

Electron–phonon effects in 4d metals: calculation of coupling constant and resistivity

I I Mazin, E M Savitskii and Yu A Uspenskii

A A Baikov Institute of Metallurgy, Academy of Sciences, Leninsky pr. 49, Moscow, 117911, USSR

Received 26 April 1983, in final form 29 June 1983

Abstract. A simple technique for calculating the phonon-limited resistivity (ρ_{ph}) of metals is described which is analogous to the Gaspari–Gyorffy method for calculating the electron–phonon coupling constant (λ). ρ_{ph} and λ are calculated for all 4d metals and silver. The HCP metals have been treated as cubic, as is common in calculations of λ . For ρ_{ph} , however, this approach turns out to be too rough because it depends strongly on the average Fermi velocity which is very sensitive to crystal structure. In all transition metals investigated the superconducting and transport electron–phonon coupling constants are nearly equal, $\lambda \approx \lambda_{\text{tr}}$. Also nearly equal are their electronic parts, $\eta \approx \eta_{\text{tr}}$. The only exception is Pd, where η_{tr} is nearly 1.5 times larger than η ; this is because the superconducting and transport properties of Pd are defined by different parts of the Fermi surface. Palladium is the only 4d metal where the Mott model of conductivity (s–d scattering) is valid.

1. Introduction

Electron–phonon interaction (EPI) in transition metals is a subject of intensive theoretical and experimental investigations. After the works of Butler (1977), Pettifor (1977) and others, considerable progress has been made in understanding the relationship between the electron–phonon coupling constant (λ) and electronic structure. For example, the origin of the old empirical law relating the superconducting transition temperature and the number of valence electrons (Matthias 1955) now has a clear theoretical explanation. However, the trends in another important EPI defined quantity, namely the phonon-limited resistivity ($\rho_{\text{ph}}(T)$), are less well studied. In spite of the fact that both λ and ρ_{ph} are defined by the strength of the EPI, they vary across the transition-metal series in a rather different manner. It can be seen from figure 1 that in most 4d metals much of the variation in ρ_{ph} is correlated to that in λ but at the beginning of the series the correlation breaks down.

With a view to understanding better the trends in these quantities we have calculated λ and ρ_{ph} *ab initio* for all 4d transition metals including silver. The calculation of ρ_{ph} was performed using the method developed in our previous paper (Mazin *et al* 1982) which is based on the spherical approximation of Gaspari and Gyorffy (1972).

2. Method of calculation of phonon-limited resistivity

In this work we shall concentrate our attention on the intermediate temperatures ($\theta_{\text{D}}/3 \leq T \leq 2\theta_{\text{D}}$; θ_{D} is the Debye temperature). These temperatures are of special

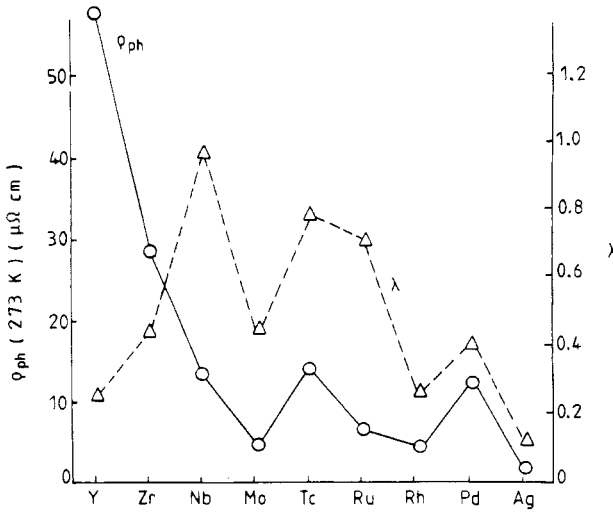


Figure 1. Variation of electron-phonon coupling constant and of phonon-limited resistivity across the 4d series (after Landolt-Börnstein 1982, Butler 1977).

importance in many applications and the most comfortable in experiments. In this temperature range the solution of the Boltzmann equation may be written as (Allen 1978)

$$\rho_{ph}(T) = \frac{12\pi k_B T \Omega}{\hbar e^2 N(0) \langle v^2 \rangle} \int \frac{d\omega}{\omega} \alpha_{tr}^2 F(\omega) \left(\frac{\omega/2k_B T}{\sinh(\omega/2k_B T)} \right)^2 \tag{1}$$

where $N(0)$ and $\langle v^2 \rangle$ are the electron density of states and the mean square velocity at the Fermi surface, Ω is the atomic volume and $\alpha_{tr}^2 F(\omega)$ is the transport spectral function of EPI. This function differs from the Eliashberg function $\alpha^2 F$ by the factor $(v_{k\lambda} - v_{k'\lambda'})^2$:

$$\alpha_{tr}^2 F(\omega) = \frac{1}{3} \sum_{\mathbf{k}\mathbf{k}', \lambda\lambda', \nu} \delta(E_{\mathbf{k}\lambda}) \delta(E_{\mathbf{k}'\lambda'}) \delta(\omega - \omega_{\mathbf{k}-\mathbf{k}', \nu}) |M_{\mathbf{k}\lambda, \mathbf{k}'\lambda'}^\nu|^2 (v_{\mathbf{k}\lambda} - v_{\mathbf{k}'\lambda'})^2 / N(0) \langle v^2 \rangle \tag{2}$$

where λ is the band index, ν numbers the phonon branches, $\omega_{\mathbf{q}, \nu}$ is the frequency of the phonon with wavevector \mathbf{q} and $M_{\mathbf{k}\lambda, \mathbf{k}'\lambda'}^\nu$ is the electron-phonon matrix element. Let us rewrite equation (1) in a factorised form:

$$\rho_{ph}(T) = \frac{6\pi k_B T \Omega}{\hbar e^2 N(0) \langle v^2 \rangle} B(T) \lambda_{tr} \tag{3}$$

$$B(T) = \int \frac{d\omega}{\omega} \alpha_{tr}^2 F(\omega) \left(\frac{\omega/2k_B T}{\sinh(\omega/2k_B T)} \right)^2 \left(\int \frac{d\omega}{\omega} \alpha_{tr}^2 F(\omega) \right)^{-1} \tag{4}$$

$$\lambda_{tr} = \eta_{tr} / M \langle \omega^2 \rangle_{tr} = 2 \int \frac{d\omega}{\omega} \alpha_{tr}^2 F(\omega) \tag{5}$$

$$\eta_{tr} = \sum_{\mathbf{k}\mathbf{k}', \lambda\lambda'} | \langle \mathbf{k}'\lambda' | \nabla V_{ei} | \mathbf{k}\lambda \rangle |^2 \delta(E_{\mathbf{k}\lambda}) \delta(E_{\mathbf{k}'\lambda'}) (v_{\mathbf{k}\lambda} - v_{\mathbf{k}'\lambda'})^2 / N(0) \langle v^2 \rangle \tag{6}$$

where λ_{tr} is the transport constant of the EPI, η_{tr} is the electronic part of λ_{tr} and $E_{\mathbf{k}\lambda}$, $|\mathbf{k}\lambda\rangle$ and $v_{\mathbf{k}\lambda}$ are the energy, the wavefunction and the velocity of the electron with wavevector \mathbf{k} in the band λ ; energy is measured from the Fermi level and ∇V_{ei} is the change in crystal potential per unit displacement of an ion: $\delta V(\mathbf{r} - \mathbf{R}) = \delta \mathbf{R} \nabla V_{ei}(\mathbf{r} - \mathbf{R})$. These formulae are analogous to the commonly used formulae for $\lambda = \eta / M \langle \omega^2 \rangle$ and η .

We shall compute η , η_{tr} and $N(0)\langle v^2 \rangle$ *ab initio*, while $\langle \omega^2 \rangle$, $B(T)$ and $\langle \omega^2 \rangle_{tr}$ will be obtained from the experimental phonon densities of states. This technique imposes strong limitations on the temperature dependence of $\rho_{ph}(T)$. Nevertheless it is known that even the Bloch-Grüneisen formula describes $\rho_{ph}(T)$ sufficiently accurately at intermediate temperatures. In fact, $B(T)$ is close to one and the phonon characteristics affect primarily the value of $\langle \omega^2 \rangle_{tr}$. Therefore the factorisation of λ_{tr} into electronic and phonon contributions is as adequate as the analogous factorisation of λ .

By rewriting the factor $(v_{\mathbf{k}\lambda} - v_{\mathbf{k}\lambda'})^2$ in equation (6) as $(v_{\mathbf{k}\lambda}^2 + v_{\mathbf{k}\lambda'}^2) - 2v_{\mathbf{k}\lambda}v_{\mathbf{k}\lambda'}$, one can obtain an obvious separation of η_{tr} : $\eta_{tr} = \eta_{20} - \eta_{11}$ so that η_{20} and η_{11} depend on $v_{\mathbf{k}\lambda}^2 + v_{\mathbf{k}\lambda'}^2$ and $v_{\mathbf{k}\lambda}v_{\mathbf{k}\lambda'}$ respectively.

Equation (6) for λ may be greatly simplified by using the rigid muffin-tin approximation (RMTA) and the spherical approximation (SA) (Gaspari and Gyorffy 1972).

The main idea of the SA is as follows. When the electron wavefunction inside the muffin-tin sphere is expanded in spherical harmonics ($L \equiv \{l, m\}$)

$$\Psi_{\mathbf{k}\lambda}(r) = \sum_{\mathbf{R}} \exp(i\mathbf{k}\mathbf{R}) \sum_L A_L(\mathbf{k}, \lambda) i^l Y_L(\widehat{\mathbf{r}-\mathbf{R}}) R_l(|\mathbf{r}-\mathbf{R}|, E_{\mathbf{k}\lambda}) \quad (7)$$

the selection rules for matrix elements in equation (6) are supposed to be the same as for free electrons, where $A_L(\mathbf{k}, \lambda) \sim Y_L^*(\hat{\mathbf{k}})$, $E_{\mathbf{k}\lambda} = E(|\mathbf{k}|, \lambda)$ and $v_{\mathbf{k}\lambda} = kv(|\mathbf{k}|, \lambda)/|\mathbf{k}|$. Then the selection rules for η_{20} will be the same as for η , giving

$$\eta_{20} = \sum_l W_{l,l+1}^2 (N_l \langle Nv^2 \rangle_{l+1} + N_{l+1} \langle Nv^2 \rangle_l) / N(0) \langle v^2 \rangle \quad (8)$$

where $W_{l,l+1}$ is the RMTA matrix element and N_l is the partial Fermi energy density of states,

$$\langle Nv^2 \rangle_l = \sum_{\mathbf{k}\lambda} \delta(E_{\mathbf{k}\lambda}) v_{\mathbf{k}\lambda}^2 \sum_m |A_{lm}(\mathbf{k}, \lambda)|^2 / 3(2l+1).$$

It was shown by Butler (1977) that the SA introduces an error of a few per cent into the calculation of η . The selection rules for η_{11} are more complicated. The final result is ($\langle Nv \rangle_{l,l+1}$ are the matrix elements of $v_{\mathbf{k}\lambda}$)

$$\eta_{11} = \frac{2}{3} \sum_l \frac{l+1}{2l+3} [2(l+2)W_{l,l+1}W_{l+1,l+2} \langle Nv \rangle_{l,l+1} \langle Nv \rangle_{l+1,l+2} - W_{l,l+1}^2 \langle Nv \rangle_{l,l+1}^2 / (2l+1)] / N(0) \langle v^2 \rangle. \quad (9)$$

Because of the complex shape of the Fermi surface the assumption that $v_{\mathbf{k}\lambda} = (\mathbf{k}/|\mathbf{k}|)v(|\mathbf{k}|, \lambda)$ is not quite correct. In transition metals it often gives rise to an error of more than 100% in the calculation of η_{11} . However, for the same reason, $\langle Nv \rangle_{l,l+1}$ is found to be rather small since it is a kind of average of the electron velocity over the Fermi surface. Hence η_{11} is small in comparison with η_{20} (tables 1 and 2) and the error introduced by η_{11} in η_{tr} is found to be insignificant (a few per cent). In simple metals η_{11} may be as large as 10–20%, but in these metals the SA is quite adequate and the method remains accurate enough in this case too. Therefore the method we use provides an accuracy of a few per cent in the computation of expression (1) at temperatures $\theta_D/3 \lesssim T \lesssim 2\theta_D$. Further details are given by Mazin *et al* (1982)†.

† In that paper there is a misprint (the fault of the authors). In the definition of $t_{ll}^{(l)}$ (p K31) the factor $\sqrt{4\pi/3}$ is omitted ($T_{LL}^{(l)} = g_{L,10}^l t_{ll}^{(l)} \sqrt{4\pi/3}$). The final formulae are quite correct.

Table 1.

Metal	s	$N(0)$	$N(0)\langle v^2 \rangle$	η	η_{tr}	η_{11}
Nb	3.072	21.07	7.480	0.183	0.188	-2.1×10^{-3}
Mo	2.905	8.36	5.675	0.116	0.126	-1.9×10^{-3}
Rh	2.818	18.19	5.780	0.101	0.0960	-2.9×10^{-4}
Pd	2.876	29.87	3.152	0.0492	0.0699	2.5×10^{-4}
Ag	3.017	3.56	6.367	0.0128	0.0146	9.3×10^{-4}

Table 2.

Metal	s	$N(0)$	$N(0)\langle v^2 \rangle$	η	η_{tr}	η_{11}
Y _{BCC}	3.79	34.6	4.03	0.0631	0.0642	-4.2×10^{-5}
Y _{FCC}		27.9	3.23	0.0536	0.0533	-5.1×10^{-5}
Zr _{BCC}	3.349	22.9	3.97	0.119	0.122	-1.1×10^{-3}
Zr _{FCC}		19.8	5.55	0.0959	0.0916	-8.3×10^{-4}
Tc _{BCC}	2.850	20.2	6.72	0.205	0.211	-1.5×10^{-3}
Tc _{FCC}		16.7	7.75	0.172	0.182	-4.6×10^{-3}
Ru _{BCC}	2.798	33.9	7.08	0.190	0.211	-1.0×10^{-3}
Ru _{FCC}		15.2	6.76	0.127	0.135	-3.6×10^{-3}

3. Results

The coupling constant λ and the resistivity have been calculated for all 4d metals and for silver. The hexagonal metals were treated as cubic (BCC and FCC). Band-structure calculations were performed using the LMTO method with $l_{\max} = 3$. The number of k points in the irreducible part of the Brillouin zone was 306 for FCC and 285 for BCC structures. We have used the self-consistent crystal potentials of Moruzzi *et al* (1978). In this book the potentials are listed for lattice parameters different from the experimental ones. We have always made calculations for the real lattice parameters, expanding or contracting the region of the constant potential.

As the RMTA leads to a significant underestimation of the EPI in simple metals, for silver we have introduced corrections to the RMTA, adding to ∇V_{ei} the expression $\delta(r-s)\Delta V = 10Z \exp(-s/\kappa)\delta(r-s)/s$ where s is the Wigner-Seitz radius and κ is the Debye screening radius[†]. This expression leads to suitable values of the corrections in simple metals (0.23 Ryd in Ag) and it vanishes in transition metals.

All integrations in k space, as well as the calculations of the Fermi velocity, were performed by the tetrahedron method. The results for η and η_{tr} are listed in tables 1 and 2 (all quantities are in atomic units, energy is in Ryd, velocity is in Ryd r_B). The calculated values of $\langle v^2 \rangle$ and η_{tr} in Nb and Pd are close to those found by Pinski *et al* (1981), but for η_{11} the agreement is only qualitative.

The calculation of the phonon quantities was performed as follows: as is common in the calculation of λ , $\alpha^2 F(\omega)$ was assumed to be proportional to $F(\omega)$ —the phonon density of states (constant α^2 approximation). For $\alpha_{tr}^2 F(\omega)$ a more sophisticated

[†] This lowest-order correction is related to the difference between the muffin-tin zero and the value of the ion potential at infinity. One can obtain this expression by describing the ion potential at a distance $r \geq s$ as a screened Coulomb potential. It should be noted that the value of the pre-factor does not significantly affect the final result.

Table 3.

Metal	$\langle \omega^2 \rangle^{1/2}$	$\langle \omega^2 \rangle_{tr}^{1/2}$	λ	λ_{exp}	λ_{tr}	$\rho_{ph}(273\text{ K})$	$\rho_{exp}(273\text{ K})$
Nb	196	204	1.40	0.97	1.32	14.3	13.5
Mo	270	265	0.45	0.44	0.50	5.8	4.9
Rh	245	245	0.44	0.27	0.42	4.1	4.3
Pd	141	192	0.62	—	0.49	10.4	9.7
Ag	156	156	0.13	0.13	0.16	1.8	1.7

Table 4.

Metal	$\langle \omega^2 \rangle^{1/2}$	$\langle \omega^2 \rangle_{tr}^{1/2}$	λ	λ_{exp}	λ_{tr}	$\rho_{ph}(273\text{ K})$	$\rho_{exp}(273\text{ K})$
Y _{BCC}	156	163	0.80	0.26	0.74	28.5	53.7
Y _{FCC}			0.68		0.67	30.0	
Zr _{BCC}	176	190	1.15	0.45	1.00	26.7	38.6
Zr _{FCC}			0.86		0.86	15.0	
Tc _{BCC}	248	248	0.92	0.78	0.94	8.8	16.7
Tc _{FCC}			0.77		0.82	6.7	
Ru _{BCC}	278	287	0.65	0.71	0.69	5.6	5.6
Ru _{FCC}			0.44		0.44	3.7	

approximation has been used. One can see from equation (2) that α_{tr}^2 differs from α^2 by the factor $(v_{k\lambda} - v_{k'\lambda'})^2$, which for $|\mathbf{k} - \mathbf{k}'| \rightarrow 0$ may be written as $(\mathbf{k} - \mathbf{k}')^2 \sim (\omega_{\mathbf{k}-\mathbf{k}'}/c)^2$, where ω_q is the phonon frequency and c is the sound velocity. Therefore $\alpha_{tr}^2 \sim \omega^2$ may be taken as the first approximation. Taking into account the difference between longitudinal and transverse phonons we divide $F(\omega)$ conditionally into two parts, $F(\omega) = F_{\parallel}(\omega) + F_{\perp}(\omega)$, which yields

$$\alpha_{tr}^2 F(\omega) \sim \omega^2 (F_{\perp}(\omega)/\omega_{\perp}^2 + F_{\parallel}(\omega)/\omega_{\parallel}^2) \tag{10}$$

where ω_{\perp} and ω_{\parallel} are the cut-off frequencies of F_{\perp} and F_{\parallel} .

The estimates of these frequencies are the positions of the first and second maxima of $F(\omega)$. The calculated values of $\langle \omega^2 \rangle$, $\langle \omega^2 \rangle_{tr}$, λ , λ_{tr} and $\rho_{ph}(273\text{ K})$ and the experimental values of λ and ρ_{ph} are shown in tables 3 and 4. The phonon densities of states are from Landolt-Börnstein (1981), excluding Rh and Tc, for which only θ_D are available. Experimental data for λ were taken from Butler (1977) and for $\rho_{ph}(273\text{ K})$ from Landolt-Börnstein (1982). The agreement between theory and experiment for λ and especially for ρ_{ph} is fairly good. For HCP metals the comparison between the calculation and experiment is questionable because of the strong dependence of λ and ρ_{ph} on crystal structure.

4. Discussion

The 4d metals investigated may be classified into three groups according to their transport properties: (i) all transition metals except Pd, (ii) Pd, in which a complicated and unusual mechanism of conductivity takes place, and (iii) Ag (a noble metal).

The main feature of the first group is the approximate equality of η and η_{tr} , λ and λ_{tr} . This may be easily explained. Assuming $\langle Nv^2 \rangle_l \approx \langle v^2 \rangle N_l$ in equation (8), one can obtain

an approximate equality $\eta_{20} \approx \eta$. In transition metals η_{11} is negligible in comparison with η_{20} ; hence $\eta \approx \eta_{tr}$. Such an assumption is reasonable when the absolute value of the electron velocity at the Fermi surface is approximately constant. It is a good approximation in all 4d transition metals (except Pd) where all sheets of the Fermi surface are due to the d bands. In these metals $\langle \omega^2 \rangle$ and $\langle \omega^2 \rangle_{tr}$ are also found to be nearly equal; hence $\lambda \approx \lambda_{tr}$.

The different variations of λ and ρ_{ph} at the beginning of the series (Y and Zr) are due to the factor $\Omega/N(0)\langle v^2 \rangle$ in equation (2). The average d-electron velocity may be estimated roughly as

$$\langle v_d^2 \rangle^{1/2} \sim 0.3 W_d s \quad (11)$$

where W_d is the width of the d band. Hence $\Omega/N(0)v^2 \sim s/W_d$. The variation of both quantities is shown in figure 2. The qualitative correlation is quite pronounced.

The minimum in the middle of the series is closely related to the well known cohesive energy maximum in metals with a half-filled d band. Nevertheless, the increase of s/W_d does not explain the whole increase of ρ_{ph} in Zr and especially in Y. Our calculation leads to an overestimation of λ in Y and Zr and to an underestimation of ρ_{ph} (tables 2 and 4). This discrepancy arises from the fact that $N(0)$ and especially $\langle v^2 \rangle$ depend strongly on the crystal structure, as well as on the position of the Fermi level. The low values of v_F at the beginning of the series are specific to the HCP structure—hence the failure of ‘cubic’ calculations. One could try to extract $N(0)\langle v^2 \rangle$ from the optical measurements, but this is also doubtful because this quantity is defined by the intensity of the intraband transitions and in many metals it is difficult to distinguish them from the interband low-energy transitions, so that the error in $N(0)\langle v^2 \rangle$ is unpredictable.

Palladium differs from other 4d metals because in Pd there are two conductivity bands: the d-like band (‘jungle gym’) with a high density of states (about 85% of $N(0)$) and a low electron velocity (about 10% of $\langle v^2 \rangle^{1/2}$), and an s-like band (Γ -centred sheet), which contains only 15% of $N(0)$ but where the electron velocity is greater than average (80% of $N(0)\langle v^2 \rangle$). Therefore η and λ are defined mainly by the parameters of the ‘d sheet’, while η_{tr} and λ_{tr} are defined by the scattering from the ‘s sheet’ to the ‘d sheet’ (the appropriate

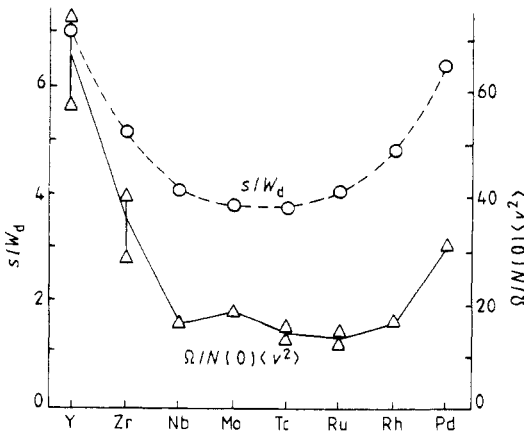


Figure 2. Variation of average d-electron Fermi velocity and of inverse d-band width across the 4d series.

term in equation (8) is proportional to $N_d \langle Nv^2 \rangle_f$). As a result η_{tr} turns out to be 1.5 times larger than η . We find λ close to λ_{tr} , as it is in other 4d metals, only because of the appreciable difference between ω^2 and ω_{tr}^2 . It is obvious that this resemblance is quite accidental. The specific mechanism of the electron-phonon scattering justifies the Mott model for conductivity in this metal, as mentioned by Pinski *et al* (1981), while in other 4d metals this model is not valid.

Silver is a typical noble metal with a nearly spherical Fermi surface. It differs from simple metals only in the fact that $N(0)$ contains some d electrons because of the hybridisation. The spherical shape of the Fermi surface causes η_{11} to be comparable with η_{tr} and λ_{tr} are defined by the scattering from the 's sheet' to the 'd sheet' (the appropriate transition metals, so that the final error does not increase. The equality $\eta_{20} \approx \eta$ is as true as in other 4d metals (except Pd). The large value of $\langle v^2 \rangle$ with the low density of states $N(0)$ yields a small λ and high conductivity.

5. Conclusion

The numerical study of the EPI in 4d metals shows that in cubic metals the RMTA is accurate enough to describe $\rho_{ph}(T)$. The discrepancy between the theory and experimental data is larger for λ than for ρ_{ph} . This is probably because the experimental determination of λ is much more problematic. Treating hexagonal metals as cubic does not allow good results to be achieved. They require band-structure calculations for the HCP lattice and probably necessitate giving up the SA.

Some specific features may be noted: (i) a considerable decrease of $N(0)\langle v^2 \rangle$ at the ends of the series and as a result the different variation of λ and ρ_{ph} , (ii) the approximate equality of λ and λ_{tr} in transition metals and (iii) the specific mechanism of conductivity in Pd.

Our calculations cannot describe the temperature dependence of ρ_{ph} at low temperatures ($T \ll \theta_D/3$). Generally speaking it is possible to describe $\rho_{ph}(T)$ at high temperatures in the framework of the method without loss of simplicity. However, it requires taking anharmonic effects and Fermi smearing into account (Pinski *et al* 1978).

Acknowledgments

Fruitful discussions with E G Maksimov are gratefully acknowledged; we are indebted to P M Petrov for his help in dealing with computers.

References

- Allen P B 1978 *Phys. Rev. B* **17** 3725-34
- Butler W H 1977 *Phys. Rev. B* **15** 5267-82
- Gaspari G D and Gyorffy B L 1972 *Phys. Rev. Lett.* **28** 801-5
- Landolt-Börnstein 1981 *New Series, Group III* vol. 13, subvol. a
- 1982 *New Series, Group III* vol. 15, subvol. a
- Matthias B T 1955 *Phys. Rev.* **97** 74-6

- Mazin I I, Savitskii E M and Uspenskii Yu A 1982 *Phys. Status Solidi b* **112** K29–33
- Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (New York: Pergamon)
- Pettifor D G 1977 *J. Phys. F: Met. Phys.* **7** 1009–28
- Pinski F J, Allen P B and Butler W H 1981 *Phys. Rev. B* **23** 5080–98
- 1978 *Phys. Rev. Lett.* **41** 431–4