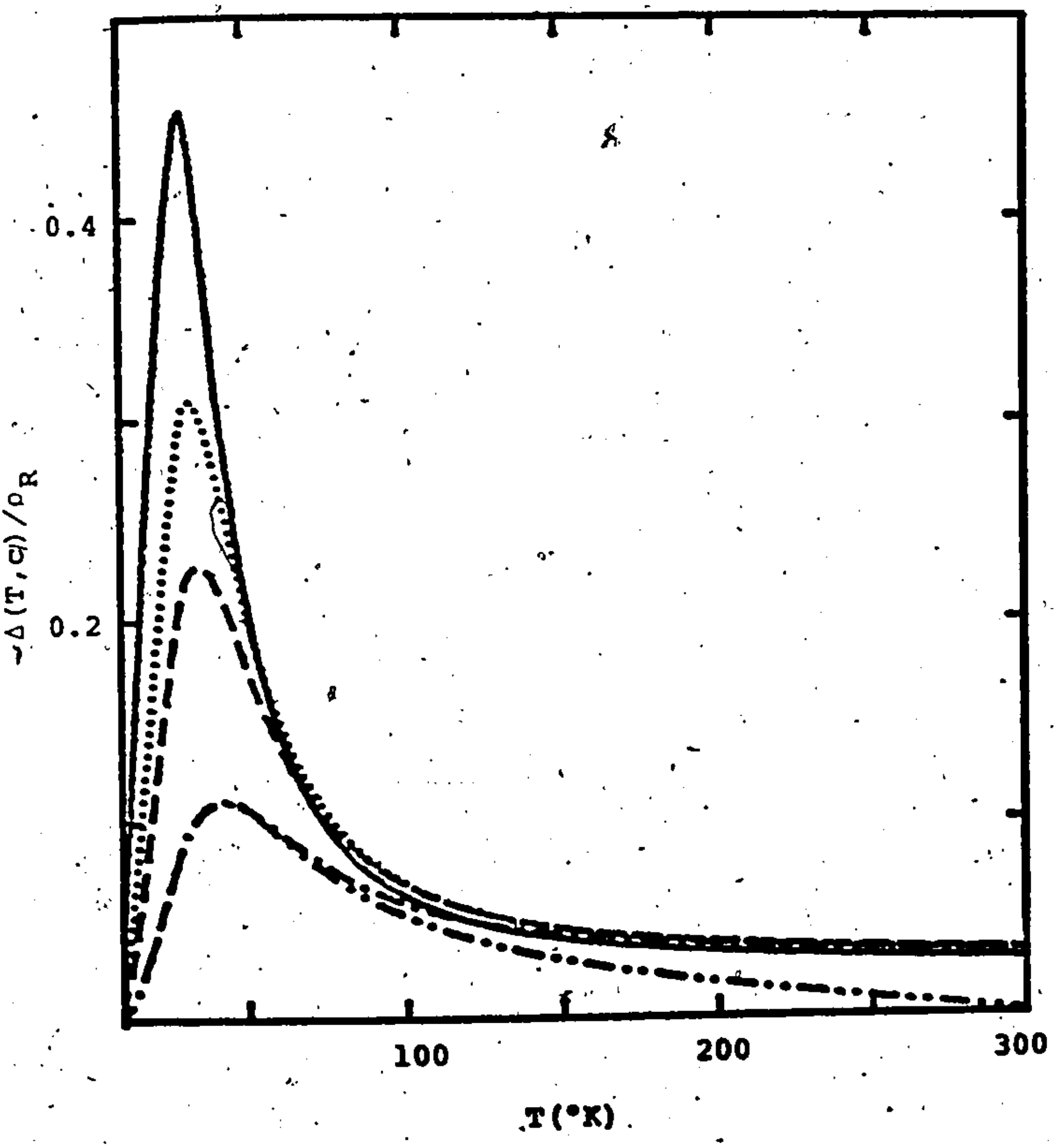


Fig. 21a: $\Delta(T,c)/\rho_R$ versus T for the Al-Ga alloys studied by Carter, with c = 0.035% (——), 0.108 (···), 0.198 (- - -), 0.664% (-·-) and 0.664% (-··-) (including the mass change). Only $\tau_0(\underline{k})$ and τ_R were included in the calculation.

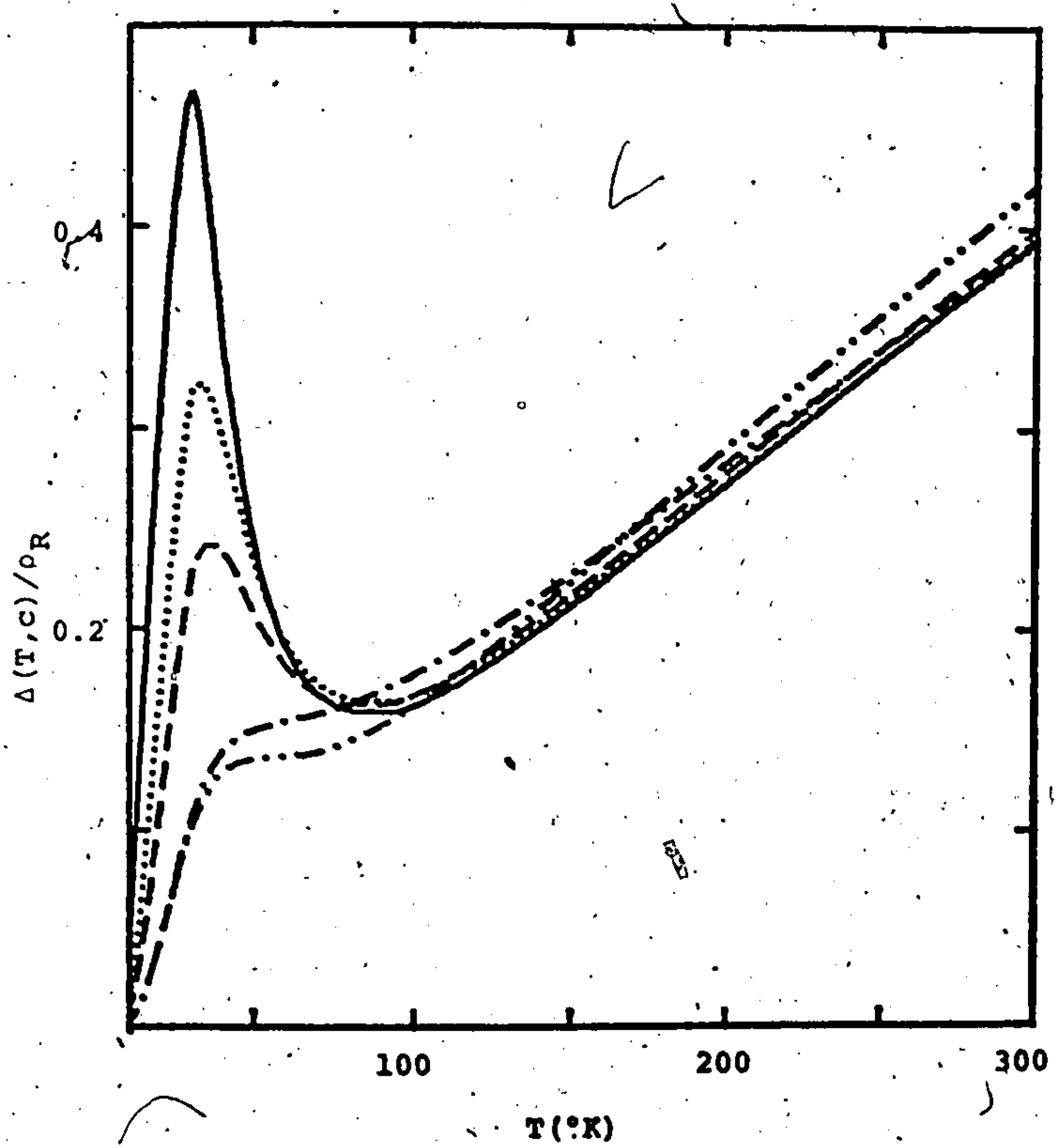


Fig. 21b: Same as Fig. 21a except that τ_1 and τ_2 as well as the Debye-Waller factor were also included in the calculation.

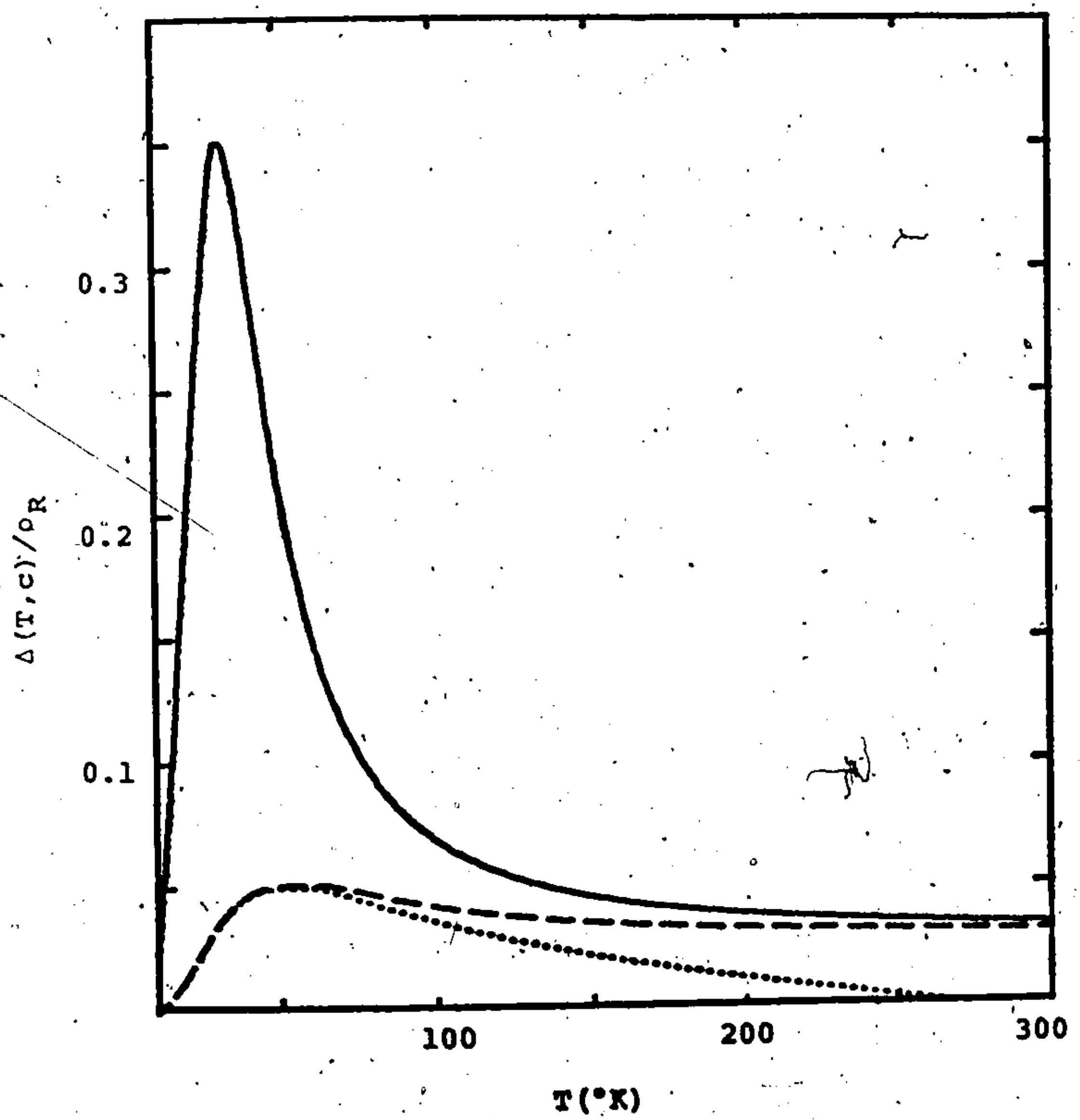


Fig. 22a: $\Delta(T,c)/\rho_R$ versus T for the Al-Zn alloys studied by Carter, with c = 0.1% (——), 2.1% (---) and 2.1% (···) (including the mass change). Only $\tau_0(\underline{k})$ and τ_R were included in the calculation.

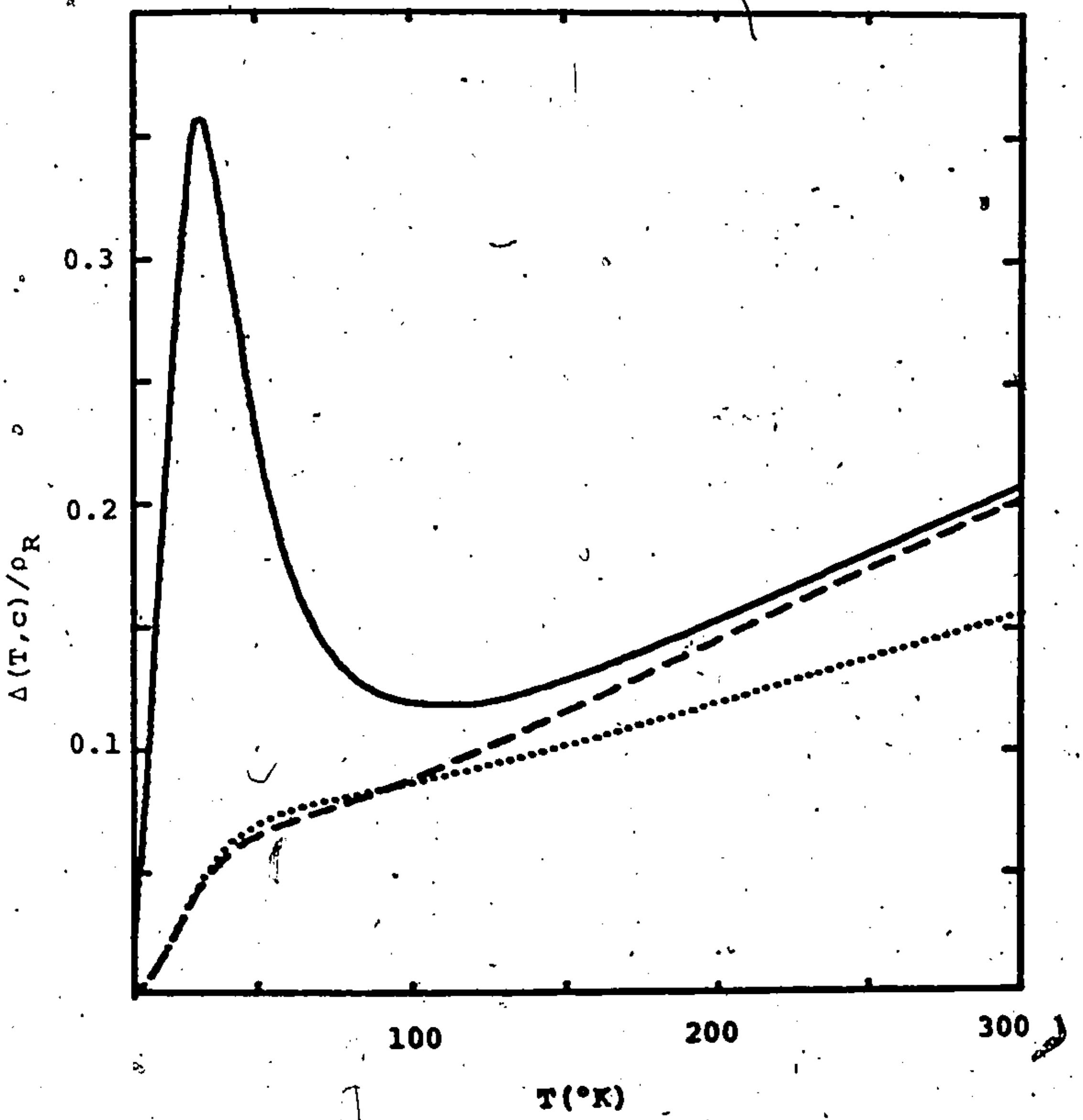


Fig. 22b: Same as Fig. 22a except that τ_1 and τ_2 as well as the Debye-Waller factor were included in the calculation.

point, so that it would be very desirable to have further experimental work in these alloys at temperatures above 100°K.

The effect of the mass changes is in general seen to be small but it must be remembered that Cu, Ga and Zn are less than three times as heavy as Al. This agrees with the conclusions of Seth and Woods (55) who did not find any significant effects that could be attributed to the mass changes. This fact is clearly shown in Fig. 23, where calculations with $c = 1\%$ for Al with Ag, Cu, Ga and Zn are shown with and without the mass change. In all cases the changes are small and, since they do not exhibit any characteristic structure, difficult to deduce from the comparison of theory and experiment in view of the many other uncertainties in the calculations which overshadow the small effect.

All of the calculated values of $\Delta(T,c)/\rho_R$ show a very sharp hump for the smallest values of ρ_R, in disagreement with the experiments which show a much broader hump which only comes down very slightly to the right of the peak before the linear rise takes over. The sharp hump in the calculations is a direct result of the form of anisotropy in $\tau_0(\underline{k})$. Since a rather arbitrary renormalization procedure, mentioned earlier, was used on the first $\frac{1}{5}$ of the effective frequency distributions, this makes the values of $\tau_0(\underline{k})$ up to $\theta_D/5 \gtrsim 85°K$ doubtful. In contrast to the case of Al, the

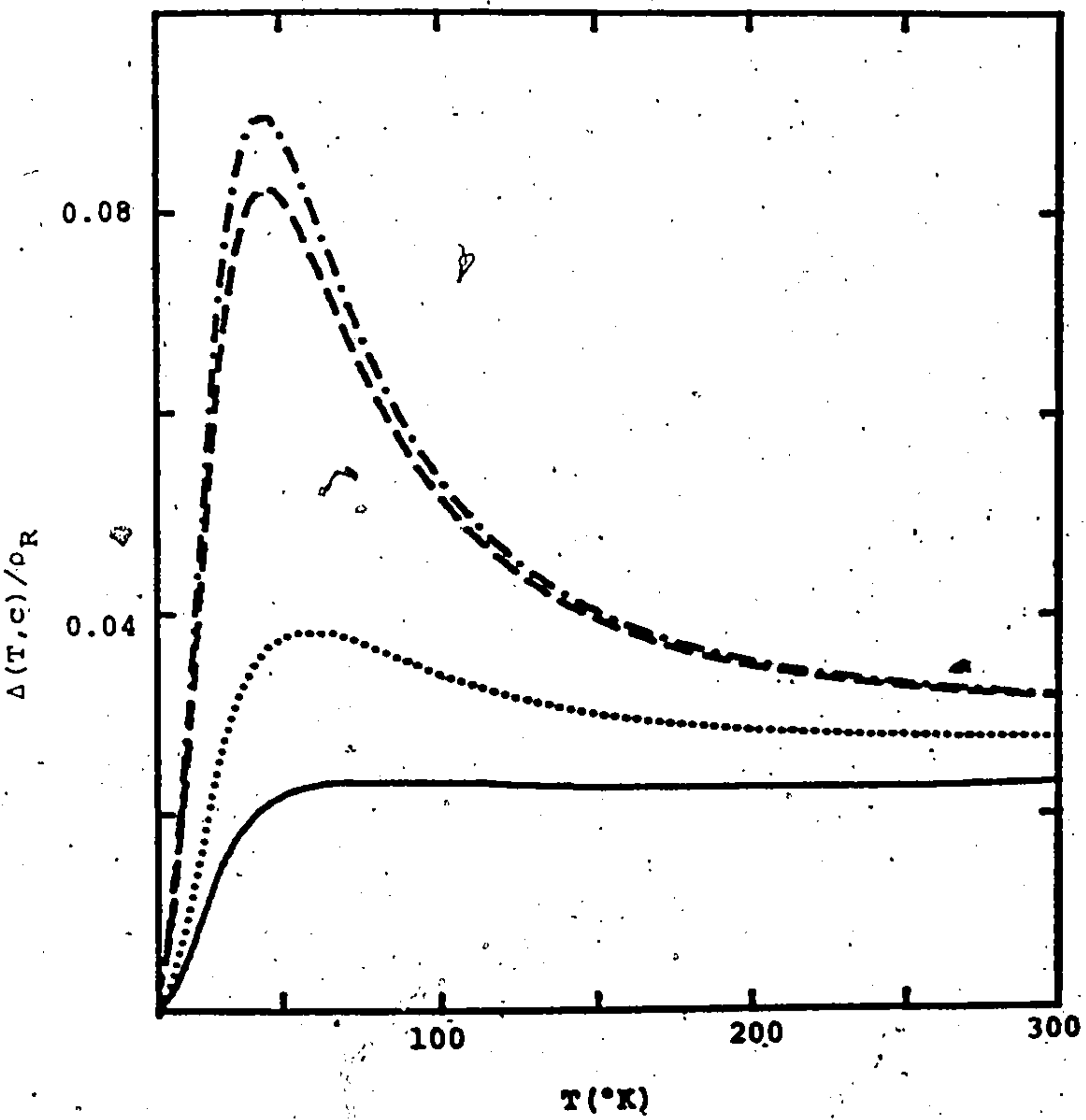


Fig. 23a: $\Delta(T,c)/\rho_R$ versus T for the study of the effect of mass changes, keeping c = 1% in all samples. This figure serves as a basis of comparison since the mass change is set equal to zero here, and only $\tau_0(\underline{k})$ and τ_R are included for Al-Ag (——), Al-Cu (···), Al-Ga (---) and Al-Zn (-·-).

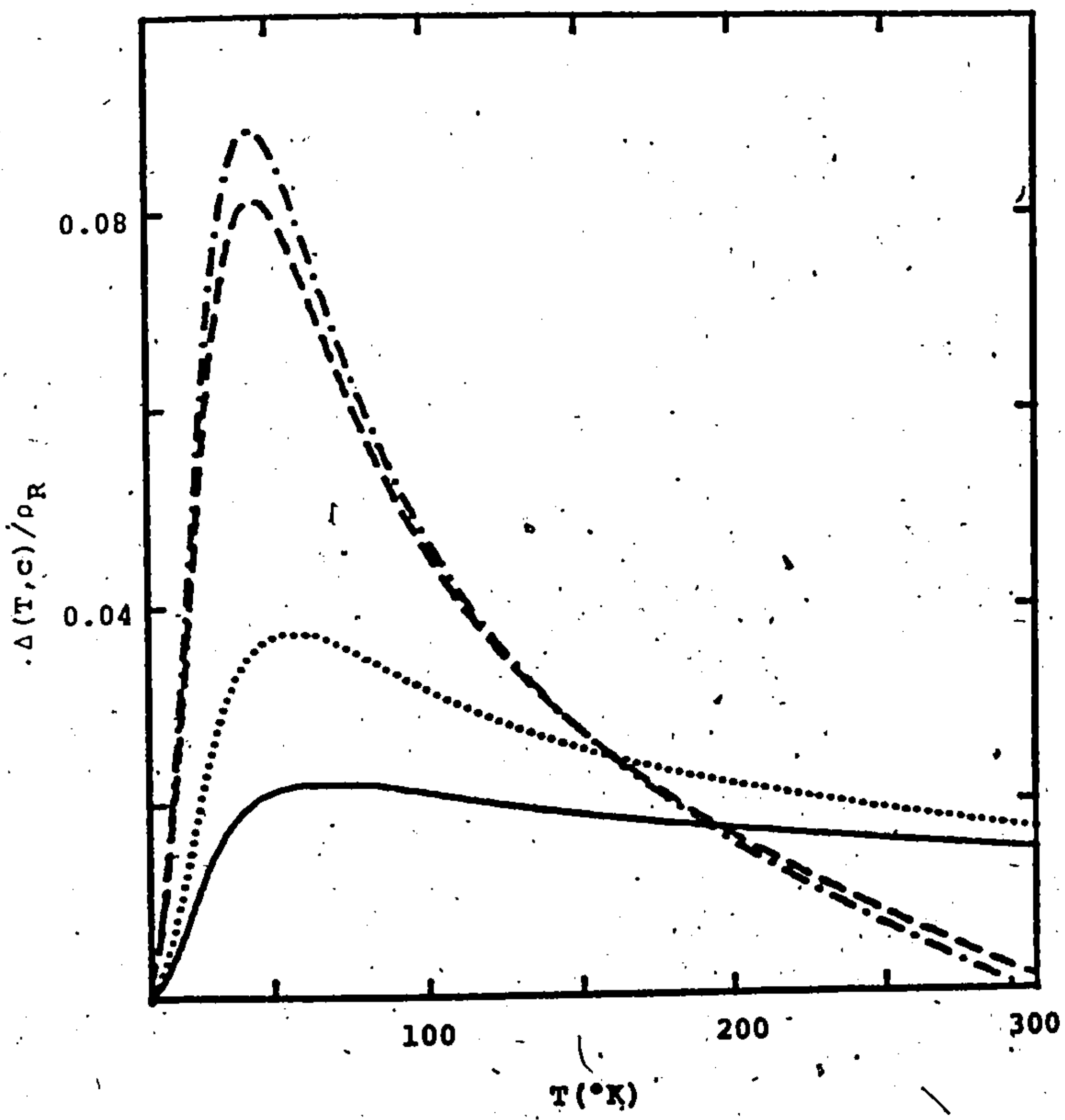


Fig. 23b: Same as Fig. 23a except that the effect of the mass change is included in $\tau_0^{(M)}(\underline{k})$.

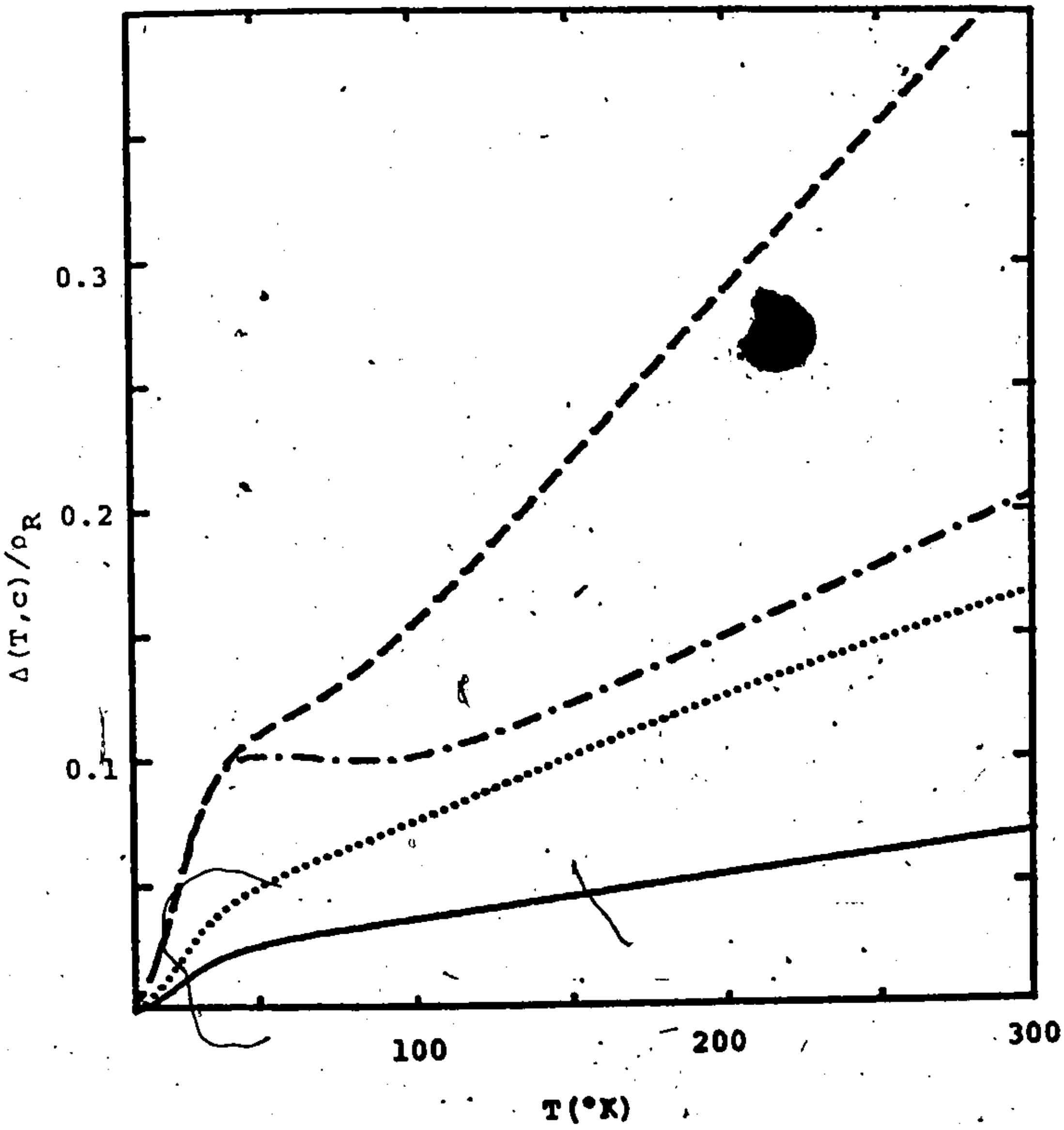


Fig. 23c: Same as Fig. 23a except that τ_1 and τ_2 as well as the Debye-Waller factor were included.

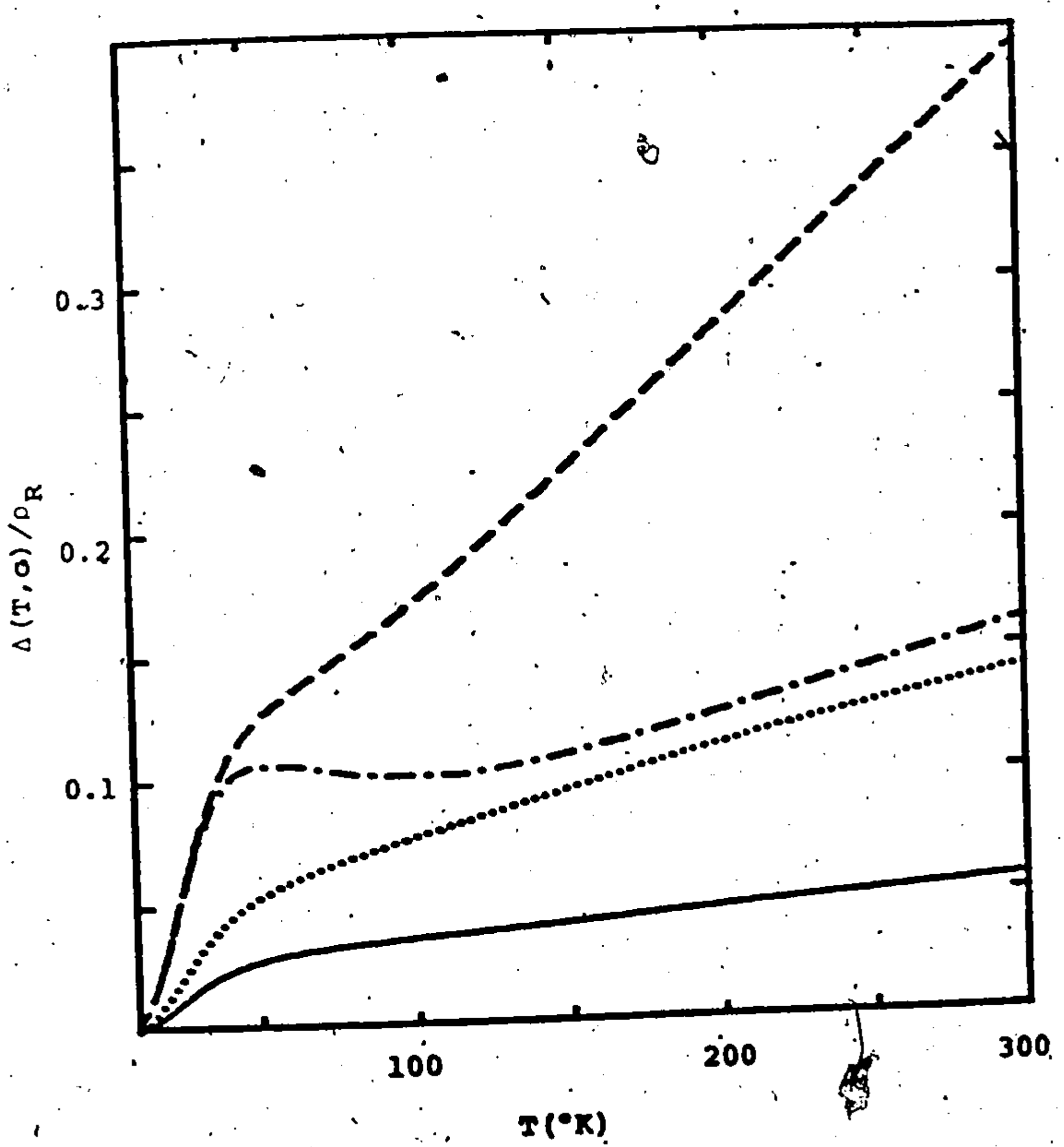


Fig. 23d: Same as Fig. 23c except that the effect of the mass change has been included.

anisotropy in Li shows a broader structure [36], persisting to higher temperature. This leads to the broader hump observed in the Li alloys. Another, more subtle effect should also be mentioned. For potassium, considered earlier, several different pseudopotentials were used in the calculation and it was found that the Bardeen pseudopotential gave a much larger amount of anisotropy than the Ashcroft form. A similar problem may also exist in aluminum.

CHAPTER IV

EFFECT OF LATTICE RELAXATION ON THE RESISTIVITY

4.1 Relation to the Lattice Statics at $T = 0$

In Chapter I it was shown that the relaxation of the host atoms around an impurity in a metal give rise to an additional scattering mechanism for the conduction electrons. This introduces a correction to the Friedel Sum Rule and to the usual expression for the residual resistivity. It was mentioned in the discussion of the D.M.R. that volume changes and strain fields, present in an alloy but not in the pure metal, can also contribute to the D.M.R. in a substantial fashion. Since the experimental values of ρ_R, which of course include the effect of the lattice relaxation, were used in the calculations, it is of interest to try to include such corrections explicitly in the finite temperature resistivity of the alloy.

Damon et al. (72) have given a simple phenomenological theory of the effect of the strain around an impurity on the resistivity. Bergmann (84) has considered the effect of ions displaced from their perfect lattice positions in a discussion of disorder in a superconductor, and Vail (85) has considered the combined effect of lattice relaxation and the thermal vibrations of ions at finite temperature in connection with the theory of polarons and F centers.

In this chapter a simple theory to include the effect of lattice relaxation both at T = 0 and at finite T will be given. The model for the lattice is similar to that used in connection with the D.M.R.: ~~one~~ impurity atom at the origin with a scattering cross section different from that of a host atom, but with the same mass as the host atoms. This is not a very severe restriction because the effects of mass changes on the D.M.R. were found generally to be small in detailed calculations.

When lattice relaxation is included, the Hamiltonian for the lattice is, to lowest order (set $\hbar \equiv 1$ for convenience)

$$H_L = \sum_{\underline{q}\lambda} g_{\underline{q}\lambda} \left(a_{\underline{q}\lambda} + a^{\dagger}_{-\underline{q}\lambda}\right) + \sum_{\underline{q}\lambda} \omega(\underline{q}\lambda) a^{\dagger}_{\underline{q}\lambda} a_{\underline{q}\lambda} \tag{4.1}$$

where $a_{\underline{q}\lambda}$ and $a^{\dagger}_{\underline{q}\lambda}$ are the phonon destruction and creation operators for a phonon with wavevector $\underline{q}$, branch index λ and energy $\omega(\underline{q}\lambda)$. The coupling constant, $g_{\underline{q}\lambda}$, for the impurity is

$$g_{\underline{q}\lambda} = \sum_{\ell\neq 0} \left(\frac{1}{2\omega(\underline{q}\lambda)NM}\right)^{1/2} \underline{\epsilon}(\underline{q}\lambda)\cdot\nabla U_{\ell}\, e^{i\underline{q}\cdot\underline{R}^{0}_{\ell}} \tag{4.2}$$

where U_{ℓ} is the potential given in Eq. (2.31) from which the force driving the host atoms to the relaxed positions may be derived. The second term in Eq. (4.1) is just the usual one for a perfect harmonic lattice while the first term, which is linear in the ionic displacement or phonon operators, would be zero in a perfect lattice. Both the force constant matrix implicit in $\omega(\underline{q}\lambda)$ and the perturbing potential U_ℓ are to be evaluated at the equilibrium sites of the perfect lattice, in contrast to the method of lattice statics$^{(7)}$ where the perturbing potential is evaluated at the relaxed positions.

It will be immediately recognized that H_L is just the Hamiltonian for a three-dimensional system of displaced harmonic oscillators which can be diagonalized by the unitary transformation$^{(86)}$

$$A = \exp\left(- \sum_{\underline{q}\lambda} \frac{g_{\underline{q}\lambda}}{\omega(\underline{q}\lambda)} (a_{\underline{q}\lambda} - a^{\dagger}_{-\underline{q}\lambda})\right) \qquad (4.3)$$

so that

$$H_D = AH_LA^{\dagger} = \sum_{\underline{q}\lambda} \omega(\underline{q}\lambda)\, a^{\dagger}_{\underline{q}\lambda} a_{\underline{q}\lambda} - \Delta\epsilon \quad . \qquad (4.4)$$

Here $\Delta\epsilon$ is a constant shift in energy given by

$$\Delta\epsilon = \sum_{\underline{q}\lambda} \frac{|g_{\underline{q}\lambda}|^2}{\omega(\underline{q}\lambda)} \quad . \qquad (4.5)$$

If the eigenstates of the harmonic Hamiltonian, H_0, i.e., just the second term of Eq. (4.1), are denoted by $|\phi\rangle$, then they are also eigenstates of H_D, but the eigenvalues of H_D differ by $\Delta\varepsilon$. Denote the eigenstates of H_L by $|\psi\rangle$ and they are related to the $|\phi\rangle$ by

$$|\psi\rangle = A^{\dagger}|\phi\rangle \tag{4.6}$$

where $\dagger$ means the hermitian conjugate.

The displacement or relaxation $\underline{\Delta}_{\ell}$ of a host ion originally at $\underline{R}^0_{\ell}$ may be calculated in terms of the displacement operator $\underline{u}_{\ell}$ by

$$\underline{\Delta}_{\ell} = \langle\psi|\underline{u}_{\ell}|\psi\rangle \tag{4.7}$$

where, in terms of the phonon operators, $\underline{u}_{\ell}$ is given by

$$\underline{u}_{\ell} = \sum_{\underline{q}\lambda}^{\mathrm{B.Z.}} \left(\frac{1}{2MN\omega(\underline{q}\lambda)}\right)^{1/2} \underline{\varepsilon}(\underline{q}\lambda)\, e^{-i\underline{q}\cdot\underline{R}^0_{\ell}}(a_{\underline{q}\lambda} + a^{\dagger}_{-\underline{q}\lambda}) \tag{4.8}$$

Using Eq. (4.6) the formula for $\underline{\Delta}_{\ell}$ may be rewritten as

$$\underline{\Delta}_{\ell} = \langle\phi|A\underline{u}_{\ell}A^{\dagger}|\phi\rangle \tag{4.9}$$

A straightforward application of the expression for A in the general result for operators C and D

$$e^{C}De^{-C} = D + [C,D] + \frac{1}{2}[C,[C,D]] + \cdots$$

gives the result

$$A\underline{u}_\ell A^\dagger = \underline{u}_\ell + \underline{f}_\ell(0) \tag{4.10}$$

where

$$\underline{f}_\ell(0) = -\sum_{\underline{q}\lambda}^{B.Z.} \left(\frac{2}{MN}\right)^{1/2} g_{-\underline{q}\lambda} \frac{\underline{\varepsilon}(\underline{q}\lambda)}{(\omega(\underline{q}\lambda))^{3/2}} e^{i\underline{q}\cdot\underline{R}_\ell^0}$$

$$= -\sum_{\underline{q}\lambda}^{B.Z.} \frac{\underline{\varepsilon}(\underline{q}\lambda)}{MN} \frac{e^{i\underline{q}\cdot\underline{R}_\ell^0}}{\omega^2(\underline{q}\lambda)} \sum_{\ell\neq 0} \underline{\varepsilon}(\underline{q}\lambda)\cdot\nabla U_\ell e^{-i\underline{q}\cdot\underline{R}_\ell^0} . \tag{4.11}$$

Since $\langle\phi|\underline{u}_\ell|\phi\rangle = 0$ and $\underline{f}_\ell(0)$ is not an operator, the following result for $\underline{\Delta}_\ell$ is obtained

$$\underline{\Delta}_\ell = \underline{f}_\ell(0) . \tag{4.12}$$

This is the same as Eq. (2.13) and the usual lattice statics result $^{(7)}$ except ∇U_ℓ is being evaluated at the perfect lattice sites instead of the relaxed lattice equilibrium sites.

4.2 Finite Temperature Formalism and Results

At finite temperature, the thermal average of various operators will be needed. For an arbitrary operator, D, this is given by

$$\langle D\rangle_T = \sum_i \frac{e^{-\beta\omega_i}}{Z_p} \langle i|D|i\rangle$$

where ω_i and $|i\rangle$ are the exact eigenvalues and eigenstates of the system and Z_p is the partition function. The important point to note in connection with thermal averages is that the eigenvalues of H_L and H_0 differ only by a constant $\Delta\varepsilon$ and this will cancel in $e^{-\beta\omega_i}/Z_p$ leaving only the eigenvalues of the harmonic lattice described by H_0. Using Eq. (4.6) and the fact that $AA^\dagger = 1$, any thermal average for a system described by H_L may be reduced to a thermal average for a system described by H_0.

The basic quantity which needs to be evaluated is

$$\langle e^{-i\underline{q}\cdot\underline{u}_\ell^{H_L}(t)}\, e^{i\underline{q}\cdot\underline{u}_\ell^{H_L}(0)}\rangle_T^{H_L}$$

where the superscript H_L is included explicitly to note that the eigenvalues and eigenstates to be used are those of H_L. The time dependence of the operators in the Heisenberg picture is given by

$$\underline{u}_{\ell}^{H_L}(t) = e^{iH_L t}\, \underline{u}_{\ell}^{H_L}(0)\, e^{-iH_L t}$$

$$= \underline{u}_{\ell}^{H_0}(t) - \underline{f}_{\ell}(t) + \underline{\Delta}_{\ell} \qquad (4.13)$$

which is obtained by using the Heisenberg equation of motion for $\underline{u}_{\ell}^{H_L}(t)$. In Eq. (4.13) $\underline{f}_{\ell}(t)$ is the generalization of $\underline{f}_{\ell}(0)$

$$\underline{f}_{\ell}(t) = -\sum_{\underline{q}\lambda}^{\text{B.Z.}} \left(\frac{2}{MN}\right)^{1/2} \frac{\underline{\varepsilon}(\underline{q}\lambda)}{(\omega(\underline{q}\lambda))^{3/2}}\, g_{-\underline{q}\lambda}\, e^{i\underline{q}\cdot\underline{R}_{\ell}^{0}} \cos(\omega(\underline{q}\lambda)t) \qquad (4.14)$$

Thus matrix elements like

$$\langle\psi_i| e^{-i\underline{q}\cdot\underline{u}_{\ell}(t)}\, e^{i\underline{q}\cdot\underline{u}_{\ell'}(0)} |\psi_i\rangle$$

$$= \langle\phi_i| A e^{-i\underline{q}\cdot\underline{u}_{\ell}(t)} A^{\dagger} A e^{i\underline{q}\cdot\underline{u}_{\ell'}(0)} A^{\dagger} |\phi_i\rangle \qquad (4.15)$$

need to be evaluated, where the superscript H_0 is dropped. By expanding $e^{-i\underline{q}\cdot\underline{u}_{\ell}(t)}$, it is easily proved that

$$A e^{-i\underline{q}\cdot\underline{u}_{\ell}(t)} A^{\dagger} = e^{-i\underline{q}\cdot(\underline{u}_{\ell}(t)+\underline{f}_{\ell}(t))}$$

Using the relations $e^{C}e^{D} = e^{C+D}e^{-\frac{1}{2}[C,D]}$ and $\langle e^{iC}\rangle_T = e^{-\frac{1}{2}\langle C^2\rangle_T}$ which are valid for a system of harmonic oscillators (43), the following result is obtained

$$\langle e^{-i\underline{q}\cdot\underline{u}_{\ell}^{H_L}(t)}\, e^{i\underline{q}\cdot\underline{u}_{\ell'}^{H_L}(0)}\rangle_T^{H_L}$$

$$= e^{-i\underline{q}\cdot(\underline{\Delta}_{\ell}-\underline{\Delta}_{\ell'})}\, e^{-2W_{D.W.}(q)}\, e^{\langle\underline{q}\cdot\underline{u}_{\ell}(t)\underline{q}\cdot\underline{u}_{\ell'}(0)\rangle_T} . \qquad (4.16)$$

Here $W_{D.W.}(q)$ is the Debye-Waller factor defined previously.

From here the derivation proceeds in the same manner as in the theory of the D.M.R. presented previously.

When the impurity at the origin is included explicitly, three more such thermal averages arise in which the motion of the impurity is correlated with the host atoms and with itself. These contributions will be very similar to Eq. (4.16) except that $\underline{\Delta}_0 = 0$, i.e., the impurity by symmetry is not relaxed, and the scattering cross sections appropriate to them are $2w(q)\Delta w(q)$ and $|\Delta w(q)|^2$ instead of $|w(q)|^2$. Expanding both the dynamic and static displacements to second order and including the factors of

$$e^{-i\underline{q}\cdot\underline{R}_{\ell}^{0}}\, e^{i\underline{q}\cdot\underline{R}_{\ell'}^{0}}$$

which have been dropped in the above discussion, the following expressions contributing to the resistivity will be obtained. From those terms containing no dynamic displacements, a correction to the residual resistivity is obtained in which $|\Delta w(q)|^2$ is replaced by

$$|\Delta w(q) - i \sum_{\ell \neq 0} e^{i\underline{q}\cdot\underline{R}_\ell^0}\, \underline{q}\cdot\underline{\Delta}_\ell|^2 .$$

This is formally the same as the expression used by Fukai (9) and Benedek and Baratoff (29) in discussing the changes in ρ_R when lattice relaxation is included. From the terms containing just the dynamic displacements, the usual terms presented in the discussion of the D.M.R. are obtained, while if both dynamic and static displacements are included, some new contributions are obtained. Writing these terms as $\alpha_{TR}^{2(i)}F(\omega)$ in analogy with the previous work, the additional terms are (neglecting the constant factors in Eq. (3.14))

$$\alpha_{TR}^{2(4)}F(\omega) = \int qd^3q|w(q)|^2 \sum_{\ell\ell'} e^{-i\underline{q}\cdot(\underline{R}_\ell^0-\underline{R}_{\ell'}^0)} (\underline{q}\cdot\underline{\Delta}_\ell)(\underline{q}\cdot\underline{\Delta}_{\ell'})$$

$$\times \frac{1}{N} \sum_{\underline{k}\lambda}^{B.Z.} \frac{|\underline{q}\cdot\underline{\varepsilon}(\underline{k}\lambda)|^2}{\omega(\underline{k}\lambda)} e^{i\underline{k}\cdot(\underline{R}_\ell^0-\underline{R}_{\ell'}^0)} \delta(\omega-\omega(\underline{k}\lambda))$$

$$\alpha_{TR}^{2(5)}F(\omega) = \int qd^3q|w(q)|^2 \sum_{\ell} (\underline{q}\cdot\underline{\Delta}_\ell)^2 \sum_{\lambda} \frac{|\underline{q}\cdot\underline{\varepsilon}(\underline{k}\lambda)|^2}{\omega(\underline{k}\lambda)} \delta(\omega-\omega(\underline{q}\lambda))$$

$$\alpha_{TR}^{2(6)}F(\omega) = c \int qd^3q w(q)\Delta w(q) \sum_{\ell} 2(\underline{q}\cdot\underline{\Delta}_\ell)$$

$$\times \sin(\underline{q}\cdot\underline{\Delta}_\ell) \frac{1}{N} \sum_{\underline{k}\lambda}^{B.Z.} \frac{|\underline{q}\cdot\underline{\varepsilon}(\underline{k}\lambda)|^2}{\omega(\underline{k}\lambda)} \delta(\omega-\omega(\underline{k}\lambda))$$

$$\alpha_{TR}^{2(7)}F(\omega) = c \int qd^3q w(q)\Delta w(q) \sum_{\ell} (\underline{q}\cdot\underline{\Delta}_\ell)^2 \frac{1}{N} \sum_{\underline{k}\lambda}^{B.Z.}$$

$$\times \frac{|\underline{q}\cdot\underline{\varepsilon}(\underline{k}\lambda)|^2}{\omega(\underline{k}\lambda)} \cos((\underline{q}-\underline{k})\cdot\underline{R}_\ell^0)\,\delta(\omega-\omega(\underline{k}\lambda)) .$$

There are no terms with $|\Delta w(q)|^2$ since they would involve only $\underline{\Delta}_0$ which is equal to zero as mentioned previously Although most of these expressions are rather complicated because of the lattice sums and the extra sum over the B.Z., it should be possible to get an estimate of these corrections by using a Debye model to simplify the $\underline{k}$ sum. The exponential factors as well as the $(\underline{q}\cdot\underline{\Delta}_\ell)(\underline{q}\cdot\underline{\Delta}_{\ell'})$, where the relaxation parameters may be positive or negative, will probably lead to a great deal of cancellation between the various terms in the double lattice sum in $\alpha^{2(4)}_{TR}F(\omega)$ so that $\alpha^{2(5)}_{TR}F(\omega)$ is expected to give a larger contribution than $\alpha^{2(4)}_{TR}F(\omega)$. The term with $\ell = \ell'$ in $\alpha^{2(4)}_{TR}F(\omega)$ should, however, be also considered. In the case of $\alpha^{2(6)}_{TR}F(\omega)$ and $\alpha^{2(7)}_{TR}F(\omega)$, they are both, approximately, dependent on Δ^2_ℓ, for small Δ_ℓ, but the latter distribution also has the factor $\cos((\underline{q}-\underline{k})\cdot\underline{R}^0_\ell)$ which will cause cancellation among the various terms in the lattice sum, so that $\alpha^{2(6)}_{TR}F(\omega)$ will probably give a more important contribution. However, it is also proportional to the concentration so that the dominant term is $\alpha^{2(5)}_{TR}F(\omega)$, together with the $\ell = \ell'$ term in $\alpha^{2(4)}_{TR}F(\omega)$. From a knowledge of the $\underline{\Delta}_\ell$'s appropriate for a given impurity, the lattice sum may be performed and the distribution calculated in an analogous manner to the one for the pure metal.

The influence of the relaxation on the finite temperature resistivity is expected to be greatest when the ionic volumes of the host and impurity ions differ substantially. This is what is found in detailed calculations of the residual resistivity of alkali impurities in alkali host metals (30). The mismatch of the ionic volumes causes a greater strain in accomodating the impurity in the host matrix, leading to larger values of the relaxation parameters $\underline{\Delta}_\ell$.

CHAPTER V

CONCLUSION AND DISCUSSION

This thesis has dealt with the problem of simple defects such as vacancies and substitutional impurities, in the dilute limit, in a metal. The effects of these defects on the system were discussed in terms of the additional scattering mechanisms they cause in the metal. This leads, at zero temperature, to a relaxation or displacement of the host ions around a defect off their perfect lattice equilibrium positions. The Friedel Sum Rule or displaced charge sum rule, which relates the phase shifts of the conduction electron at the Fermi surface due to the defect scattering to the excess charge of the defect, must be modified to include the additional scattering off the displaced host ions. Within the Born approximation, a simple, microscopic derivation was given to include the additional scattering. It was also shown that the correction term to the F.S.R. is directly related to the volume change caused by the net displacement of all the host ions inside an arbitrary large sphere in the metal. Some numerical estimates were given for the correction, and the relation of this correction to an analogous correction in the calculation of the residual resistivity was discussed. It was pointed out that the additional scattering due to the displaced ions becomes particularly important for isovalent impurities since then the ΔZ in the F.S.R. is equal to zero, and the net scattering amplitude of the impurity is thus very sensitive to the correction term.

At finite temperature, the conduction electrons are scattered by the vibrating ions or phonons as well as by any defects. Also, there are extra effects due to the thermal vibrations of the defects and possible mass differences between the host and the impurity. In a pure metal the phonons propagating in different directions often show a great deal of anisotropy. Similarly, the electron-phonon interaction is very anisotropic, particularly when umklapp processes are considered. This anisotropy, which is greatest at low temperature when the thermal population of phonons is restricted to low energy phonons, causes the scattering time associated with the electron-phonon contribution to the resistivity to be very anisotropic over the Fermi surface. The addition of a small amount of impurities can radically affect the net anisotropy in the total scattering time, leading to significant D.M.R.. Detailed calculations of the D.M.R. in potassium give good agreement with experiment (44), showing that the physical origin of the D.M.R. may be understood in terms of the washing out of the anisotropy. Similar results were also obtained for sodium and rubidium. For lithium the anisotropy is much more pronounced and persists to much higher temperatures.

Results for very dilute alloys of Li demonstrate the importance of including the effect of the impurities both in the alloy and in the purest sample. For the more concentrated alloys of Li-Mg and Li-Ag, the effect of the inelastic scattering off the impurities becomes more important, especially at high temperature, but the calculations tend to overestimate this effect, so that often better qualitative agreement is achieved by just including the elastic impurity scattering. The effect of the mass change in Li-Mg is very small while in Li-Ag, it is more significant. However, it just gives an increase to the hump in Δ(T,c) and is not the cause of the hump, as was previously thought (50). The effect of mass changes does produce some pronounced effects in the specific heat (87) and in the neutron scattering cross section (42) but in the resistivity, the effect of the washing out of the anisotropy tends to dominate the D.M.R., at least until the impurity concentration is so large that anisotropy has become negligible.

For aluminum, more substantial and systematic results are available (55,56), including alloys with Mg, Ag, Zn, Cu and Ga as impurities, covering the whole range of temperature up to room temperature. The detailed calculations give fair agreement with experiment even at low temperature where the effect of the Fermi surface anisotropy, which has been neglected, should be more important. The hump in Δ(T,c) is too sharp, especially for the most dilute alloys, and the linear rise at high temperature is usually too strong, although including the Debye-Waller factor in the scattering form factors gives some improvement. The overall agreement, however, leaves little doubt that the main causes of the D.M.R. in dilute Al alloys are the ones represented in the calculations presented in this thesis. It must be remembered that the scattering form factor for Al has one parameter, R_c, which is fitted to the pure metal resistivity at some intermediate temperature, between 120° and 150°K; it would be very useful if the impurity form factor, instead of being fitted to the residual resistivity, were fitted, also at $\sim$ 150°K, to the total resistivity of a relatively concentrated alloy, say c $\gtrsim$ 1%, so that the ρ_2 term has an appreciable magnitude compared to ρ_R. For the low temperature values of $\Delta(T,c)$, it is most important that the details of the anisotropy in $\tau_0(\underline{k})$ are calculated correctly. This depends on using a realistic scattering form factor for the host ions and the experimentally measured phonons in the density of states, $F(\omega)$, as well as including umklapp processes properly. Since the anisotropy in the scattering time is so crucial, it might be of interest to use the $\tau_0(\underline{k})$ calculated according to the prescription of Robinson and Dow (37) in an iterative fashion in the Boltzmann equation. This would have the same effect as using still higher trial wavefunctions in the variational procedure except that less computation will probably be involved since $\tau_0(\underline{k})$ already has a great deal of anisotropy.

It is interesting to note that many of the features in $\Delta(T,c)$, especially the hump at low temperature, are common to a wide variety of alloys with different host metals $^{(39)}$: simple metals like the alkalis and aluminum, valence 2 metals like cadmium and magnesium which have band overlap, and the noble metals. Although the details of the Fermi surface must be included if quantitative results are desired, the main features which must be included in the calculation are the realistic form factors, the experimentally measured phonons and the proper inclusion of umklapp processes in the electron-phonon interaction. The latter particularly will reflect differences in the Fermi surface.

The methods used in calculating $\Delta(T,c)$ using the anisotropic scattering time are probably also applicable to many other properties of metals. When an anisotropic scattering time is defined for the electronic thermal conductivity or the ultrasonic attenuation, preliminary results show that these are much less anisotropic than the scattering time for the resistivity. Nevertheless, in Li there is enough anisotropy that it should be included in a calculation. The thermal conductivity is complicated by the fact that higher order corrections to the energy dependence of the trial wavefunction are probably more important than the corrections to the anisotropy, e.g., for potassium, Ekin (88) showed that the better energy dependence can give changes of about 20% while calculations including just the anisotropy better produce changes of only ∿ 3% for K. In the ultrasonic attenuation scattering time, there is also little anisotropy but since the quantity of interest is the ratio of the times for the ultrasonic attenuation and the resistivity (46), this ratio will reflect the anisotropy and impurity dependence of the resistivity scattering time when comparison between theory and experiment is made. The effective number of electrons, n^*/n, in the Hall effect for simple metals is given by (89) $<\tau^2(k)>/<\tau(k)>^2$ where the scattering times are the same as those for the resistivity. Recently, Ekin and Bringer (41) found that the magnetoresistance may be used to obtain information about the anisotropy in resistivity scattering time since this will be decreased by the magnetic field. Another field of application of these basic ideas is to the infrared properties of metals: Allen (35) has shown that the a.c. conductivity may be expressed in terms of $\alpha^2_{TR}F(\omega)$.

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