

If we keep only the terms proportional to N we obtain:

$$\begin{aligned}
 -\beta F = & \frac{\beta J}{N} [L^2 - K^2 - S^2] - \beta \Delta \cdot n + \frac{1}{2} \beta \Delta \cdot N \\
 & - \left(\frac{n - B_1}{2} \right) \log \left(\frac{n - B_1}{2} \right) - \left(N - \frac{n + B_1}{2} \right) \log \left(N - \frac{n + B_1}{2} \right) \\
 & - \left(\frac{n - B_2}{2} \right) \log \left(\frac{n - B_2}{2} \right) - \left(N - \frac{n + B_2}{2} \right) \log \left(N - \frac{n + B_2}{2} \right) \quad (32) \\
 & - \left(\frac{B_1}{2} - S_1 \right) \log \left(\frac{B_1}{2} - S_1 \right) - \left(\frac{B_1}{2} + S_1 \right) \log \left(\frac{B_1}{2} + S_1 \right) \\
 & - \left(\frac{B_2}{2} - S_2 \right) \log \left(\frac{B_2}{2} - S_2 \right) - \left(\frac{B_2}{2} + S_2 \right) \log \left(\frac{B_2}{2} + S_2 \right) \\
 & - \left(\frac{cN}{2} - K \right) \log \left(\frac{cN}{2} - K \right) - \left(\frac{cN}{2} + K \right) \log \left(\frac{cN}{2} + K \right) + \text{const.}
 \end{aligned}$$

For fixed K and $J > 0$ the maximum value of $-\beta F$ is

$$\begin{aligned}
 -\beta F(K) = & 2N \log \left\{ \cosh \left[\beta \cdot J \frac{K}{N} \right] + \cosh \left[\frac{1}{2} \beta \Delta \right] \right\} \\
 & - \left(\frac{cN}{2} - K \right) \log \left(\frac{cN}{2} - K \right) - \left(\frac{cN}{2} + K \right) \log \left(\frac{cN}{2} + K \right) + \text{const.} \quad (33)
 \end{aligned}$$

In the limit of large N we can take the sum on the right of Eq. (30) to be equal to its largest term.

The condition for $-\beta F$ to be an extremum with respect to K is

$$-\beta \frac{\partial F(K)}{\partial K} = 2\beta J \frac{\sinh \left[\beta \cdot J \frac{K}{N} \right]}{\cosh \left[\beta \cdot J \frac{K}{N} \right] + \cosh \left[\frac{1}{2} \beta \Delta \right]} - \log \frac{cN + K}{cN - K} = 0^* \quad (34)$$

This equation for the magnetization $M = 2K/cN$ is identical with the one (Eq. (13)) derived with the molecular field method.

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* Note that for $J < 0$ we obtain exactly the same Eq. (34) for the magnetization, whereas THOMPSON [7], (special case $\Delta = 0$) due to a mathematical error finds a different result for $J < 0$.

An Analysis of the Temperature and Pressure Dependence of the Electrical Resistivity in Lead

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The volume dependence of the high temperature electrical resistivity has been treated in detail for lead. Volume changes caused by external pressure as well as thermal expansion have been considered. Experiments on the volume dependence of the effective electron mass have been reanalysed with an inclusion of electron-phonon interaction. Finally, we have found no experimental support for a net effect from a Debye-Waller factor and multi-phonon processes.

Die Volumenabhängigkeit des elektrischen Widerstandes von Blei bei hohen Temperaturen ist ausführlich behandelt. Volumenänderungen, hervorgerufen sowohl durch äußeren Druck als auch durch Wärmeausdehnung, wurden betrachtet. Experimente über die Volumenabhängigkeit der effektiven Elektronenmasse sind neu überprüft worden unter Einbezug der Elektron-Phonon-Wechselwirkung. Eine experimentelle Bestätigung für einen Nettoeffekt, herrührend von einer unvollständigen Kompensation eines Debye-Waller-Faktors durch Multi-phonon-Prozesse, konnte nicht gefunden werden.

Nous avons calculé la résistance électrique de plomb à haute température en fonction du volume. Des changements de volume, aussi bien causés par la pression extérieure que par l'expansion thermique, ont été considérés. Nous avons réanalysé des expériences sur la variation de la masse effective de l'électron en fonction du volume, en tenant compte de l'interaction électron-phonons. Finalement, nous n'avons trouvé aucune preuve expérimentale pour un effet dû à une compensation incomplète d'un facteur de Debye-Waller et de collisions multi-phonons.

Introduction

The purpose of this paper is threefold. We will try to account for the volume (i.e. pressure) dependence of the electrical resistivity in a detailed calculation based not on models but on data from experiments on other metallic properties. Secondly, it has been conjectured that the Debye-Waller factor and multiphonon processes might cancel in the electrical resistivity and we will therefore analyse this question with the help of available experimental data. Finally we reanalyse experiments on the volume dependence of the effective electron mass and take into account the variation in the electron-phonon enhancement factor. We will consider lead, because of lack of relevant data for other elements.

Theory

There are numerous calculations in the literature [1] of the volume dependence of the electrical resistivity in metals. Although some of them are very elaborate, they make use of models and assumptions that we now know are much too crude.

We will base our analysis on ZIMAN's [2] well known solution of the transport problem obtained with a variational method:

$$\rho = \frac{3\pi k}{2e^2 M N k T S^2 k_F^3} \sum_{\lambda} \iint \frac{q^2 (\epsilon_{\lambda, q} \cdot q)^2 \mathcal{V}^2(|q|)}{[\epsilon^2 \omega_{\lambda, q} k T - 1][1 - e^{\epsilon^2 \omega_{\lambda, q} k T}]} \frac{dS}{v} \frac{dS'}{v'} \quad (1)$$

$q = k - k'$. The integration dS extends over the Fermi surface, whose free area is S . Phonons of branch λ and wavevector q have frequencies $\omega_{\lambda}(q)$ and polarization vectors ϵ_{λ} . The electron-phonon interaction has been approximated by the form factor $\mathcal{V}(|q|)$ that only depends on the magnitude of the momentum transfer $q = k - k'$. M is the ion mass, N the number of unit cells per unit volume and v and v' the velocities of an electron at the Fermi surface. The rest of the quantities have their usual meaning. An earlier calculation of resistivities for some polyvalent metals [3] with the use of Eq. (1) was in good agreement with experiments and the results obtained in this paper are also reasonable, so we believe that Eq. (1) is accurate enough in this context. It is interesting to note that we could in principle make a self-consistent treatment, if we knew how the pseudo-potential changed with pressure. Once we had this information we could calculate changes in the phonon frequencies, the shape of the Fermi surface and the density of states of the conduction electrons, but such a procedure would not only be very difficult but also in practice give inaccurate results. Instead we shall use all available information to see how different parts in Eq. (1) contribute to a change in ρ . For a discussion of the volume dependence it is very convenient to consider $(d \ln \rho / d \ln V)$ and we write

$$\frac{d \ln \rho}{d \ln V} = \frac{2 d \ln m_b}{d \ln V} - \frac{2 d \ln \Theta_R}{d \ln V} + \frac{d \ln I_R}{d \ln V} + 1. \quad (2)$$

The first term on the right hand side of Eq. (2) comes from the volume dependence of the band density of states at the Fermi level, i.e. essentially from dS/v , and we have taken an average over the Fermi surface in the form of an effective mass. We will always consider the resistivity at high temperatures (i.e. $T \gg \Theta_D$) and then the phonon frequencies come in as $1/\omega_{\lambda}^2(q)$ in the integrand of Eq. (1). This leads to the term

$$- 2(d \ln \Theta_R / d \ln V).$$

The phonon spectrum is differently weighted in different properties like e.g. the electrical resistivity and the vibrational specific heat. The relative frequency shift is not the same for all phonons and we must therefore be careful to specify which experiment we are considering. This is why we use the notation Θ_R and it does not imply the use of a Debye model or any other model. $(d \ln I_R / d \ln V)$ contains the effect of a variation in the form factor $\mathcal{V}(q)$. Finally there remain some terms that we assume to vary linearly with the lattice dimension and this gives +1 in the right hand side of Eq. (2). We shall later consider volume changes caused by external pressure and by the thermal expansion so we do not yet specify whether the temperature or the pressure is to be kept constant in the derivatives in Eq. (2).

The thermal expansion coefficient β can be written

$$\beta / K_T = \left(\frac{\partial S}{\partial V} \right)_T \quad (3)$$

where K_T is the isothermal compressibility and S the entropy. At low temperatures the thermal expansion of a non-magnetic metal consists of one contribution from the conduction electrons, which is linear in T , and one phonon contribution which goes like T^3 . The entropy of the electrons is proportional to the total effective electron mass and it is evident from Eq. (3) that a measurement of the low temperature thermal expansion can give information about the volume dependence of the effective mass. A review of this method has been given by COLLINS and WHITE [4]. A measurement of the pressure dependence of the critical field of a superconductor can in principle give the same information about the effective mass. At present this latter type of experiment seems to be less accurate than the first method [5]. In both cases the change in the total effective mass m_{eff} is obtained. If we neglect the influence of electron-electron interaction, we can write

$$m_{eff} = m_b(1 + \lambda) \quad (4)$$

where $1 + \lambda$ is the factor by which the band mass m_b is increased due to electron-phonon interaction. For λ we can write [6]

$$\lambda = \frac{1}{(2\pi)^3 M N k} \sum_{\lambda} \iint \frac{(\epsilon_{\lambda, q} \cdot q)^2 \mathcal{V}^2(|q|)}{\omega^2(q)} \frac{dS}{v} \frac{dS'}{v'} / \int \frac{dS}{v}. \quad (5)$$

Therefore, in analogy with Eq. (2)

$$\frac{d \ln m_{eff}}{d \ln V} = \frac{d \ln m_b}{d \ln V} + \frac{\lambda}{1 + \lambda} \frac{d \ln \lambda}{d \ln V} \quad (6)$$

where

$$\frac{d \ln \lambda}{d \ln V} = \frac{d \ln m_b}{d \ln V} - \frac{2 d \ln \Theta_{\lambda}}{d \ln V} + \frac{d \ln I_{\lambda}}{d \ln V}. \quad (7)$$

Like in Eq. (2) the term $-2(d \ln \Theta_{\lambda} / d \ln V)$ is the effect of shifts in the phonon frequencies but now they are averaged according to Eq. (5). The last term, $(d \ln I_{\lambda} / d \ln V)$, is the result of a change in $\mathcal{V}(q)$ in Eq. (5). The derivatives in Eq. (6) are to be taken at constant temperature (cf. Eq. (3)). There is no a priori reason why the various band masses we have introduced should have the same volume dependence, as they correspond to different averages over the Fermi surface. However, we do not expect them to behave in a very different way, and moreover this point is not crucial for any of the conclusions in this paper.

Pressure Dependence of the Resistivity

The resistance of various metals under pressure has been measured by BRIDGMAN [7]. After taking into account that we want resistivity instead of resistance, we have at room temperature and in the limit of small volume changes $(d \ln \rho / d \ln V)_T = 6.9$. FISHER [8] obtained the value 6.5, but BRIDGMAN considers his experimental method to be somewhat uncertain. Throughout this paper we will use the compressibility and thermal expansion coefficient given by GSCHNEIDER [9] to convert from experimentally determined pressure or temperature derivatives to the corresponding volume derivatives.

The phonon term, $(d \ln \Theta_R / d \ln V)_T$, could in principle be obtained from measurements of phonon frequencies in lead under pressure. The experimental

uncertainties are, however, very large, and we defer a closer discussion of this experiment to the later comparison between effects of an external pressure and of thermal expansion. The standard approach in the literature has been to take $(d \ln \Theta_R/d \ln V)_T$ equal to the well known Grüneisen constant, γ_G , without any further justification. In appendices 1 and 2 we show that the use of γ_G is a reasonable approximation for lead.

The term $(d \ln I_R/d \ln V)$ is very difficult to discuss accurately. In order to make any further progress possible, we already in Eq. (1) made the approximation with a form factor $\mathcal{V}(q)$ which only depends on the magnitude of the momentum transfer. In a polyvalent metal this leads to erroneous results for those scattering processes where k and k' differ by a reciprocal wave vector [10]. On the other hand, recent calculations by CARBOTTE and DYNES [11], using the form factor for all scattering processes, has given quite good results for both lead and aluminium, indicating that this approximation could give a good over all description. There are recent measurements of the de Haas-van Alphen effect in lead under pressure [14]. From this experiment, the two derivatives $d\mathcal{V}_{111}/dp$ and $d\mathcal{V}_{200}/dp$ of the form factor can be deduced. It turns out that a simple model, like HARRISON's pseudopotential, gives a value for these derivatives which is correct in sign but too small by a factor five. The Fermi level shifts in opposite direction to what is expected from the free electron case. One must therefore be very careful in drawing conclusions from simple models. There are several complications in a calculation of $(d \ln I_R/d \ln V)$ from the de Haas-van Alphen data. The volume dependence of the resistivity is even more sensitive than the resistivity itself to the location of the node of the form factor, for there is a cancellation effect from the contributions from either side of the node. The Fermi surface is not spherical, so we are not strictly limited to scattering processes with $(q/2 k_F) \leq 1$. Experimental errors in the de Haas-van Alphen data and the breakdown of the form factor description at reciprocal wavevectors add to the difficulties. Therefore we do not find a detailed numerical calculation very significant. Instead we use the de Haas-van Alphen data for \mathcal{V}_{111} and \mathcal{V}_{200} and their pressure derivatives to estimate $(d \ln I_R/d \ln V)$, as it comes from Eq. (1). With allowance for the uncertainties mentioned we find $0.5 \leq (d \ln I_R/d \ln V) \leq 3$.

Some quantities (the number of unit cells per unit volume, the free Fermi surface area and the length of q -vectors) were assumed to scale with the lattice spacing. One can have some doubt about this point, for the de Haas-van Alphen measurements mentioned gave a net change in the cross sectional area for some orbits that was twice that which would result from a pure scaling. However, we do not believe that the orbits considered are typical for the average behaviour of the Fermi surface. Remember that the number of electrons per unit cell is constant, so the Fermi surface encloses a constant volume in the reciprocal space.

For the remaining term, $(d \ln m_b/d \ln V)$, we have no reliable information. We will therefore assign to it a value which makes Eq. (2) hold. The result is summarized in the table. The errors given are somewhat arbitrary. They only serve the purpose of indicating which terms are best known, and the order of magnitude of the uncertainties. We will comment on the results in the next section.

Pressure Dependence of the Effective Mass

The value of $(d \ln m_{eff}/d \ln V)_T$ obtained from measurements of the low temperature thermal expansion of lead [4] is 1.0 ± 0.5 . The value of λ for lead has been obtained by McMILLAN and ROWELL [6] from tunneling experiments in superconductors. They find $\lambda = 1.5$. The term $(d \ln \Theta_R/d \ln V)_T$ will be set equal to γ_G . The appendices should be seen, for a justification. Finally we make an estimate of $(d \ln I_R/d \ln V)$ analogous to that used for the resistivity. In fact the only difference is an additional factor, q^2 , in the integral for ρ as compared to the integral for λ . Proceeding in the same way as for the resistivity we have estimated $1 \leq (d \ln I_R/d \ln V) \leq 3$.

Several interesting conclusions can now be drawn. Although $(d \ln I/d \ln V)$ is very uncertain, there is no doubt that it is positive and can be quite large. The experimental results for $(d \ln \rho/d \ln V)_T$ and $(d \ln m_{eff}/d \ln V)$ then both require that $(d \ln m_b/d \ln V)$ is negative and not very small in magnitude. The band mass is closely related to the form factor so it is natural that a strong volume dependence in one of them also leads to a strong volume dependence in the other. For a long time it has been thought that shifts in the phonon frequencies give the essential contribution to $(d \ln \rho/d \ln V)$ in simple metals. Our analysis shows that there are other important contributions in lead but that they come in with opposite signs and almost cancel.

Nonlinear Temperature Dependence of the Resistivity

As the temperature is increased, the resistivity will increase due to the explicit temperature dependence as it appears in Eq. (1), but there will also be an additional effect coming from changes in the other quantities in the same relation. This additional variation will be very similar to the volume effect at constant temperature discussed above. At high temperatures the explicit temperature dependence gives a linear increase in the resistivity. For lead at room temperature there still remains a small correction to this linear behaviour from the exponential terms, but this correction can easily be estimated if the phonon spectrum is approximated by two Einstein peaks that are given the weights found in appendix 2. The explicit temperature dependence so evaluated is subtracted from the measured temperature coefficient for the resistivity. The rest can conveniently be expressed in the same form as Eq. (2) if we remember that the experiment is performed under constant pressure instead of constant temperature, i.e. if we consider that $(d \ln \rho/d \ln V)_P$ and therefore $(d \ln \Theta_R/d \ln V)_P$ should contain both a volume effect and an additional purely anharmonic effect (cf. appendix 1). The rest of the terms in Eq. (2) comes only from the thermal expansion of the lattice. There are, however, some other differences as compared to the pressure effect at constant temperature. In our starting formula, Eq. (1), we have not included any Debye-Waller factor or multiphonon scattering processes. These two effects come in with opposite signs and it is still an open question whether they cancel exactly or not [13]. If they do not cancel, we can tentatively include them with an additional multiplicative factor $\exp(-\alpha T)$ in Eq. (1), leading to a term $-\alpha T (d \ln T/d \ln V)_P$ in Eq. (2). Simple estimates show [13] that any of the two effects considered separately gives a contribution to $(d \ln \rho/d \ln V)_P$ which can be even larger than that coming from

the thermal expansion, so it is not a small correction we are discussing. As the temperature is raised, there will also be an increase in the resistivity due to thermally created lattice imperfections. It has been shown experimentally [14] for lead that such effects are negligible at room temperature.

From resistivity measurements we have calculated $(d \ln \rho / d \ln V)_P$ at room temperature and find 4.5 (HOLBORN [15]), 4.7 (LEADBETTER, NEWSHAM and PICTON [14]) and 5.0 (POCHAPSKY [16]). As an average we take $(d \ln \rho / d \ln V)_P = 4.7 \pm 0.3$. It should be remarked that this value stays constant within 10% up to about 500 °K. There is a significant difference

$$(d \ln \rho / d \ln V)_T - (d \ln \rho / d \ln V)_P = 2.2 \pm 0.6$$

which can come from the fact that $(d \ln \Theta_R / d \ln V)_T$ and $(d \ln \Theta_R / d \ln V)_P$ are not equal, but also from a Debye-Waller factor and multiphonon processes. We first consider phonon shifts. The electrical resistivity is a scattering phenomenon. Therefore data from inelastic neutron scattering at different temperatures could give us the correct shifts to be used in $(d \ln \Theta_R / d \ln V)_P$. Such experiments have been performed by STEDMAN, ALMQVIST and NILSSON [17], and also by BROCKHOUSE et al. [18]. The two sets of data agree within experimental uncertainties. There is also a general agreement with specific heat measurements on lead by LEADBETTER [19].

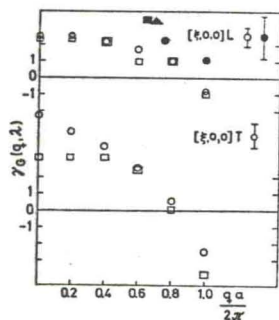


Fig. 1. Experimentally determined microscopic Grüneisen parameters $\gamma(q, \lambda)$ for the longitudinal and transverse branch in the [100]-direction. Unfilled symbols are from inelastic neutron scattering measurements by STEDMAN et al. [17] (○) and BROCKHOUSE [18] (□) at different temperatures and constant pressure. Inelastic neutron scattering under hydrostatic pressure by LECHNER and QUITNER [20] (●) and tunneling experiments on superconductors under pressure by ZAVARITSKII (■) et al. [21] and FRANK and KEELER [22] (▲) give shifts that do not contain any explicit anharmonic effects. Typical experimental errors are indicated by the error bars.

In Fig. 1 we summarize some experimentally determined $\gamma_q = (d \ln \omega_q / d \ln V)_P$ for the longitudinal and transverse branches in the [100]-direction. Other branches and directions show a similar behaviour. In the same figure we include the corresponding values $\gamma_q = (d \ln \omega_q / d \ln V)_T$ obtained by QUITNER and LECHNER [20] from neutron scattering experiments under pressure. We also give points from tunneling experiments in superconductors under pressure by ZAVARITSKII, ISTKEVICH and VORONOVSKII [21] and FRANK and KEELER [22]. In tunneling experiments one can measure the location in energy of the van Hove singularities in the phonon spectrum. The resolution in the tunneling experiments is not very

Table. Calculated contributions to the measured values of $(d \ln \rho / d \ln V)$ and $(d \ln m_{eff} / d \ln V)_T$. The value of $(d \ln I / d \ln V)$ is very uncertain but it is positive and large. $(d \ln m_b / d \ln V)$ has not been calculated but has instead been given a value to make the relations above hold. The errors given for the rest of the quantities are somewhat arbitrary and serve the purpose of indicating which terms are best known

$$\begin{aligned} (d \ln \rho / d \ln V)_T &= 2(d \ln m_b / d \ln V) - 2(d \ln \Theta_R / d \ln V)_T + (d \ln I_R / d \ln V) + 1 \\ 6.9 \pm 0.3 &= 2(-2 \leq \dots \leq 0) + 2(2.7 \pm 0.3) + (0.5 \leq \dots \leq 3) + 1 \\ (d \ln m_{eff} / d \ln V)_T &= \frac{1+2\lambda}{1+\lambda} (d \ln m_b / d \ln V) - \frac{2\lambda}{1+\lambda} (d \ln \Theta_R / d \ln V)_T + \frac{\lambda}{1+\lambda} (d \ln I_R / d \ln V) \\ 1.0 \pm 0.5 &= \frac{8}{5} (-2.5 \leq \dots \leq -1.5) + \frac{6}{5} (2.7 \pm 0.3) + \frac{3}{5} (1 \leq \dots \leq 3) \end{aligned}$$

good, and the points in Fig. 1 represent some average of the shifts in the van Hove singularities for the longitudinal branch. Therefore this method is not useful for our purposes, although it is an experiment that is much easier to perform than inelastic neutron scattering under pressure. Even though the experimental uncertainties are large, it is evident that the relative frequency shift varies considerably with the wave vector q , and it would be very misleading to base an analysis on shifts in the elastic constants. The shifts in the pressure experiments (i.e. a pure volume effect) are in general larger than the shifts obtained when the lattice expands under constant pressure. Theoretical calculations confirm these conclusions [22]. From STEDMAN et al. [17] we estimate $(d \ln \Theta_R / d \ln V)_P = 1.4 \pm 0.5$. We have then given all modes equal weight just as for the high temperature γ_G . This leads to a difference $2(d \ln \Theta_R / d \ln V)_T - 2(d \ln \Theta_R / d \ln V)_P = 2.7 \pm 1$ while $(d \ln \rho / d \ln V)_T - (d \ln \rho / d \ln V)_P = 2.2 \pm 0.6$. The non-linear temperature dependence of the high temperature resistivity in lead can thus be naturally explained as the effect of thermal expansion and a shift in the phonon frequencies of purely anharmonic origin without any net effect from a Debye-Waller factor and multiphonon processes.

Conclusions

We have treated the temperature and volume (pressure) dependence of the high temperature electrical resistivity of a simple metal (lead) in considerably more detail than has been done before. We have been forced to make a lot of approximations, and the quantitative results should not be taken too seriously. However, the following qualitative results hold.

(i) It is well known that the volume dependence of the resistivity, $(d \ln \rho / d \ln V)_T$ is in quantitative agreement with $2\gamma_G$, γ_G being the standard Grüneisen parameter which describes the volume dependence of the phonon frequencies. This approximate agreement holds also for lead, and it has therefore been thought that the volume dependence of the resistivity in this metal is essentially due to shifts in the phonon frequencies. We have found that there might be considerable contributions from shifts in the electron density of states at the Fermi surface and in the electron-phonon interaction described by the form factor, but these two effects come in with opposite signs and happen to almost cancel.

(ii) SHAM and ZIMAN [12] have suggested that one should look for a non-linearity in the high temperature electrical resistivity to see if there is any net

effect from a Debye-Waller factor and the opposing multiphonon processes. In addition to the effect of thermal expansion we find a non-linearity which, however, agrees both in sign and magnitude with the effect of purely anharmonic shifts in the phonon frequencies.

(iii) Finally we have reanalysed experiments on the volume dependence of the effective electron mass. In the literature on this subject it has not been recognized how large the electron-phonon enhancement of the mass is for lead. When we take this fact into account, we find that the band mass decreases when the lattice expands, instead of a supposed increase.

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Appendix 1

We follow COWLEY and COWLEY [24] and write for the phonon frequency $\omega(\mathbf{q}, \lambda)$ as measured e.g. with inelastic neutron scattering

$$\omega(\mathbf{q}, \lambda) = \omega_0(\mathbf{q}, \lambda) + \Delta_1(\mathbf{q}, \lambda) + \Delta_2(\mathbf{q}, \lambda) + \Delta_3(\mathbf{q}, \lambda). \quad (\text{A1})$$

The three last terms represent anharmonic corrections. Δ_1 takes into account the effect of thermal expansion. Δ_2 and Δ_3 represent purely anharmonic effects, they originate from the third and fourth order derivatives of the effective interatomic potential. At high temperatures Δ_2 and Δ_3 are linear in T and they are also volume dependent. The standard Grüneisen γ_G can be expressed in the isothermal compressibility K_T and the thermal expansion coefficient β , but also as a derivative of the entropy

$$\gamma_G = \frac{\beta V}{C_v K_T} = \frac{V}{C_v} \left(\frac{\partial S}{\partial V} \right)_T. \quad (\text{A2})$$

COWLEY and COWLEY find for the volume dependent part ΔS of the entropy

$$\Delta S = -k \sum_{\lambda, \mathbf{q}} \frac{\partial}{\partial T} \left[\frac{1}{\exp(\omega(\mathbf{q}, \lambda)/kT) - 1} \right] [\Delta_1(\mathbf{q}, \lambda) + \Delta_2(\mathbf{q}, \lambda) + \Delta_3(\mathbf{q}, \lambda)]. \quad (\text{A3})$$

Therefore the high temperature γ_G measures the average of the relative volume dependence of the phonon frequencies

$$\gamma_G \approx \frac{1}{3N} \sum_{\lambda=1}^{3N} (d \ln \omega_{\lambda} / d \ln V)_T. \quad (\text{A4})$$

The result above is valid when $T \geq \Theta_D$, but it only represents the lowest correction and must not be used at higher temperatures where the frequency shifts are more complicated and the frequencies less well defined because of damping effects. Experiments on lead by LEADBETTER [19] suggest that the range of validity for lead is $\Theta_D \leq T \leq 3\Theta_D$ ($\Theta_D \approx 90^\circ\text{K}$). From the measurements of LEADBETTER we find $\gamma_G(270^\circ\text{K}) = 2.7$ and we use this value for $(d \ln \Theta_D / d \ln V)_T$. (cf. appendix 2) $(d \ln \Theta_D / d \ln V)_T$ refers to very low temperatures but the weighting of different modes is the same as for the high temperature γ_G . At low temperatures Δ_2 and Δ_3 are small (although not zero). This fact leads us to consider γ_G calculated without the terms Δ_2 and Δ_3 , and at crystal volume $V_0 = V(T=0)$. Leadbetter gives the value 2.7 for this quantity and we thus have $(d \ln \Theta_D / d \ln V) = 2.7$ (cf. Appendix 2).

Appendix 2

From tunneling experiments in superconductors one can obtain a quantity $\alpha^2(\omega) F(\omega)$ [6], giving the product of the strength of electron-phonon interaction $\alpha^2(\omega)$ as a function of energy, and the phonon density of states $F(\omega)$. Using this function, it is possible to rewrite Eq. 1 for the electrical resistivity in the form [3]

$$\rho = \left(\frac{S}{S_0} \right)^2 \frac{N_{bs}(0)}{N_{fs}(0)} \frac{4\pi m \hbar (1 - \cos \Theta)}{n e^2 k T} \int \frac{\alpha^2(\omega) F(\omega) \omega d\omega}{[\exp(\hbar\omega/kT) - 1][1 - \exp(-\hbar\omega/kT)]} \quad (\text{A5})$$

where S/S_0 is the ratio between the true free area of the Fermi surface and the area in the free electron case. $N_{bs}(0)/N_{fs}(0)$ is the corresponding ratio for the density of electron states at the Fermi level. $1 - \cos \Theta$ denotes the average of the usual factor $1 - \cos \Theta$ that enters expressions for the resistivity. This factor has been rewritten in Eq. 1, using $q^2 = 2k_F(1 - \cos \Theta)$. Let us now make the assumption that $1 - \cos \Theta$ is approximately the same if it is considered separately for transverse phonons and for longitudinal phonons. In a polyvalent metal, where the resistivity is totally dominated by Umklapp scattering, this should be a reasonable approximation. We then take the high temperature limit of Eq. A1 and find that the relative importance of phonons of energy ω in the resistivity is given by $\alpha^2(\omega) F(\omega)/\omega$.

In the high temperature Grüneisen γ_G , all individual $\gamma(\mathbf{q}, \lambda)$ are equally weighted

$$\gamma_G = \int F(\omega) \bar{\gamma}(\omega) d\omega = \frac{2}{3} \bar{\gamma}_T + \frac{1}{3} \bar{\gamma}_L \quad (\text{A6})$$

where $\bar{\gamma}(\omega)$ is an average over all individual phonon modes with energy in $[\omega, \omega + d\omega]$. $\bar{\gamma}_T$ and $\bar{\gamma}_L$ are averages for the transverse and longitudinal branches. For $\gamma_R = (d \ln \Theta_R / d \ln V)$ we could write

$$\gamma_R \approx \int \frac{\alpha^2(\omega) F(\omega)}{\omega} \bar{\gamma}(\omega) d\omega. \quad (\text{A7})$$

The function $\alpha^2(\omega) F(\omega)$ has been obtained by McMILLAN and ROWELL [6]. It turns out that $\alpha^2(\omega)/\omega$ does not vary very much with ω in the region of typical phonon energies. From a study of the experimentally determined $\alpha^2(\omega) F(\omega)/\omega$ we have found it reasonable to take

$$\gamma_R = \frac{3}{4} \bar{\gamma}_T + \frac{1}{4} \bar{\gamma}_L. \quad (\text{A8})$$

The individual $\gamma(\mathbf{q}, \lambda)$ can vary very much with \mathbf{q} , but the general behaviour is the same for the transverse and the longitudinal branches (Fig. 1). Therefore γ_G should not be too bad as an approximation for γ_R .

If we make a series expansion in the denominator of Eq. 1, the first non-vanishing term gives a linear temperature dependence for the resistivity at high temperatures. The small correction for lead at room temperature from higher order terms can easily be estimated if we approximate $\alpha^2(\omega) F(\omega)/\omega$ by two sharp peaks at characteristic transverse and longitudinal frequencies and give them weights in the ratio 3:1 (cf. Eq. A9). We finally turn to $(d \ln \Theta_D / d \ln V)_P$. One has rigorously [6]

$$\lambda = 2 \int \frac{\alpha^2(\omega) F(\omega)}{\omega} d\omega. \quad (\text{A9})$$

We therefore have approximately the same weighting of different frequencies as in the high temperature electrical resistivity.

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Specific Heat of $Tb_xY_{1-x}Sb$ Mixed Crystals

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The specific heat of $Tb_xY_{1-x}Sb$ mixed crystals ($x = 0, 0.103, 0.383, 0.428, 0.467, 0.635, 0.928$ and 1.0) has been measured between 1.6 and $20^\circ K$ using an adiabatic calorimeter. The crystal field potential is described well taking into account only 4th order terms, and the overall splitting of the ground multiplet 7F_6 of the Tb^{3+} ion has been found to be $115^\circ K$ independent of the concentration x . For $x > 0.46$ the specific heat curves exhibit a behaviour typical for a second order phase transition. For lower concentrations a normal Schottky anomaly is found and no evidence for magnetic order was detected. The experimental results which are in agreement with magnetic measurements are compared with molecular field calculations including crystal field and exchange interaction.

La chaleur spécifique des composés mixtes $Tb_xY_{1-x}Sb$ ($x = 0, 0.103, 0.383, 0.428, 0.467, 0.635, 0.928$ et 1.0) a été mesurée entre 1.6 et $20^\circ K$ dans un calorimètre adiabatique. Le potentiel du champ cristallin peut être décrit en ne tenant compte que des termes du quatrième ordre et la décomposition totale du multiplet fondamental vaut $115^\circ K$, indépendamment de la concentration x . Pour $x > 0.46$, les courbes de la chaleur spécifique ont la forme caractéristique d'un changement de phase de deuxième espèce. Pour des concentrations plus petites, on mesure l'anomalie de Schottky normale, sans qu'aucun ordre magnétique se manifeste. Les résultats expérimentaux, compatibles avec les mesures magnétiques sont comparés aux courbes calculées dans l'approximation du champ moléculaire, en tenant compte du champ cristallin et de l'interaction d'échange.

Die spezifische Wärme von $Tb_xY_{1-x}Sb$ Mischkristallen ($x = 0, 0.103, 0.383, 0.428, 0.467, 0.635, 0.928$ und 1.0) wurde zwischen $1,6$ und $20^\circ K$ mit einem adiabatischen Kalorimeter gemessen. Das Kristallfeldpotential läßt sich allein durch Terme 4. Ordnung beschreiben, und die Gesamtaufspaltung des Grundmultiplets 7F_6 des Tb^{3+} Ions wurde zu $115^\circ K$ unabhängig von der Konzentration x bestimmt. Für $x > 0.46$ zeigen die Kurven der spezifischen Wärme das für einen Phasenübergang 2. Ordnung typische Verhalten. Für kleinere Konzentrationen findet man eine gewöhnliche Schottky-Anomalie ohne Anzeichen für eine magnetische Ordnung. Die experimentellen Ergebnisse, die mit magnetischen Messungen übereinstimmen, werden mit Kurven verglichen, die in Molekularfeldnäherung unter Einschluss des Kristallfeldes und der Austauschwechselwirkung berechnet wurden.

I. Introduction

The magnetic and caloric properties of compounds containing rare earth ions are strongly influenced by the symmetry and the strength of the crystal field [1]. Rare earth ions having an even number of f -electrons may have a singlet ground state in a crystal field. Recently the properties of the singlet ground state have been examined by several authors [1–3]. BLEANEY [9] and TRAMMELL [1] have shown that the ground state moment is zero until the exchange interaction exceeds a critical value. Specific heat measurements of rare earth nitrides have demonstrated that the condition given by TRAMMELL is fulfilled [4].

A singlet ground state is expected in the compounds of the type RE-X (RE = rare earth ion, X = N, P, As, Sb and Bi). These compounds crystallize in the