Superconductivity and Phonon Softening

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(Received 21 August 1972)

A new formula is derived which relates changes in electron-phonon coupling strength λ to shifts in phonon frequencies. Using this formula, the superconducting transition temperature T_c is discussed for bcc transition metals and rock-salt–structure transition-metal carbides.

Among superconducting elements and compounds, it is common to find pairs of metals with the same crystal structure, made of elements in neighboring columns of the periodic table, in which the transition temperature T_c differs greatly. Good examples are the rock-salt–structure materials HfC (with $T_c < 0.015$°K) and TaC (with $T_c \sim 11$°K). Recently Smith and Gläser[1] and Smith[2] have reported inelastic neutron scattering studies of the phonon dispersion in these two compounds. The spectra are very similar except for sharply defined softening of the acoustic modes of TaC at large wave vector $\vec{q}$. Similar but less dramatic anomalies have been known for some time to occur in the phonon spectra of transition elements.[3] In addition to connecting large values of T_c with phonon softening, these data provide insight into the little understood relation between superconductivity and lattice instabilities. Several qualitative discussions[4,5] have been given of the data of Ref. 1. The aim of this paper is to provide a new and quantitative formulation of the relation between high T_c's and lattice softening.

A phenomenological shell-model fit of the TaC dispersion curves by Weber, Bilz, and Schröder[6] has successfully[7] predicted a previously unobserved softening of a TA(110) branch. In spite of this impressive accomplishment, it should be emphasized that a microscopic understanding of these dispersion curves is still unavailable. Such an understanding would require knowing the energy bands and solving the screening problem; this latter problem remains almost unexplored for d-band materials.[8] Therefore we attempt to circumvent the problem of identifying the precise mechanism for phonon softening; we construct instead a direct relation between the amount of softening and the enhancement of the electron-phonon coupling parameter λ. Specifically, the difference in λ between closely related materials will be related to the difference in phonon frequencies.

For our purposes, the relation between T_c and microscopic parameters is given adequately by the McMillan equation,[9,10]

$$T_c = \frac{\Theta}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right], \qquad (1)$$

which relates T_c to λ, the Coulomb repulsion strength μ^*, and a temperature Θ characteristic of the phonons. Specific values of these parameters are given in Table I for the materials we will discuss.

The calculation of λ from microscopic quantities is very complicated in general, although it has been carried out successfully for nontransition materials.[11] In this paper we begin with an identity[12] which has not previously been exploited,

$$\lambda = 4[\pi N(0)]^{-1} \textstyle\sum_q \gamma_q / \omega_q^2, \qquad (2)$$

which expresses λ in terms of the phonon frequencies ω_q and linewidths γ_q. The symbol q is used to represent both the wave vector q and a mode index. The density of states at the Fermi surface, $N(0)$, is for both spin orientations. The linewidth is assumed to arise completely from electron-phonon interactions, and is twice the decay rate as calculated from Fermi's "golden rule." If the values of γ_q were known, λ could be calculated directly from the phonon spectra. In principle the widths could be observed directly from the intrinsic line shape[12]

$$\pi^{-1}\gamma_q / [(\omega - \omega_q)^2 + \gamma_q^2]. \qquad (3)$$

In particular, because the anomalies in the phonon spectra of high-T_c materials are likely to arise from strong electron-phonon coupling, the

TABLE I. Data for various pairs of metals (A,B); also shown are the experimental and theoretical values of $\Delta\lambda$.

Metals	T_c [a] (°K)	Θ [b] (°K)	μ^*	λ(expt) [c]	$\Delta\lambda$(expt)	$\Delta\lambda$(theory)
A NbC	~10 [d]	355	0.1	0.69	>0.29	0.26[e]
B ZrC	<1.28[d]	384	0.1	<0.40		
A TaC	<11 [d]	255	0.1	0.84	>0.59	0.33[g]
B HfC	<0.015[f]	288	0.1	<0.25		
A V	5.30	399	0.13	0.60	...[h]	0.29[i]
B Cr	...[h]	598	...[h]	...[h]		
A Nb	9.22	277	0.13	0.82	0.41	0.42[i]
B Mo	0.92	460	0.13	0.41		
A Ta	4.48	258	0.11[j]	0.69[j]	0.41	0.49[i]
B W	0.012	390	0.13	0.28		

[a] Ref. 7 unless otherwise noted.

[b] Ref. 7 for elements. For compounds, the maximum frequency of the LA(100) modes is used, as given in Refs. 1 and 2.

[c] Ref. 7 for elements; for compounds, λ is calculated using Eq. (1).

[d] B. W. Roberts, *Superconductive Materials and Some of their Properties*, National Bureau of Standards Technical Note No. 482 (U. S. GPO, Washington D. C., 1969).

[e] Average of longitudinal modes in three directions. The transverse modes probably contribute at least 0.1 extra.

[f] K. Andres, unpublished.

[g] Average of longitudinal modes in two directions.

[h] Chromium is nonsuperconducting because it is antiferromagnetic. Therefore an experimental upper limin on λ is not available.

[i] LA mode only; a spherical model based on the ⟨100⟩ direction.

[j] From the tunneling measurement of L. Y. L. Shen, Phys. Rev. Lett. 24, 1104 (1970).

line shapes should be relatively broad. However, the widths have not yet been observed directly. A more practical scheme would be to deduce the width γ_q from the easily measured shift or softening of the phonon. The shifts and the widths are related by Kramers-Kronig relations, because they are given by the real and imaginary parts of the phonon self-energy

$$\Pi(q,\omega) = -\delta(q,\omega) + i\gamma(q,\omega). \qquad (4)$$

The observed frequency ω_q is related to a bare frequency Ω_q (in the absence of electron-phonon interactions) via a shift parameter δ_q:

$$\omega_q^{\,2} = \Omega_q^{\,2} - 2\omega_q\delta_q. \qquad (5)$$

The width and the shift are given by the value of Π at the physical frequency:

$$\gamma_q = \gamma(q,\omega_q), \qquad (6)$$

$$\delta_q = \delta(q,\omega_q). \qquad (7)$$

We now introduce a model to allow us to estimate γ_q. Let A denote the high-T_c member of the pair of materials, and B denote the low-T_c member. First consider the bare frequencies Ω_q, which are in general unequal if A and B have different valences. The self-energy renormalization results in frequencies ω_q which are very similar for A and B. But A has some extra renormalization which gives the anomalous softening. We need to know something about the frequency dependence of this extra renormalization. It is easy to show[13] that $\omega_q\gamma$ is similar to the imaginary part of the inverse dielectric function $\epsilon^{-1}(q,\omega)$. This latter function ought to be quite similar for A and B. Of course, the f sums will differ if A and B have different valences. However, we regard this aspect of ϵ^{-1} as irrelevant to superconductivity, as the extra contribution to the f sum serves to screen the extra ionic charge resulting in new frequencies which are the same for A and B. Furthermore we believe that the observed differences in phonon frequencies can be associated with differences in $\mathrm{Im}\,\epsilon^{-1}(q,\omega)$ at small ω, i.e., transitions within a few eV of the Fermi energy. Thus we conjecture that (after adjusting the "bare" frequencies until they are equal) the function $\omega_q\gamma$ is the same for A and B except at low frequencies, where they are both linear functions of ω, but with different slopes.

As a simple realization of the picture described above, we choose the following model:

$$\Delta(\omega_q\gamma) \equiv [\omega_q\gamma(q,\omega)]_A - [\omega_q\gamma(q,\omega)]_B = \begin{cases} \omega\,\Delta\gamma_q & \text{if } |\omega| < \omega_c \\ 0 & \text{otherwise,} \end{cases} \tag{8}$$

where $\Delta\gamma_q$ is the increase in linewidth and ω_c is the cutoff frequency. The Kramers-Kronig relations then give

$$\Delta(\omega_q\delta_q) = 2\pi^{-1}\Delta\int_0^\infty d\omega'\,\omega'(\omega'^2-\omega_q^2)^{-1}\omega_q\gamma(q,\omega') \cong 2\pi^{-1}\omega_c\Delta\gamma_q \equiv \tfrac{1}{2}\Delta(\omega_q^2). \tag{9}$$

This is the desired relation between the shift and the width. We have assumed $\omega_q \ll \omega_c$ and used Eq. (5). An obvious choice for the cutoff ω_c is the difference in Fermi levels

$$\omega_c = |\epsilon_F^A - \epsilon_F^B|, \tag{10}$$

which, in a rigid band picture, is given by

$$\left|Z^{-1}\int_{\epsilon_F^A}^{\epsilon_F^B} d\epsilon\, N(\epsilon)\right| = 1 = fN_A(0)\omega_c, \tag{11}$$

where Z is the valence difference and f is a numerical factor defined by Eq. (11). In the materials we will consider Z is unity and the choice $f=\frac{1}{2}$ seems appropriate because material A has a much higher density of states $N_A(0)$ than material B, and a linear behavior of $N(\epsilon)$ can be assumed. Finally let us compute the difference $\lambda_A - \lambda_B$ which we call $\Delta\lambda$. From Eq. (2) this can be written

$$\Delta\lambda = \frac{4}{\pi N_A(0)}\sum_q \frac{\Delta\gamma_q}{\omega_q^2(A)} + \frac{4}{\pi}\sum_q \gamma_q(B) \times\left[\frac{1}{N_A(0)\omega_q^2(A)} - \frac{1}{N_B(0)\omega_q^2(B)}\right]. \tag{12}$$

The last term is typically quite small, so we neglect it. With the help of Eqs. (9), (10), and (11), our final equation for $\Delta\lambda$ is

$$\Delta\lambda = fN^{-1}\textstyle\sum_q[\omega_q^2(B)/\omega_q^2(A) - 1]. \tag{13}$$

The new result can be used to discuss chemical trends in λ; it should be contrasted with the much used formula due to McMillan,[7]

$$\lambda = N(0)\langle I^2\rangle/M\langle\omega^2\rangle, \tag{14}$$

where $\langle I^2\rangle$ is an averaged matrix element, $\langle\omega^2\rangle$ an averaged phonon frequency (weighted by the matrix elements in a complicated way), and M is the ionic mass. The usefulness of McMillan's formula rests upon two assumptions: first, that the numerator is constant in a class of materials, and second, that $\langle\omega^2\rangle$ is a mean squared frequency which does not depend on the matrix elements. The first assumption is believed[9,14] to be farily good for most elements but has not been tested for compounds. The second assumption is probably less valid.[11] If both assumptions are accepted, then Eq. (14) yields

$$\Delta\lambda = \lambda_B\left[\textstyle\sum_q\omega_q^2(B)/\sum_q\omega_q^2(A) - 1\right]. \tag{15}$$

In general it can be expected that Eq. (13) will give values of $\Delta\lambda$ which are much larger than Eq. (15) gives. We believe that Eq. (13) is on firmer theoretical ground as the effects of the matrix elements have been included in deriving it. However, our formula applies only to differences between related compounds; we do not have an analogous improvement to offer for Eq. (14), which remains the best known simple way of studying λ for a single material.

We have used Eq. (13) to calculate theoretical values of $\Delta\lambda$ for five pairs of metals. The results are compared with experiment in Table I. The values of $\Delta\lambda$ for the transition-metal carbides were found by averaging $\Delta(\omega^2)$ for the LA modes in the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ directions. The results are somewhat lower than the experimental values. Considerable softening of the TA modes also occurs and would increase $\Delta\lambda$; however, we are unable to evaluate this because the data for transverse modes is incomplete. Optical modes contribute a small negative amount to $\Delta\lambda$. In the pair NbC, HfC[15] this is of order -0.005 or less for each mode.

For the bcc transition elements we have estimated $\Delta\lambda$ for the LA modes by using only the (100) data and assuming spherical symmetry. Thus the entries in Table I cannot be regarded as precise, but should be fairly good for depicting trends. In particular, the trend indicates a value ~ 0.3 for λ in chromium, which would give $T_c \sim 0.2$°K if magnetic effects were absent.

We regard the comparison between theory and experiment in Table I as encouraging confirmation of our model. A more stringent test would occur if the natural broadening of the phonons were measured. From Eqs. (9)–(11) the difference $\gamma_A - \gamma_B$ is

$$\Delta\gamma_q = \tfrac{1}{4}\pi fN_A(0)[\omega_q(B)^2 - \omega_q(A)^2]. \tag{16}$$

Values of $\Delta\gamma$ based on this equation are shown in

TABLE II. Predicted electron-phonon broadening $\Delta\gamma_q$ for various modes. Anharmonic contributions are neglected, as is the broadening γ_B of the "hard" metal; γ is the half width at half-maximum.

Metal	Mode	$(\zeta,\eta,\xi) = (a/2\pi)\vec{q}$	$N(0)$ (states/eV/molecule)	ω_q (10^{12} Hz)	$\Delta\gamma_q/\omega_q$
NbC	LA	(0.5,0.5,0.5)	0.75[a]	6.0	0.013
	TA	(0.5,0.5,0.5)		4.0	0.005
TaC	LA	(0.6,0.6,0)	0.73[a]	4.5	0.005
V	LA	(0.65,0,0)	2.62[b]	7.5	0.017
Nb	LA	(0.7,0,0)	1.82[b]	5.5	0.016
Ta	LA	(0.6,0,0)	1.54[b]	4.3	0.012

[a] J. K. Hulm, M. S. Walker, and N. Pessal, in *Proceedings of the International Conference on the Science of Superconductivity, Stanford, 1969,* edited by F. Chilton (North-Holland, Amsterdam, 1971).

[b] Ref. 9.

Table II. The modes have been picked in an attempt to find the maximum $\Delta\gamma/\omega$. Instrumental resolution tends to be best for transverse modes; we suspect that the predicted[6,7] soft TA(110) modes in TaC (and NbC by analogy) might have the most favorable $\Delta\gamma/\omega$, but the absence of data prohibits a specific prediction in this case.

We are grateful to H. G. Smith for a helpful discussion and for sending unpublished data, and to J. P. Maita and E. Bucher for help with low-temperature data.

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*Work supported in part by the National Science Foundation under Grant No. GP 13632.

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[7] H. G. Smith, Phys. Rev. Lett. 29, 353 (1972).

[8] Preliminary steps in this direction have been taken. See, for example, L. J. Sham, Phys. Rev. Lett. 27 1725 (1971).

[9] W. L. McMillan, Phys. Rev. 167, 331 (1968).

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[14] J. J. Hopfield, Phys. Rev. 186, 443 (1969).

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