RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 5 15 AUGUST 1987-I

Empirical electron-phonon λ values from resistivity of cubic metallic elements

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(Received 17 April 1987; revised manuscript received 11 May 1987)

Band-theory values of $N(E_F)$ and Ω_p (density of states and Drude-plasma frequency) are used to extract dimensionless electron-phonon parameters λ_{tr} from the measured resistivity ρ and λ_γ from the measured low-T electronic specific heat γT for 25 cubic elements. In cases where independent reliable estimates of λ are available from the superconducting transition temperature T_c, λ_{tr} is consistent, and λ_γ, although more uncertain, seems meaningful. Empirical estimates of λ for the nonsuperconducting metals Ca, Ba, Fe, Ni, and Rh are suggested.

I. INTRODUCTION

Papaconstantopoulos[1] has included in his recent handbook of energy bands the values of $N(E_F)$ and Ω_p for all cubic elemental metals, where $N(E_F)$ is the density of states of electrons of both spins at the Fermi energy, and Ω_p is the Drude-Plasma energy $[4\pi e^2 N(E_F)\langle v^2\rangle/3]^{1/2}$, and $\langle v^2\rangle$ is the mean-square band velocity at E_F. These numbers enable independent determinations of the electron-phonon coupling parameters λ_{tr} and λ_γ from experimental resistivity ρ and specific-heat coefficient γ, respectively. Technically, both $N(E_F)$ and Ω_p should be derived from quasiparticle (QP) rather than density-functional (DF) bands. Thus, the consistency of various determinations of λ tests our knowledge of QP properties.

The resistivity and Drude-plasma frequency determine λ_{tr} via the formula

$$\lambda_{tr}=(\hbar\Omega_p^2/8\pi^2)(\rho/k_BT)F_{th} \quad (1)$$

$$=(0.8422\times10^{-3})[\rho(\mu\Omega\,\mathrm{cm})]\{[\Omega_p(\mathrm{eV})]^2\}F_{th}\ . \quad (2)$$

This equation assumes the impurity resistivity ρ_0, as well as any other contributions, to be small compared to the electron-phonon contribution described by standard Boltzmann theory. The temperature T must be about $0.7\Theta_D$ or greater, and F_{th} is the leading correction factor in powers of Θ/T,

$$F_{th}=(1-\theta^2/12T^2)^{-1}\ , \quad (3)$$

$$\theta^2=\hbar^2\langle\Omega^2\rangle/k_B^2\simeq(0.68\Theta_D)^2\ . \quad (4)$$

These equations have been tested in various ways[2] and rest on approximations which are quite safe for nearly all the elements. The approximate value $\theta\sim0.68\Theta_D$ in Eq. (4) is based on detailed numerical work for four elements[2] and may vary by $\pm10\%$, but leads to only small errors in λ_{tr} since $F_{th}\approx1$.

The experimental specific-heat coefficient γ is proportional to a quasiparticle density of states $N_\gamma(E_F)$, and is larger than the band quasiparticle density of states $N(E_F)$ by the electron-phonon mass enhancement parameter λ,

$$1+\lambda_\gamma\equiv N_\gamma(E_F)/N(E_F)\ , \quad (5)$$

$$N_\gamma(E_F)(\mathrm{states/Ry\,atom})=5.769\,\gamma(\mathrm{mJ/mole\,K^2})\ . \quad (6)$$

In Eq. (5), λ_γ equals λ provided $N(E_F)$ comes from an exact quasiparticle band structure which includes all many-body effects except electron phonon.[3] Finally, λ appears in the McMillan[4] equation for the superconducting transition temperature, and in favorable cases can be extracted from superconducting quasiparticle tunneling.[5] The resulting empirical values of λ are shown in the last four columns of Table I. The estimated reliability of the right-hand side of Eqs. (1) and (5) is about 10%, which means that for small λ, Eq. (1) is much more accurate than Eq. (5). The results will now be discussed.

II. RESULTS

A. Alkali metals

None of these metals are superconducting. In all cases except Li, the empirical values λ_{tr} and λ_γ are so small that T_c as predicted by the McMillan equation would be unmeasurably low. There is quite close correspondence between λ_{tr} and λ as calculated from single plane-wave pseudopotential theory,[6] and qualitative agreement with the "corrected rigid muffin-tin" calculation of Zdetsis, Economou, and Papaconstantopoulos.[7] Empirical values λ_{tr} for these and several other metals were also found in Ref. 7 and agree fairly well with the present ones. The negative value for Cs simply reflects the $\sim10\%$ uncertainty in $1+\lambda_\gamma$ and is not to be taken seriously.

For lithium, the empirical values of λ and also the calculated values[6] suggest that it should be a superconductor. The absence of superconductivity[8] can be attributed[9] to the fact that the low-temperature structure differs from the bcc structure seen at room temperature and used in the band calculations.[4] Then a value $\lambda\sim0.35$ would be a property only of the high-T phase, and the low-temperature value λ_γ would no longer be 0.40, but would require a new band calculations to determine and would presumably be small.

TABLE I. The present empirical values of λ_{tr} and λ_γ are given in columns 6 and 7, as extracted from the data or calculations in columns 1–4. The values λ_{McM} are from McMillans's paper (Ref. 4) except for the values of Th and Rh which were calculated using $\mu^* = 0.13$.

	$N(E_F)$ (states/ Ryatom) (Ref. 1)	$N_\gamma(E_F)$[a] (States/ Ryatom)	$\hbar\Omega_p$ (eV) (Ref. 1)	$\rho(295)$[a,b] ($\mu\Omega$ cm)	F_{th}[a]	λ_{tr}	λ_γ	λ_{McM} (Ref. 4)	λ_{tun}
Li	6.73	9.4	6.53	9.32	1.05	0.35	0.40		
Na	6.72	8.0	5.81	4.75	1.01	0.14	0.18		
K	10.49	12.0	4.21	7.19	1.004	0.11	0.14		
Rb	12.52	13.9	3.75	12.5	1.001	0.15	0.11		
Cs	20.43	18.5	3.11	20.0	1.001	0.16	−0.09		
Cu	4.03	4.01	9.11	1.70	1.05	0.13	−0.01		
Ag	3.59	3.7	9.28	1.61	1.02	0.12	0.04		
Au	4.08	4.2	8.84	2.20	1.01	0.15	0.05		
Ca	17.14	16.7	4.20	3.6	1.02	0.05	−0.02		
Ba	15.51	15.6	2.87	39	1.005	0.27	0.00		
Al	5.46	7.8	12.44	2.74	1.09	0.39	0.43	0.38	
Pb	6.86	17.2	9.12	21.0	1.005	1.48	1.51	1.12	1.55[c]
V	24.83	53.4	7.80	19.9	1.07	1.09	1.15	0.60	~0.8[d]
Nb	19.86	44.9	9.12	14.5	1.03	1.06	1.26	0.82	~1.0[e]
Mo	8.05	11.5	8.06	5.3	1.10	0.32	0.43	0.41	
Ta	17.08	34.0	8.77	13.1	1.03	0.87	0.99	0.65	0.69[f],0.73[g]
W	5.73	7.5	7.39	5.3	1.08	0.26	0.31	0.28	
Ir	12.71	17.9	10.33	5.1	1.08	0.50	0.41	0.34	
Th	15.17	23.5[h]	6.33	15.2	1.01	0.52	0.55	0.56	
Cr	9.63	8.1	6.41	12.9	1.21	0.55	−0.16		
Fe	15.16	28.7	6.11[i,j]	9.8	1.11	0.34	0.90		
Ni	23.79	40.5	6.96[j]	7.0	1.10	0.31	0.70		
Rh	18.68	28.3	9.57	4.8	1.11	0.41	0.51	0.24	
Pd	32.16	54.3	7.18	10.5	1.03	0.47	0.69		
Pt	29.90	39.2	8.56	10.4	1.03	0.66	0.31		

[a]From values tabulated by C. Kittel, *Introduction to Solid State Physics,* 5th ed. (Wiley, New York, 1976), pp. 167, 170, 126.
[b]J. Bass, in *Metals: Electronic Transport Phenomena,* edited by H. Klupper, Landolt-Börnstein, Group 3, Vol. 17, Pt. a (Springer-Verlag, Berlin, 1982), Sec. 1-2.2.
[c]W. L. McMillan and J. M. Rowell, Phys. Rev. Lett. **14**, 108 (1965).
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[h]Based on $\gamma = 4.08$ mJ/moleK [C. A. Luengo, J. M. Cotignola, J. G. Serini, A. R. Sweedler, M. B. Maple, and J. G. Huber, Solid State Commun. **10**, 459 (1972)].
[i]The values $\Omega_{p\uparrow} = 7.31$ eV and $\Omega_{p\downarrow} = 4.63$ eV were accidentally omitted from Ref. 1 [D. A. Papaconstantopoulous (private communcation)].
[j]Ω_p^2 is defined as the average $\frac{1}{2}(\Omega_{p\uparrow}^2 + \Omega_{p\downarrow}^2)$ of majority- and minority-spin values.

B. Noble metals

These are similar to the alkalis. None are superconducting. There is an extrapolation of $T_c \sim 0.0002$ K in Au based on alloy trends[10] which suggests $\lambda \sim 0.2$, consistent with $\lambda_{tr} \sim 0.15$. Similar, but less reliable extrapolations[10] for Cu and Ag suggest $\lambda \sim 0.16$, consistent with $\lambda_{tr} = 0.13$ and 0.12. Since λ_γ has an uncertainty of order ± 0.1 from uncertainties in band theory, λ_{tr} and λ_γ are consistent.

C. Ca, Ba, Al, Pb

The polyvalent *sp* metals have a variety of noncubic structures, and only Ca, Sr, Ba, Al, and Pb are cubic. Sr is not included because the bands of Ref. 1 correspond to a zero-gap semiconductor (disagreeing with experiment which suggest semimetallic or metallic behavior.) Both transport and specific heat give small values of λ for Ca and Ba, consistent with the absence of superconductivity.

As usual, Al and Pb fall perfectly into place, and seem to be the best understood of metals. The McMillan value $\lambda=1.12$ for Pb is apparently an underestimate. McMillan's prefactor $\Theta_D/1.45$ is almost always too large, causing underestimates of λ.

D. Superconducting transition metals and actinides

There is remarkable consistency between λ_γ and λ_{tr} for these metals, and decent agreement with McMillan if we allow that his estimates are generally low. The worst in this respect is vanadium. Independent theoretical estimates[11] have also given values of $\lambda\sim1.0$ which has supported a suggestion that T_c is somewhat suppressed by spin fluctuations.[12]

There is a slight problem with Ta, where the present values of λ_{tr} and λ_γ are significantly higher than McMillan or tunneling values. A previous estimate[2] gave lower and more consistent values of λ_{tr}. The value of Ω_p in Ta seems especially sensitive to the fine details of the energy bands, and differs between the calculation of Ref. 1 (8.77 eV, Hedin-Lunqvist exchange correlation) and the calculation used in Ref. 2 (7.1 eV, potential from Boyer *et al.*[13] using the $X\alpha$ method). Both calculations were self-consistent and fully relativistic except for spin-orbit interactions. Fortunately, this sensitivity to energy bands does not seem to occur frequency.

It is worth mentioning that for transition metals, theoretical calculations based on a rigid muffin-tin or similar model apparently give quite reliable values of λ (Ref. 11) and λ_{tr} (Ref. 1).

E. Nonsuperconducting transition metals

These metals are antiferromagnetic (Cr), ferromagnetic (Fe, Ni), or nearly magnetic (Rh, Pd, Pt), which explains the absence of superconductivity and a corresponding ignorance of electron-phonon coupling strengths. Rh actually is superconducting[14] below 325 μK, but can still be classified with Pd and Pt because of the very strong suspicion that its T_c has been suppressed by spin fluctuations. The values of λ_{tr} and λ_γ in Cr differ widely and both should be ignored, because the calculated energy bands do not include the antiferromagnetic order. This order apparently reduces $N(E_F)$ significantly below the calculated value, as is necessary to have $\lambda_\gamma>0$. This will presumably alter Ω_p and hence λ_{tr}. In all three magnetic metals (Cr, Fe, and Ni) the value of λ_{tr} is distorted by the presence of spin-disorder scattering in $\rho(T)$, but for Fe and Ni the effect may be fairly small at 295 K, which is well below the Curie temperature where maximum spin-disorder scattering appears. Thus the values $\lambda_{tr}=0.34$ and 0.31 in Fe and Ni are probably upper limits but may accurately reflect the size of electron-phonon coupling. The method of extracting λ_{tr} for Fe and Ni needs explaining. Making the usual variational ansatz to solve the Boltzmann equation yields the formula

$$\sigma_{dc}=(\Omega_{p\uparrow}^2\tau_\uparrow+\Omega_{p\downarrow}^2\tau_\downarrow)/8\pi\ , \tag{7}$$

where Ω_p is a Drude plasma for the up-spin electrons normalized so as to equal Ω_p for a paramagnetic metal in the nonmagnetic limit. The scattering rates $1/\tau_\sigma$ are determined by electron-phonon scattering for decoupled spin species, and equal $2\pi\lambda_{tr,\sigma}k_BT/\hbar$ in the high-T limit. The parameters $\lambda_{tr,\sigma}$ can be different for the two-spin species, but cannot both be extracted from $\rho(T)$. By defining Ω_p^2 as the average value of $\Omega_{p\sigma}^2$ and using Eq. (1), we obtain an average value of

$$\lambda_{tr}=(\Omega_{p\uparrow}^2+\Omega_{p\downarrow}^2)/(\Omega_{p\uparrow}^2\lambda_{tr\downarrow}^{-1}+\Omega_{p\downarrow}^2\lambda_{tr\downarrow}^{-1})\ . \tag{8}$$

For the case of Ni where $\Omega_{p\sigma}^2$ is very similar for both bands, λ_{tr} is $2(\lambda_\uparrow^{-1}+\lambda_\downarrow^{-1})^{-1}$. For Fe, where $\Omega_{p\uparrow}^2$ is bigger than $\Omega_{p\downarrow}^2$, the average is pulled closer to $\lambda_\uparrow$. If $\lambda_{tr,\sigma}$ is independent of σ, then it is correctly given by λ_{tr}, but there is no reason why this should hold; the rough rule of thumb is that λ_σ should scale with the density of state N_σ which is quite different for the two bands. Independent of these complications, the transport data show a fairly weak electron-phonon interaction, $\lambda\sim0.3$. This disagrees with the mass renormalization $\lambda_\gamma\sim0.8$, which may signal a significant electron-magnon enhancement of γ, or else possibly some extra heat capacity coming directly from magnetic collective excitations.

The nearly ferromagnetic metals Rh, Pd, and Pt have large values of $N(E_F)$ which prevents λ from being very small. The value $\lambda\sim0.4\pm25\%$ seems a reasonable guess. The weakness (Rh) or absence (Pd, Pt) of superconductivity[14] can be blamed on long-lived spin fluctuations, which apparently[2] contribute little to $\rho(295\ \mathrm{K})$ but may enhance λ_γ somewhat. The anomalous ordering $\lambda_\gamma<\lambda_{tr}$ in Pt seems suspicious and may reflect a special sensitivity to band structure as was seen in Ta. The "McMillan" value of λ for Rh given in Table I neglects the influence of spin fluctuations. Buchal *et al.*[14] suggest a value $\lambda=0.34$ after estimating a spin-fluctuation contribution $\lambda_{SF}\sim0.1$. No special reliability can be attached to any current theory relating T_c to λ_{SF}, but the trend is clear: λ may be significantly bigger than 0.24, and the present value 0.41 is reasonable.

F. Others

For completeness, it is worth mentioning the calculations of Pickett, Freeman, and Koelling[15,16] for cubic phases of La and Ce. For fcc La, theoretical values[15] of $N(E_F)=27.47$ states/Ry atom and $\Omega_p=3.17$ eV were found. These were translated into values $\lambda_\gamma=1.42$, $\lambda_{tr}=1.08$, which compare with $\lambda\approx0.8$–0.9 from tunneling. Difficulties were encountered both for λ_γ (the low-T sample had an admixture of *dhcp* structure) and λ_{tr} (the data exhibit non-Boltzmann-type "saturation"[17] as a function of T). For Ce, the values[16] $N(E_F)=31.6$ states/Ry atom and $\Omega_p=4.7$ eV were calculated with a lattice constant (4.790 Å) corresponding to a pressure of 15 kbar at $T=0$. From these values $\lambda_\gamma=0.9$ and $\lambda_{tr}=0.45$ were estimated. Since α-Ce is not superconducting, no independent value of λ is known. In common with La, complications in data analysis weaken the reliability of these λ values.

III. CONCLUSIONS AND PROVISOS

Overall, the values found for λ_{tr} seem very reasonable and can be taken as an accurate semiempirical measure of electron-phonon coupling. This provides new information for the nonsuperconductors Ca, Ba, Fe, Ni, and Rh where empirical values were not previously available. There are several subtle points in the use of Eq. (1), which are described in Ref. 2. Perhaps the most serious proviso is the warning that λ_{tr} is not exactly like λ. For Ta, simultaneous microscopic calculations[2] of λ and λ_{tr} give $|\lambda_{tr}-\lambda|/\frac{1}{2}(\lambda_{tr}+\lambda)=40\%$, while for Cu, Pd, and Nb the relative separation was $\sim 7\%$. The empirical values for λ_{tr} and λ_γ are consistent with the view that λ_{tr} and λ are usually quite similar.

A second proviso is that we have used local-density-approximation (LDA) theory rather than QP theory to calculate Ω_p and $N(E_F)$. The present results indicate that the size of the discrepancy between LDA and QP values of metallic properties is not large at the Fermi surface. Examining Table I suggests that Li, Ba, Rh, Pd, and Pt have strong enough interactions to drive some form of ordering at low enough temperatures. In Li this may be preempted by a structural instability,[9] but Ba might be a candidate for a very low-T singlet BCS state. In Rh, Pd, and Pt, pure enough samples ought to have some sort of BCS instability (singlet or triplet) if not preempted by magnetic ordering.

ACKNOWLEDGMENTS

I thank D. A. Papaconstantopoulos for help and encouragement. I also acknowledge a sabbatical stay at the Naval Resarch Laboratory with support under the Intergovernmental Personnel Act.

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