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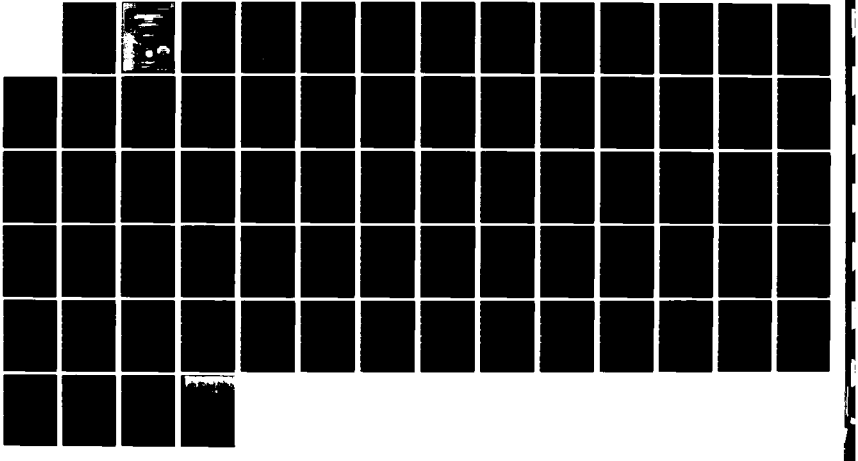

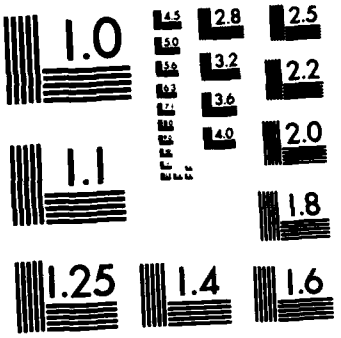

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This report presents several contributions to the formulation, calculation and understanding of the effects of electron-phonon interaction in metals with variation in the electronic density of states on the scale of a typical phonon energy. The A15 compound Nb_3Sn is studied in detail with this theory.

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CONTENTS

EXTENSIONS OF THE THEORY OF THE ELECTRON-PHONON INTERACTION IN METALS: A COLLECTION

ANNOTATED BIBLIOGRAPHY

1. "ELECTRON-PHONON INTERACTION IN THE f-BAND METALS La, Ce and Th: ELECTRONIC ASPECTS INCLUDING THE SPIN-ORBIT INTERACTIONS." Physica 111B, 1 (1981).

An important parameter reflecting the strength of the electron-phonon interaction is $\eta=N(E_F)\langle I^2\rangle$, where N(F) is the Fermi level density of states and $\langle I^2\rangle$ is the Fermi level mean square electron-ion matrix element. The parameter η is calculated for the f-band metals La, Ce and Th using self-consistent muffin-tin potentials. The corrections within the rigid muffin-tin approximation (RMTA) due to spin-orbit coupling derived by John and Hamann are found to increase η by 1% in La and 4% in Th, and by 10% and 33% in the α and γ phases of Ce, respectively. The RMTA expression is reinterpreted to provide an understanding of the low values of η in Ce (0.7 to 1.1eV/$\AA^2$) in spite of an extremely large density of states at the Fermi level. Using moments of the measured phonon spectra, the superconducting transition temperature is calculated and compared with experiment. The RMTA appears to overestimate η by approximately 25% in these metals, although spin fluctuations may be contributing to this apparent discrepancy with experiment.

Manuscript approved September 2, 1983.

2. "TRANSFERABILITY AND THE ELECTRON-PHONON INTERACTION: A REINTERPRETATION OF THE RIGID-MUFFIN-TIN APPROXIMATION." Phys. Rev. B25, 745 (1982).

The expression for the McMillan-Hopfield constant $\eta=N(E_F)\langle I^2\rangle$ within the rigid-mufin-tin approximation (RMTA) is reinterpreted in terms of single-channel electron-ion matrix elements $I^2_{\ell,\ell+1}$ and angular-momentum-character fractions f_ℓ of the electronic states at the Fermi level. Reexamination of Nb- and V-based A15 compounds suggests that $I^2_{\ell,\ell+1}$ is more nearly an atomic property, and thus transferable from system to system, than other commonly used quantitities. The fractions f_ℓ are dependent on bonding character and crystal structure but tend to be constant within a class of compounds. Criteria for increasing η within RMTA are discussed.

3. "EFFECT OF A VARYING DENSITY OF STATES ON SUPERCONDUCTIVITY." Phys. Rev. B21, 3897 (1980).

A microscopic treatment of the consequences for superconductivity of a nonconstant electronic density of states is presented. Generalized Eliashberg gap equations valid for a varying density of states are presented, from which the change of T_c with static or thermal disorder can be calculated. The temperature dependence of the effective mass is shown to be altered by disorder. Use of these results provides a possible experimental approach for deducing the energy variation of the density of states of superconductors.

4. "INFLUENCE OF ELECTRONIC STRUCTURE ON SUPERCONDUCTING PROPERTIES OF COMPLEX CRYSTALS: THEORY AND APPLICATION TO Nb_3Sn." Solid State Commun. 38, 95 (1981). With B.M. Klein.

A thermodynamic theory valid for complex crystalline superconductors is applied to Nb_3Sn. It is shown how the structure of the Eliashberg equation and the solution is altered by density of states fine structure. One important implication is that the current method of inversion of tunneling data can be only approximate.

5. "PARAMETER-FREE CALCULATION OF THE ENHANCED SPIN SUSCEPTIBILITY OF Nb_3Sn INCLUDING ELECTRON-PHONON EFFECTS." Physica 107B, 703 (1981).

A parameter-free calculation of the spin susceptibility $\chi_{sp}(T)$ of Nb_3Sn, which includes static and dynamic disorder as well as exchange-correlation enhancement, is presented. It is found that χ_{sp} is only 15% of the measured susceptibility, and its small temperature dependence cannot account for the experimental findings.

6. "GENERALIZATION OF THE THEORY OF THE ELECTRON-PHONON INTERACTION: THERMODYNAMIC FORMULATION OF SUPERCONDUCTING- AND NORMAL-STATE PROPERTIES." Phys. Rev. B26, 1186 (1982).

A thermodynamic formulation for the electron self-energy is given which is applicable when the electronic spectrum posseses structure on the scale of phonon frequencies, provided only that the ratio of phonon phase velocity to electron Fermi velocity is small. Electron-phonon, Coulomb, and electron-

defect interactions are included on an equal footing and it is shown that their different frequency dependencies lead to specific effects on the Eliashberg self-energy: (a) The Coulomb interaction contributes nothing of essence to the normal-state self-energy (in this isotropic approximation) but retains its usual depairing effect upon the superconducting gap function, (b) defects affect superconducting properties primarily through a broadening of the electronic spectrum, and (c) phonons contribute a thermal shift and broadening as well as the mass enhancement. A generalization to intensive electron-phonon, electron-electron, and electron-defect interaction constants is necessary to redevelop an intuition into the effects of these interactions. The change in the structure of the Eliashberg equation due to a nonconstant density of states (DOS) and the consequent interplay between static and thermal disorder is analyzed in detail, with a central feature being the change in frequency dependence of the self-energy compared to a constant DOS solution. The effect of DOS structure on the superconducting transition temperature T_c, which is manifested in the defect dependence of T_c, is analyzed in detail. Further it is proposed that an extension of the self-consistent Eliashberg approach be extended above T_c to determine the normal-state self-energy and thereby the electronic contribution to thermodynamic quantities. Phonon broadening is shown to affect the spin susceptibility at finite temperature. Reinterpretation of several of the anomalous properties of A15 compounds in terms

of the present theory is suggested. Several aspects of the theory are compared to experimental data for Nb_3Sn.

7. "RENORMALIZED THERMAL DISTRIBUTION FUNCTION IN AN INTERACTING ELECTRON-PHONON SYSTEM." Phys. Rev. Lett. 48, 1548 (1982).

The electron-phonon interaction is used to demonstrate the important effect of interactions on the electronic distribution function at finite temperature. It is shown that the usual picture of "thermal (Fermi) smearing" is a greatly oversimplified one. The distribution function resulting from an Einstein spectrum with various coupling strengths is presented and interpreted, and an exact expression for the spin susceptibility is used to illustrate the utility of this novel viewpoint for thermodynamics.

8. "THEORY OF THE NORMAL STATE HEAT CAPACITY OF Nb_3Sn." Superconductivity in d- and f-band metals, Edited by W. Buchel and W. Weber (Kernforschungszentrum Karlsruhe GmbH, 1982), p.97. With B.M. Klein.

The experimental α^2F of Wolf et al. is applied to calculate the T-dependence of the electronic heat capacity. It is found that, if the phonon spectrum is Debye-like (which is not the case in Nb_3Sn), this T-dependence results in an extrapolated value of $N(E_F)\ (1 + \lambda)$ which is overestimated by an amount which is proportional $N(E_F)\lambda$, equal to 13% for Nb_3Sn. It is further shown that the change in slope of C/T found by Stewart, Cort and Webb can be modeled by a combined Debye and Einstein spectrum with Θ_D=267 K and having 1.5% of the acoustic modes at an Einstein frequency Ω=40 K.

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ELECTRON–PHONON INTERACTION IN THE f-BAND METALS La, Ce AND Th: ELECTRONIC ASPECTS INCLUDING THE SPIN–ORBIT INTERACTIONS

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The electron–ion scattering parameter η is calculated for the f-band metals La, Ce and Th using self-consistent muffin-tin potentials. The corrections within the rigid muffin-tin approximation (RMTA) due to spin–orbit coupling derived by John and Hamann are found to increase η by 1% in La and 4% in Th, and by 10% and 33% in the α and γ phases of Ce, respectively. The RMTA expression is reinterpreted to provide an understanding of the low values of η in Ce (0.7 to 1.1 eV/Å^2) in spite of an extremely large density of states at the Fermi level. Using moments of the measured phonon spectra, the superconducting transition temperature is calculated and compared with experiment. The RMTA appears to overestimate η by approximately 25% in these metals, although spin fluctuations may be contributing to this apparent discrepancy with experiment.

1. Introduction

In his classic work on the theory of the electron–phonon (EP) interaction McMillan [1] showed that the EP coupling constant λ can be expressed as

$$\lambda = \frac{N(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle} \equiv \frac{\eta}{M\langle\omega^2\rangle}, \tag{1}$$

where $N(E_F)$ is the electronic (single spin) density of states at the Fermi energy E_F, $\langle I^2\rangle$ is a mean square electron–ion matrix element averaged over the Fermi surface, M is the ionic mass and $\langle\omega^2\rangle$ is an appropriately defined [1] mean square phonon frequency. Specifically $\langle I^2\rangle$ is given by

$$\langle I^2\rangle = \sum_{kn}\sum_{k'n'}\left|\left\langle kn\left|\frac{\delta V}{\delta R}\right|k'n'\right\rangle\right|^2 \times \delta(E_{kn}-E_F)\delta(E_{k'n'}-E_F)/N(E_F)^2, \tag{2}$$

where k, n are, respectively, the wavevector and band index of the state $|k, n\rangle$ with $E_{k,n}$ and $\delta V(r)/\delta R$ is the change in crystal potential per unit displacement δR of an ion at position R. Up to this point the expression for λ is rigorous. However, for all but weak scattering ions $\delta V/\delta R$ is very difficult to compute precisely, and further progress in the understanding of $\langle I^2\rangle$ or the McMillan–Hopfield [2] parameter η necessitates approximations of $\delta V/\delta R$.

Noting that the muffin-tin approximation for $V(r)$ has been very successful in describing the electronic structure of transition metals, Gaspari and Gyorffy [3] suggested that the local environment of a vibrating strongly scattering ion would be *modeled* realistically by rigidly displacing the muffin-tin potential for that ion. Within this rigid muffin-tin approximation (RMTA), Gaspari and Gyorffy obtained the relation (in Rydberg units $\hbar = 2m = e^2/2 = 1$ throughout this paper)

$$\eta^{(0)} = \frac{E_F}{\pi^2}\frac{1}{N(E_F)}\sum_l 2(l+1) \times \sin^2(\delta_l - \delta_{l+1})\nu_l\nu_{l+1}, \tag{3}$$

where δ_l is the phase shift for the lth partial wave scattering from the muffin-tin potential. The crystalline enhancement ratio $\nu_l = N_l(E_F)/N_l^{(1)}(E_F)$ of the density of states is defined in terms of the single scatterer partial density of

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states

$$N_l^{(1)}(E_F) = \frac{\sqrt{E_F}}{\pi}(2l+1)\int_0^{r_s} dr\, r^2 R_l^2(r, E_F)$$

$$= \frac{\sqrt{E_F}}{\pi}(2l+1)\, r_s^2 r_l^2(r_s, E_F)|\dot{\gamma}_l| . \qquad (4)$$

Here r_s is the muffin-tin radius, R_l is the radial function and $\dot{\gamma}_l$ is the energy derivative of the logarithmic derivative of the radial function evaluated at r_s and E_F. Eq. (3) has been applied widely [3–5] in the study of elemental transition metals. Often it is found that the results of the RMTA in this form seem to agree with empirically determined values to within 10–20% and to reproduce trends with pressure [6] rather well.

Aside from the approximation of rigidly displaced muffin-tin potentials, eq. (3) contains two simplifying assumptions. The first is the so-called "spherical band" approximation [3] in which the angular dependence of the bands is ignored. This is not an essential approximation, and recent studies [5, 7] have generalized eq. (3) appropriately and shown the corrections to be small in elemental systems with cubic symmetry. The second approximation in eq. (3) is that of ignoring the spin–orbit interaction (denoted by the superscript '0'). John and Harmann [8] have shown how this restriction can be removed (within the spherical band approximation) but to date no numerical test has been performed to test the size of corrections.

In this paper the RMTA will be applied to the fcc phases of La, Ce and Th, each of which has f bands [9–11] near or at E_F. Since spin–orbit contributions to η may not be negligible in systems with large atomic number ($Z = 57$, 58 and 90, respectively, for these atoms), the expression of John and Hamann will be evaluated in section 2 and compared to the zero spin–orbit limit in eq. (3). Contrary to the expectations of Butler [5], the contribution to η from d-to-f scattering in Ce is surprisingly small in spite of a huge $l = 3$ partial density of states $N_l(E_F)$. This finding leads to a reinterpretation [12] of the contributions to η in terms of a rearrangement of terms in eq. (3). This reinterpretation and a discussion of its implications for states which are nearly confined to the muffin-tin sphere are given in section 3. The results for the superconducting transition temperature T_c, which is found to be overestimated, are presented in section 4.

2. Spin–orbit effects in the RMTA

The expression for η given by John and Hamann [8], which includes spin–orbit effects, is

$$\eta = \frac{E_F}{\pi^2 N(E_F)}\sum_l 2(l+1)$$

$$\times\left\{\frac{l+2}{2l+3}\sin^2(\delta_l^+ - \delta_{l+1}^+)\nu_l^+\nu_{l+1}^+\right.$$

$$+\frac{l}{2l+1}\sin^2(\delta_l^- - \delta_{l+1}^-)\nu_l^-\nu_{l+1}^-$$

$$\left.+\frac{1}{(2l+1)(2l+3)}\sin^2(\delta_l^+ - \delta_{l+1}^-)\nu_l^+\nu_{l+1}^-\right\}. \qquad (5)$$

The superscripts $\pm$ indicate the corresponding quantity for total angular momentum $j = l \pm \frac{1}{2}$ and the "single scatterer" density of states is given by

$$N_l^{(1)+}(E_F) = \frac{\sqrt{E_F}}{\pi}(l+1)\int_0^{r_s} dr\, r^2 |R_l^+(r, E_F)|^2 , \qquad (6a)$$

$$N_l^{(1)-}(E_F) = \frac{\sqrt{E_F}}{\pi} l \int_0^{r_s} dr\, r^2 |R_l^-(r, E_F)|^2 . \qquad (6b)$$

The large component $R_l^\pm$ of the radial wave function is normalized according to

$$R_l^\pm(r_s, E_F) = j_l(\kappa_F r_s)\cos\delta_l^\pm - n_l(\kappa_F r_s)\sin\delta_l^\pm , \qquad (7)$$

where $\kappa_F \equiv \sqrt{E_F}$, in terms of the spherical Bessel (j_l) and Newmann (n_l) functions. Eqs. (6) can be expressed in terms of logarithmic derivatives $\gamma_l^\pm$ analogously to eq. (4).

Eq. (5) has been evaluated in detail for La, Ce and Th using the results of self-consistent, spin–orbit, linearized-augmented-plane-wave band structure calculations [9–11]. To compare with the corresponding zero spin–orbit limit the following identifications have been made:

$$\delta_l = [l\delta_l^- + (l+1)\delta_l^+]/(2l+1)\,, \tag{8a}$$

$$N_l(E_F) = N_l^+(E_F) + N_l^-(E_F)\,, \tag{8b}$$

$$N_l^{(1)}(E_F) = N_l^{(1)+}(E_F) + N_l^{(1)-}(E_F). \tag{8c}$$

It is easily shown that in the zero spin–orbit limit ($\delta_l^\pm \to \delta_l$ and $\nu_l^\pm \to \nu_l$) eq. (5) reduces to eq. (3). It is instructive also to introduce the quantities

$$\Delta_l = \delta_l^- - \delta_l^+\,, \tag{9a}$$

$$\nu_l = [l\nu_l^- + (l+1)\nu_l^+]/(2l+1)\,, \tag{9b}$$

$$\epsilon_l = \nu_l^- - \nu_l^+\,. \tag{9c}$$

in terms of which the relativistic quantities are given by

$$\delta_l^+ = \delta_l - \frac{l}{2l+1}\Delta_l\,, \tag{10a}$$

$$\delta_l^- = \delta_l + \frac{l+1}{2l+1}\Delta_l\,, \tag{10b}$$

and similarly for $\nu_l^\pm$ in terms of ν_l and ϵ_l. Respectively, Δ_l and ϵ_l represent the spin-orbit splitting of the phase shift and the crystalline enhancement of the partial density of states. It has not been emphasized previously that the corrections to η in eq. (5) which are first order in the spin–orbit corrections Δ_l and ϵ_l *vanish identically*. This may be due to the traceless nature of the spin–orbit operator and it is in keeping with the picture that *quantitative* changes in observables tend to be second order in the spin–orbit splitting.

In table I phase shifts $\delta_l^\pm$, crystalline enhancements $\nu_l^\pm$ and partial and total values of η (with and without spin–orbit effects) are presented. In each case η is increased by spin–orbit corrections (this is *not* a general requirement), by 0.03, 0.08, 0.10 and 0.18 eV/Å^2 (or 1%, 4%, 10% and 33%, respectively) in fcc La, Th, α-Ce and γ-Ce. (This is a fictitious "paramagnetic γ-Ce" which, however, illustrates spin–orbit effects more clearly than the other metals.) In thorium the increase arises from corrections

Table I.
Relativistic phase shifts $\delta_l^\pm$ (in radians), crystalline density of states enhancements $\nu_l^\pm$ and the resulting contributions to η(eV/Å^2); the $\pm$ sign indicates $j = l \pm \frac{1}{2}$ and $\eta^{(0)}$ is the value of the McMillan-Hopfield parameter neglecting spin–orbit corrections

	La		γ-Ce		α-Ce		Th	
$\delta_l^-, \delta_l^+ l = 0$	–	−0.96	–	−0.98	–	−1.23	–	−1.14
1	−0.42	−0.50	−0.43	−0.51	−0.60	−0.69	−0.56	−0.82
2	0.59	0.54	0.56	0.51	0.63	0.58	0.75	0.61
3	0.026	0.024	0.142	0.067	0.187	0.109	0.095	0.079
$\nu_l^-, \nu_l^+ l = 0$	–	0.71	–	1.33	–	2.30	–	1.05
1	2.46	2.65	1.41	1.50	1.16	1.17	0.74	1.01
2	1.20	1.45	0.63	0.77	0.48	0.57	0.58	0.82
3	3.10	3.61	0.99	7.01	0.65	2.75	1.44	2.24
4	7.86	7.74	6.89	5.94	4.30	3.77	3.12	2.51
η_{l+1}, η_{l-1}								
sp	0.12	0.12	0.07	0.07	0.29	0.29	0.10	0.10
pd	1.58	1.57	0.24	0.24	0.41	0.41	0.93	0.87
df	1.08	1.08	0.30	0.14	0.23	0.15	0.85	0.83
fg	0.02	0.02	0.11	0.09	0.16	0.15	0.10	0.10
total	2.81	2.78	0.72	0.54	1.10	1.00	1.99	1.91

to p–d scattering while the channels involving f states are unaffected. In the two phases of cerium the increase occurs in the d–f channel.

The spin–orbit correction is seen most clearly in γ-Ce. Using an obvious notation from eq. (5), $\eta_{df} = \eta_{df}^{\uparrow\uparrow} + \eta_{df}^{\downarrow\downarrow} + \eta_{df}^{\uparrow\downarrow}$, it can first be noted that, for $l \geq 2$, $\eta^{\uparrow\downarrow}$ becomes negligible with respect to $\eta^{\uparrow\uparrow}$ and $\eta^{\downarrow\downarrow}$ due to the factor $[(2l+1)(2l+3)]^{-1}$. The large increase in η in γ-Ce arises from the large crystalline enhancement of $\nu_l^{\uparrow}$ at the expense of $\nu_l^{\downarrow}$. This leads to $\eta_{df}^{\uparrow\uparrow} = 0.28$, $\eta_{df}^{\downarrow\downarrow} = 0.02$ compared to their zero spin–orbit counterparts 0.08 and 0.05 (all in eV/Å^2). Ultimately the spin–orbit increase results from the shifting of states at E_F by crystallinity (solid state effects) from one member of the pair $j = l \pm \frac{1}{2}$ to the other. The central requirement for a large correction of this type to occur is that $\nu_l^{\uparrow}$ and $\nu_l^{\downarrow}$ be as dissimilar as possible (i.e., that one be maximized at the expense of the other), and that this skewing be in the same direction for both l and $l+1$, thereby maximizing either $\nu_l^{\uparrow}\nu_{l+1}^{\uparrow}$ or $\nu_l^{\downarrow}\nu_{l+1}^{\downarrow}$. To obtain the maximum ratio $\nu_l^{\uparrow}$ requires that the crystal density of states (numerator) and the single scatterer density of states (denominator) be oppositely skewed. In γ-Ce this occurs only for $l = 3$, with normal ratios ($\nu_l^{\uparrow} \approx \nu_l^{\downarrow}$) for $l = 2$ and $l = 4$. This opposite skewing of the f states $N_l^{\uparrow}/N_l^{\downarrow} = 13.3/7.0$, $N_l^{(1)\uparrow}/N_l^{(1)\downarrow} = 1.9/7.0$ leads to $\nu_l^{\uparrow}/\nu_l^{\downarrow} = 7.08$ and a factor of 2.5 increase in η_{df}.

An interesting limiting case occurs when all the crystal states (for *both* l and $l+1$) are shifted to either $j = l + \frac{1}{2}$ or $j = l - \frac{1}{2}$. Assuming equal single scatterer densities of states for $j = l \pm \frac{1}{2}$, the value of η_{ll+1} is increased by the factor $(2l+3)/(l+1)$. Further increase may result from oppositely skewing the single scatterer density of states as noted above, which will require a narrow l resonance in the vicinity of E_F.

In the next section the problem of understanding the small values of η in Ce, which possesses an extremely large f density of states at E_F, is addressed in terms of a reinterpretation of the RMTA expressions eqs. (3) and (5). It should be noted that the small values of η calculated from the Ce band structure persist only for values of E_F lying within the 4f bands. If E_F is artificially placed above the f bands (say 0.05 to 0.50 Ry above), larger values of $\eta \sim 3$ to 5 eV/Å^2 result, just as obtained from a similar treatment using the La band structure.

3. Reinterpretation of the RMTA expression

The discussion in the previous section did not address the cause of the small values of η in Ce, compared to La, in spite of much larger values of $N(E_F)$. The following rearrangement and reinterpretation of the RMTA expression for η or $\langle I^2 \rangle$ provides insight into this puzzle.

Begin by defining a rigid muffin-tin matrix element for the $l \to l+1$ channel by (see also Butler [5] for the non-relativistic analog)

$$I_{ll+1}^{\sigma\sigma'} = \int_0^{r_s} R_l^{\sigma} \frac{dV}{dr} R_{l+1}^{\sigma'} r^2 dr / \tau_l^{\sigma} \tau_{l+1}^{\sigma'}, \tag{11}$$

$$(\tau_l^{\sigma})^2 \equiv \int_0^{r_s} (R_l^{\sigma})^2 r^2 dr, \qquad \sigma = \pm. \tag{12}$$

Evidently $I_{ll+1}^{\sigma\sigma'}$ is independent of the normalization of the radial functions and depends only on dV/dr and the *shapes* of the radial functions. Using the normalization in eq. (7) the numerator in eq. (11) is $\sin(\delta_l^{\sigma} - \delta_{l+1}^{\sigma'})$, and the normalization integral can be expressed as

$$(\tau_l^{\sigma})^2 = r_s^2 |R_l^{\sigma}(r_s, E_F)|^2 |\dot{\gamma}_l^{\sigma}|, \tag{13}$$

where $\dot{\gamma}_l^{\sigma}$ denotes the energy derivative of the logarithmic derivative of R_l^{σ}. Finally, eq. (11) becomes

$$(I_{ll+1}^{\sigma\sigma'})^2 = \sin^2(\delta_l^{\sigma} - \delta_{l+1}^{\sigma'}) / [r_s^4 (R_l^{\sigma} R_{l+1}^{\sigma'})^2 (\dot{\gamma}_l^{\sigma} \dot{\gamma}_{l+1}^{\sigma'})]. \tag{14}$$

In terms of these matrix elements $\langle I^2 \rangle$ can be

expressed as

$$\langle I^2\rangle = \sum_l \frac{2}{(2l+1)(2l+3)} \times \Big\{(2l+1)(I^{+}_{ll+1})^2 f^{+}_l f^{+}_{l+1} + (2l+3)(I^{-}_{ll+1})^2 f^{-}_l f^{-}_{l+1} + \frac{1}{l+1}(I^{+-}_{ll+1})^2 f^{+}_l f^{-}_{l+1}\Big\}, \quad (15)$$

which in the zero spin–orbit limit becomes

$$\langle I^2\rangle^{(0)} = \sum_l \frac{2l+2}{(2l+1)(2l+3)} I^2_{ll+1} f_l f_{l+1}. \quad (15')$$

In these relations $\langle I^2\rangle$ is expressed in terms of the *fraction* $f^{\sigma}_l = N^{\sigma}_l(E_F)/N(E_F)$ of states at E_F, and $f_l = f^{+}_l + f^{-}_l$. This form for $\langle I^2\rangle$ has the desirable property [12] that the atomic-like quantity I^2_{ll+1}, which depends only on the logarithmic derivative and varies smoothly and predictably with E_F, is separated from the crystalline property f_l. Although it requires a full band structure calculation to ascertain $\{f_l\}$, these fractions typically vary much more smoothly [12] than $N_l(E_F)$ and $N(E_F)$ separately which generally possess Van Hove singularities at the same energies. This behavior is strikingly illustrated for γ-Ce in fig. 1 in a 20 mRy region centered on the calculated value of E_F. In this region there is strong hybridization among the s, p, d and f bands and $N(E)$ varies non-monotonically by more than a factor of 2 whereas the fractions f_l vary more smoothly.

The form for I_{ll+1} given by

$$I_{ll+1} = \sin(\delta_l - \delta_{l+1})/\tau_l\tau_{l+1} \quad (11')$$

is useful for understanding the contribution of f states to $\langle I^2\rangle$ as E_F is varied. As a result of the boundary condition eq. (7) "fixing" R_l at r_s, the normalization integrals τ_l are unbounded ($0 < \tau_l < \infty$) and they become the principal determining factors in the magnitude of I_{ll+1}. Near the bottom of the bands derived from the atomic l states, R_l peaks at or near r_s and τ_l will be small. Near the top of the bands, R_l assumes very large values for $r < r_s$ compared to $R_l(r_s)$, resulting in large values of τ_l and smaller values of I_{ll+1} (and $I_{l-1,l}$). Schematic radial functions are shown in fig. 2. The boundary condition of fixed $R_l(r_s)$ results in "the dog (τ_l) being wagged by the tail [$R_l(r_s)$]"[13]. Physically, the small values of I_{ll+1} at the top of the bands reflects the poor coupling to plane waves of states which are too strongly confined to the muffin-tin sphere. (This discussion is somewhat oversimplified: the "fixed" value of $R_l(r_s)$ and the numerator $\sin(\delta_l - \delta_{l+1})$ both vary with E_F, but these variations usually are secondary effects.)

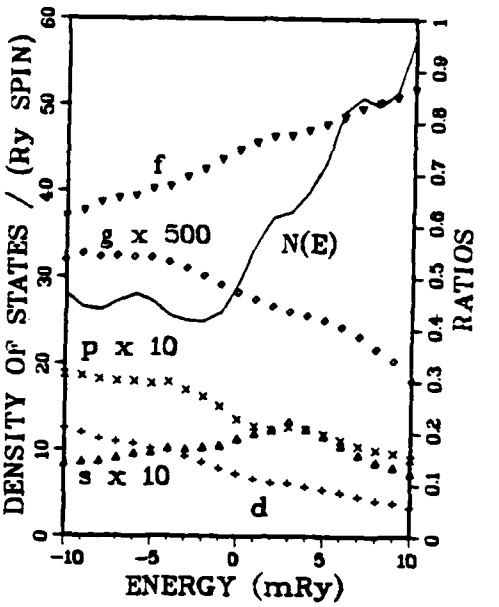

Fig. 1. The total density of states (left scale) and partial wave ratios f_l, $l = 0, \ldots, 4$ (right scale) in a 20 mRy region centered at the Fermi energy (0.450 Ry) in γ-Ce. In this region $N(E)$ has fine structure and varies by a factor of two, whereas the ratios f_l vary much more smoothly.

This description of τ_l and its influence on I_{ll+1} applies to wide bands such as s, p and 4d, 5d bands in transition metals. The narrow 4f bands in La and Ce (and the late 3d bands) present a different behavior however. For these metals the f bands are only 1–2 eV wide and, even at the

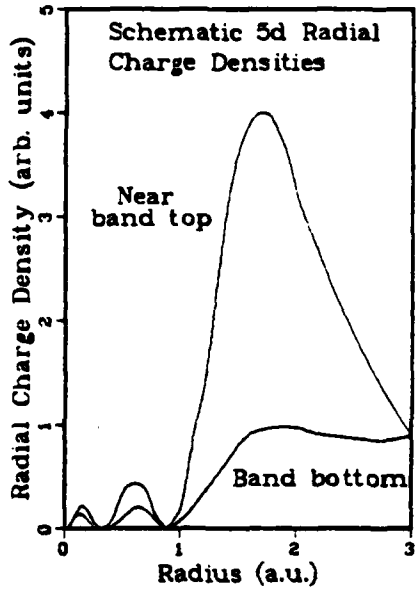

Fig. 2. Schematic 5d radial charge densities $r^2R_2^2(r,E)$ illustrating the bonding behavior at the bottom of the band and the antibonding behavior at the top of the band. The radial wavefunctions (R_2) have been normalized to the same value at the sphere radius (taken as 3 a.u.).

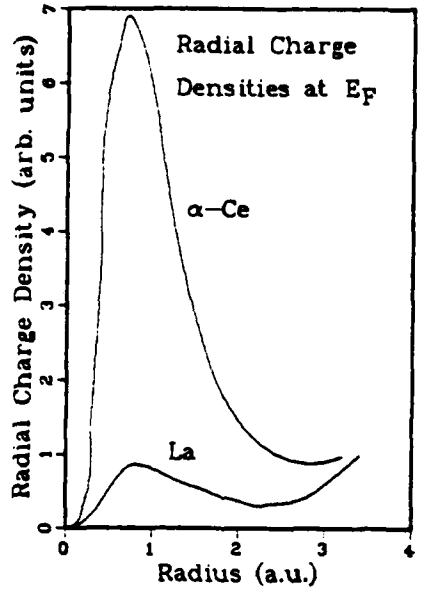

Fig. 3. The $l = 3$ radial charge densities at E_F for La and α-Ce, normalized to the same value at the muffin-tin sphere boundary. In La it is clear that E_F is far off the 4f resonance, resulting in a small atomic 4f character (peak at 0.75 a.u.). This graph clearly illustrates the order of magnitude difference in normalization integrals τ_l between La and Ce.

bottom of the f bands, the 4f radial function is strongly confined to the muffin-tin sphere. This is illustrated in fig. 3 for α-Ce, where E_F lies near the bottom of the 4f bands. Due to the strong peaking of $R_{l=3}$ at 0.75 a.u., $\tau_{l=3}$ is correspondingly larger, and I_{Ll+1} smaller, than for the s–p–d bands. The detrimental effect only subsides at or below about 2 eV below the 4f bands, which is where E_F lies in La. The radial charge density at E_F in La is shown in comparison with that of α-Ce in fig. 3, normalized such that the radial functions are equal at r_s. Although the $l = 3$ radial function in La shows a mild peak at 0.75 a.u. due to the incipient 4f bands, it is insufficient to decrease τ_3 significantly.

The squared normalizations at E_F for La, Ce and Th are included in table II. La and Ce differ significantly only in the values of $(\tau_3^{\pm})^2$, which for Ce are more than an order of magnitude larger than those of La. In the magnitude of τ_3, as in the value of T_c, Th is much more similar to La than to the isoelectronic element Ce. This of course reflects the similar position of the f bands with respect to E_F in La [9] and Th [11].

The small df contribution to η in Ce, compared to both La and Th, can be attributed to the dramatically decreased value of I_{df} (see table II). This small value is illustrated graphically in fig. 4; I_{df}^2 is *two orders of magnitude smaller* than that for the other channels in α-Ce. The extremely small value results from E_F lying "near" the center of both d and f bands giving large values of τ_2 and τ_3 as well as a reduced numerator $\sin(\delta_2 - \delta_3)$.

A second important feature is illustrated in fig. 4. The quantities I_{Ll+1}^2 are seen to be slowly and smoothly varying with energy, while η_{Ll+1} reflects the sharp structure which may occur in $N(E_F)$ and, to a lesser extent, in f_l. The fact that I_{Ll+1}^2 can be written solely in terms of the phase shifts (or equivalently, logarithmic derivatives) and their energy derivatives [eqs. (11)–(13)] guarantees their smooth variation with energy. Fur-

Table II

Relativistic crystalline density of states ratios f_l^j, normalization integrals τ_l^j, single channel matrix elements $I_{l,l+1}^j$ and average matrix elements (in $eV^2/Å^2$) for La, Ce and Th; the ± sign indicates $j = l \pm \frac{1}{2}$ and $\langle I^2 \rangle^0$ is the value of $\langle I^2 \rangle$ neglecting spin–orbit corrections

	La		γ-Ce		α-Ce		Th	
$f_l f_l^j$								
$l = 0$	–	0.022	–	0.019	–	0.040	–	0.044
1	0.032	0.059	0.008	0.015	0.010	0.018	0.014	0.029
2	0.207	0.333	0.048	0.079	0.056	0.092	0.143	0.240
3	0.041	0.053	0.253	0.485	0.242	0.438	0.106	0.152
4	0.0012	0.0014	0.0005	0.0005	0.0008	0.0009	0.0017	0.0017
$\tau_l \tau_l^j$								
$l = 0$	–	2.02	–	1.79	–	1.13	–	1.42
1	0.85	0.74	0.76	0.65	0.54	0.49	0.66	0.49
2	5.72	5.06	4.97	4.37	3.82	3.45	4.15	3.29
3	0.29	0.24	10.97	2.23	8.06	2.59	0.83	0.57
4	0.0024	0.0024	0.0022	0.0022	0.0030	0.0030	0.0045	0.0045
$I_{l,l}^{j,j}, I_{l,l+1}^{j,j}, I_{l,l+1}^{j,j+1}$								
$l = 0$	86 –	100	117 –	135	319 –	384	94 –	212
1	133 98	124	169 123	157	355 285	329	404 225	326
2	132 115	110	13 2.0	1.8	16 4.0	3.6	90 72	59
3	628 620	628	601 552	601	993 938	993	1553 1563	1553
$\langle I_l \rangle$	2.78		0.36		0.95		3.26	
$\langle I^2 \rangle^0$	2.76		0.27		0.86		3.13	

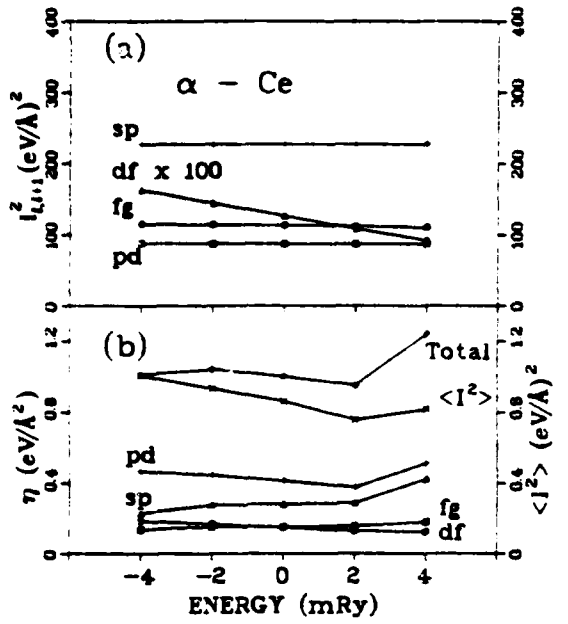

Fig. 4. (a) The squared matrix element $I^2_{l,l+1}$ for scattering from l to $l+1$ versus energy. Note that I^2_{df} is smaller by a factor of 100 than for the other channels, and also that the variation with energy is smooth for all channels. (b) Contributions $\eta_{l,l+1}$ to η (left scale) and average squared electron–ion matrix element $\langle I^2 \rangle$ (right scale) versus energy. Both $\langle I^2 \rangle$ and (to a greater extent) η show rapid variation with energy between 2 and 4 mRy which comes solely from density of states factors.

thermore, its atomic-like nature suggests that for a given atom $I^2_{l,l+1}$ will possess a transferability, from element to compound and compound to compound, which the crystal structure related quantities f_l and ν_l can never attain. These properties have been investigated in detail elsewhere [12] for the case of niobium and vanadium.

4. The transition temperature

In this section the calculated values of T_c, with and without the spin–orbit correction discussed in Section 2, are compared with experimental values. For T_c we use the Allen–Dynes [14] modification of the McMillan [1] equation

$$T_c = (\omega_{\log}/1.2)\exp\left\{-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right\}$$

with $\omega_{\log}$ defined as usual [14] and $\mu^* = 0.13$. For the phonon moments $\omega_{\log}$ and $\langle\omega^2\rangle$ of Th, the Butler [5] prescription

$$\omega_{\log} = 0.60\,\theta_c\,,$$

$$\langle\omega^2\rangle^{1/2} = 0.69\,\theta_c\,,$$

has been applied, with the high-temperature Debye temperature θ_c taken from the inelastic neutron scattering measurements of Reese et al. [15]. The same prescription has been used [16] for La and Ce.

Table III summarizes the results. (Note that no comparison is possible between the theoretical "paramagnetic γ-Ce" and the actual high temperature magnetic phase.) In each of the metals T_c is substantially overestimated. It is not the purpose of the present paper to investigate these discrepancies in detail, but a few observations can be noted. For La and Th, the empirical values of λ which give the experimental value of T_c (1.15 and 0.60, respectively) suggest that the RMTA overestimates η by 0.5–0.6 eV/Å² in these similar metals. These overestimates have

Table III
Experimental and theoretical quantities determining the superconducting transition temperature T_c. The superscript zero indicates quantities calculated disregarding spin–orbit corrections to the RMTA expressions

	La	γ-Ce	α-Ce	Th
$\omega_{\log}$(K)	74	70	104	86
$\langle\omega^2\rangle^{1/2}$(K)	86	81	119	99
M/ω^{2}(eV Å⁻¹)	1.84	0.92	1.99	2.28
$\eta,\eta^{(0)}$(eV/Å²)	2.65,2.62	0.72,0.54	1.10,1.00	1.99,1.91
$\lambda,\lambda^{(0)}$	1.44,1.42	0.77,0.58	0.55,0.50	0.87,0.84
$T_c, T_c^{(0)}$(K)	8.4,8.3	2.8,1.0	1.3,0.8	3.9,3.6
$T_{c\,\mathrm{exp}}$	6.05	–	~0.01	1.4

been discussed elsewhere, for La by Pickett et al. [9] and for Th by Winter [17]. For α-Ce a good case can be made [10] for invoking a paramagnon contribution λ_{spin} detrimental to spin pairing, which need only be of the order of 0.15 to explain the overestimate of T_c by two orders of magnitude. Indeed, recent careful estimates by Rietschel and Winter [18] point to a probable value of $\lambda_{spin} \approx 0.2$ for Nb and V, so this effect may be contributing to the overestimate of T_c in La and Th as well.

5. Conclusions

The specific conclusions of this study are twofold. Firstly, spin–orbit corrections to η (within RMTA) may become important in metals with large atomic numbers Z. One condition which can lead to an appreciable correction is for the spin–orbit interaction to be large enough to result in a net displacement of $j = l + \frac{1}{2}$ states with respect to $j = l - \frac{1}{2}$ states, viz., a deviation of the ratio $f_l^{\downarrow}/f_l^{\uparrow}$ from the zero spin–orbit value $l/(l+1)$. These deviations are small (see table II) in La ($Z = 57$) and even Th ($Z = 90$) at E_F. Due to the proximity of E_F to the 4f bands, deviations in Ce become significant. Perhaps a more important criterion for spin–orbit correction to η may be that the spin–orbit splitting ΔE_l of the l-resonance [$\Delta E_l = |E_l^{\uparrow} - E_l^{\downarrow}|$, where $\delta_l^{\uparrow}(E_l^{\uparrow}) = \delta_l^{\downarrow}(E_l^{\downarrow})$], be comparable to the distance of the l band center from E_F. This leads to a variation of the ratio $\tau_l^{\downarrow}/\tau_l^{\uparrow}$ from unity (table II) which is large for Ce. As a result the matrix elements $I_{l,l+1}^{\uparrow\uparrow}$ and $I_{l,l+1}^{\downarrow\downarrow}$ differ. In the systems studied here $I_{l,l+1}^{\uparrow\uparrow} \geq I_{l,l+1}^{\downarrow\downarrow}$, and $f_l^{\uparrow}$ is generally increased at the expense of $f_l^{\downarrow}$, resulting in increased values of η.

Secondly for each of the "f-band metals" La, Ce and Th, the RMTA appears to overestimate η by approximately 25%. In this respect these f-band metals resemble d-band metals, where similar overestimates [4, 5, 19] by the RMTA are common.

Acknowledgments

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Transferability and the electron-phonon interaction: A reinterpretation of the rigid-muffin-tin approximation

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The expression for the McMillan-Hopfield constant $\eta = N(E_F)\langle I^2\rangle$ within the rigid-muffin-tin approximation (RMTA) is reinterpreted in terms of single-channel electron-ion matrix elements $I^2_{l,l+1}$ and angular-momentum-character fractions f_l of the electronic states at the Fermi level. Reexamination of Nb- and V-based $A15$ compounds suggests that $I^2_{l,l+1}$ is more nearly an atomic property, and thus transferable from system to system, than other commonly used quantities. The fractions f_l are dependent on bonding character and crystal structure but tend to be constant within a class of compounds. Criteria for increasing η within RMTA are discussed.

I. INTRODUCTION

In his classic study of the electron-phonon interaction parameter λ and its relation to the superconducting transition temperature T_c, McMillan[1] showed that λ can be written

$$\lambda = \frac{N(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle} \tag{1}$$

in terms of the density of states $N(E_F)$ per spin at the Fermi energy E_F, a mean-square electron-ion matrix element $\langle I^2\rangle$, and an appropriately defined lattice stiffness $M\langle\omega^2\rangle$. A topic of particular interest in the ensuing decade has been the discussion of high T_c metals in terms of one or the other of the factors $N(E_F)$, $\langle I^2\rangle$, or $M\langle\omega^2\rangle$ as most important in leading to high-temperature superconductivity. With one of these factors [say, $N(E_F)$] as the principal determinant of the high T_c, a natural procedure which could be tried to produce a higher temperature superconductor is to "transfer" this large value of $N(E_F)$ to a metal with more favorable values of $\langle I^2\rangle$ and $M\langle\omega^2\rangle$.

The limited data available to McMillan[1] [all empirical except for a few calculated values of $N(E_F)$] suggested that the product $N(E_F)\langle I^2\rangle$ is roughly constant within a class of materials, in which case the search for high T_c materials should concentrate on soft lattices with small values of $M\langle\omega^2\rangle$. Although this approach was used by several investigators in the following years, often with apparent success in understanding trends in T_c, more recently it has been called into question by a number of calculations. Based upon the "rigid-muffin-tin approximation" (RMTA) of Gaspari and Gyorffy,[2] Papaconstantopoulos *et al.*,[3] and Butler[4] have shown that, within isostructural elemental transition metals, $N(E_F)\langle I^2\rangle$ can vary by as much as a factor of 3. Furthermore, these estimates appear to agree rather well with more recent experimental data. Thus variations of $N(E_F)$ and $\langle I^2\rangle$ separately must be taken into account.

Another early attempt to correlate superconducting properties was made by Hopfield,[5] who introduced the notational convenience $\eta = N(E_F)\langle I^2\rangle$ (the "McMillan-Hopfield parameter"). Analysis by Hopfield which emphasized only the p-d scattering led him to anticipate that, in transition metals which had a large d partial density of states, η would be essentially an atomic parameter. As such, η would be transferable, from element to alloy and within a class of compounds, and Hopfield used this idea in an attempt to understand superconductivity in transition-metal alloys and within $A15$ compounds. However, the startling discovery by Klein and Papaconstantopoulos[6] that the d-f contribution[7] to η is not only appreciable but in fact *dominant* in transition metals, and the ensuing realization that the f contribution is a property of the environment rather than atomic in nature, has pointed out the limited usefulness of Hopfield's approach.

There have also been suggestions that, within

limited classes or subclasses of compounds, there may be an "atomic λ" which is more or less transferable. Phillips[8] suggested that, within the NaCl-structure NbN family of compounds, the sum of atomic contributions $\lambda=\lambda_A+\lambda_B$ should be a useful concept. However, RMTA calculations by Klein, Papaconstantopoulos, and Boyer[9] indicate λ_C for carbon varies by more than a factor of 5 in the compounds NbC, TaC, and HfC. This idea of "transferable λ" was then further restricted to the subclass "NaCl-structure compounds with phonon anomalies" by Haufe, Kerker, and Benneman.[10] However, at such a specialized level the concept of transferability loses much of its usefulness in understanding superconductivity as well as for predicting higher T_c materials.

In view of these largely unfruitful attempts to identify transferable quantities related to superconductivity, and also the difficulty in calculating the phonon spectrum and hence the lattice stiffness $M\langle\omega^2\rangle$, emphasis has shifted to attempting to understand the behavior of η within rigid-ion models, chiefly the RMTA. Notably, the group at the Naval Research Laboratory has published extensive RMTA calculations for elements[3,6] and for NaCl-structure[9,11] compounds and $A15$ (Ref. 12) compounds, among others. Butler[4] has provided a detailed RMTA study of the 4d transition metals, noting in particular the dependence of $\langle I^2\rangle$ on atomic number (i.e., valence) and volume in this class of metals. A simultaneous examination of the behavior of η across the 4d series was given by Pettifor,[13] who related RMTA quantities to band-structure parameters.

In this paper I present a reinterpretation of the original Gaspari-Gyorffy expression for $\langle I^2\rangle$ which results from a simple regrouping of terms. In addition to providing more physical insight into the quantities which determine $\langle I^2\rangle$, this reinterpretation has two other favorable consequences. One is that atomiclike quantities are identified, these being the electron-ion matrix elements $I_{l,l+1}$ for scattering, from partial wave l to partial wave $l+1$, by an atomic displacement. The atomiclike nature of $I_{l,l+1}$ suggests an approximate transferability which seems to hold at least in systems with common bonding characteristics. The other is that the *fraction* of states $f_l=N_l(E_F)/N(E_F)$ with angular momentum l, which multiplies $I^2_{l,l+1}$ is a much smoother quantity (in several senses to be discussed below) than the original crystalline enhancement factors. Results of various previous calculations are reviewed in terms of these ideas.

II. REARRANGEMENT OF THE GASPARI-GYORFFY EXPRESSION

Gaspari and Gyorffy derived an expression for $\langle I^2\rangle$ which can be written (in atomic units $\hbar=2m=e^2/2=1$)

$$\langle I^2\rangle=\frac{E_F}{\pi^2 N(E_F)^2}\sum_l 2(l+1)\times\sin^2(\delta_l-\delta_{l+1})\nu_l\nu_{l+1}\,, \tag{2}$$

where δ_l is the Fermi-energy phase shift for partial wave l. The "crystalline enhancement" of the density of states is given by

$$\nu_l=N_l(E_F)/N_l^{(1)}(E_F)\,,$$

where $N_l^{(1)}(E_F)$ is the corresponding density of states for a single scatterer rather than for a lattice of scatterers. Specifically,

$$N_l^{(1)}(E_F)=\frac{\sqrt{E_F}}{\pi}(2l+1)\times\int_0^{R_S}dr\,r^2R_l^2(r,E_F)\,, \tag{3}$$

where R_l is the radial wave function and R_S is the muffin-tin radius. The trigonometric factor in Eq. (2) arises from the RMTA matrix element

$$\int_0^{R_S}dr\,r^2R_l\frac{dV}{dr}R_{l+1}=\sin(\delta_l-\delta_{l+1})\,, \tag{4}$$

with the radial function normalization chosen to be

$$R_l(R_S,E_F)=j_l(\kappa_F R_S)\cos\delta_l-n_l(\kappa_F R_S)\sin\delta_l\,. \tag{5}$$

Here j_l and n_l are the spherical Bessel and Neumann function and $\kappa_F^2=E_F$.

Several features of Eq. (2) should be noted. First, the factor $\sin^2(\delta_l-\delta_{l+1})$ which is bounded between 0 and 1, depends, from Eq. (4), on the muffin-tin potential V, on its overlap with radial functions, and on the radial function normalization, which is not bounded [see Eq. (6) below]. Secondly, the rather unphysical single scatterer density of states tends to obscure the physical interpretation. Thirdly, the factor E_F, which seems to imply an overt dependence on the zero of energy, is in fact artificial, being canceled by the $\sqrt{E_F}$ factors from Eq. (3). This last feature points to the fact that the factor $(\sqrt{E_F}/\pi)(2l+1)$ was *introduced* into the expression (2) to convert the *normalization integral*

$$\tau_l^2 = \int_0^{R_S} dr\, r^2 R_l^2 \tag{6}$$

to a density of states.

Although the original expression (2) may be desirable from some points of view, the following reinterpretation in many ways provides a simpler, and thereby more illuminating picture. Begin by defining a rigid-muffin-tin matrix element for the $l \to l+1$ channel by (see also Butler[4])

$$I_{l,l+1} = \int_0^{R_S} dr\, r^2 R_l \frac{dV}{dr} R_{l+1}/(\tau_l \tau_{l+1}) \,. \tag{7}$$

Evidently $I_{l,l+1}$ is independent of the normalization of the radial functions and depends only on dV/dr and the *shapes* of the radial functions. This form of matrix element has been used previously by Pickett and Gyorffy,[14] Pettifor,[13] and to some extent by Butler,[4] and was also preferred by Allen.[15] In terms of these matrix elements and the fraction f_l of states of angular momentum l, $\langle I^2 \rangle$ can be expressed as

$$\langle I^2 \rangle = \sum_l \frac{(2l+2)}{(2l+1)(2l+3)} I_{l,l+1}^2 f_l f_{l+1} \,. \tag{8}$$

This expression provides a more straightforward and useful interpretation for primarily two reasons. The first reason is that $I_{l,l+1}$ will be, to a degree to be discussed in Sec. III, an *atomic* property as it depends only on the muffin-tin potential, through its derivative dV/dr and its radial functions, but not explicitly on the crystalline arrangement of neighboring atoms. This in fact is essentially the idea of Hopfield,[5] but restricted to the muffin-tin region and making no attempt to simplify the ratios f_l out of the expression.

The second desirable feature of the summand in Eq. (8) is its dependence on energy E_F. From Eqs. (4) and (7) and the expression

$$\tau_l^2 = R_S^2 R_l(R_S, E_F)^2 \, |\dot{\gamma}_l| \,, \tag{9}$$

where $\dot{\gamma}_l$ is the energy derivative of the logarithmic derivative, $I_{l,l+1}^2$ is seen to be very smooth, varying as do δ_l and γ_l on the scale of the l and $(l+1)$ bandwidths. This energy variation has been discussed previously by Pettifor.[13] Although it is somewhat less obvious, the ratios f_l are much more smoothly varying then either its numerator or denominator alone. This is the result of (i) $N_l(E)$ and $N(E)$ having canceling van Hove singularities at the same energies, and (ii) f_l depending only on the character of eigenstates, rather than on the density of states which may vary rapidly. It follows that $\langle I^2 \rangle$ is slowly varying with energy, a characteristic which was not evident in the original Gaspari-Gyorffy expression.

The behavior of f_l in La (Ref. 16) is shown in Fig. 1 and it can be compared with N_l and N in Fig. 2. La is a good metal in which to illustrate this behavior because, although over most of its spectrum it is typical of a $5d$ transition metal, it possesses $4f$ ($l=3$) bands centered 2.5 eV above E_F which provide an extreme example of the features mentioned above. Figures 1 and 2 show dramatically how the sharply structured behavior of $N_3(E)$ is translated into a smooth, almost resonance-like behavior of $f_3(E)$. Likewise, the structured d spectrum $N_2(E)$ is converted into a smoother form in $f_2(E)$ which, however, is nearly split by the f bands. [In the absence of the f bands, as in more typical transition metals, only a minor minimum in $f_2(E)$ will occur in the low density-of-states bonding-antibonding "gap."]

Deviation of $f_l(E)$ from *very* smooth behavior results primarily from hybridization, as mentioned above for the d-f interaction effect on $f_2(E)$. This effect is more clearly drawn in $f_0(E)$ and $f_1(E)$, each of which show structure due to hybridization with d bands (at -2 eV) and f bands (~ 1.5 eV). However, the resulting variation with energy in

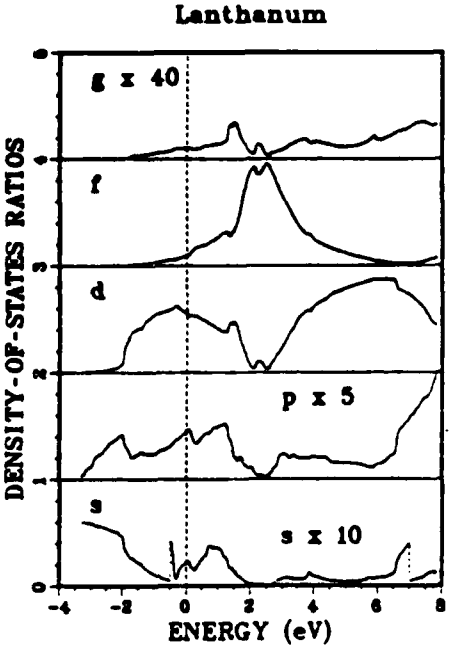

FIG. 1. The electronic density-of-states ratios f_l versus energy for fcc La, $l=0, 1, 2, 3, 4$. Successive plots are displaced by one unit ($0 \le f_l \le 1$). The zero of energy is fixed at the Fermi level.

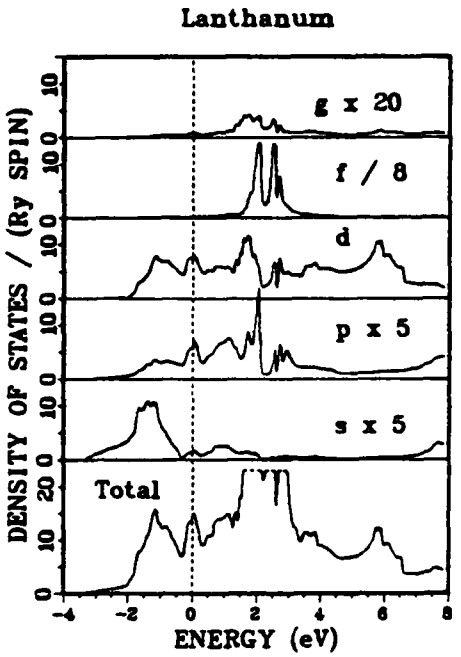

FIG. 2. The total and partial densities of states of fcc La. Rescalings of the various partial densities of states are as noted.

each case remains much smaller than that of $N_l(E)$.

To give a full picture of the present approach to $\langle I^2 \rangle$, the quantities δ_l, τ_l, and $I^2_{l,l+1}$ for La are shown in Fig. 3. [For δ_l and τ_l the $(2j+1)$-weighted averages of the corresponding fully relativistic quantities for $j = l \pm \frac{1}{2}$ have been used for $l=1$, 2, and 4. For $l=3$ this averaging results in unphysical behavior in the energy region between the $j=\frac{5}{2}$ and $j=\frac{7}{2}$ resonances, so only the $j=\frac{7}{2}$ quantities are shown in Fig. 3. The full relativistic treatment of $\langle I^2 \rangle$ will be presented elsewhere.[17]] The phase shifts for $l=0$, 1, and 2 are typical of an early $5d$ transition metal, but the sharp $l=3$ resonance (where $\delta_3 = \pi/2$) at 2.1 eV gives rise to flat $4f$ bands not present (or rather, fully occupied) in heavier $5d$ transition metals. The $l=4$ phase shift is positive but less than 7×10^{-3} throughout this range.

The normalizations τ_l calculated from Eq. (6) and shown in Fig. 3(b) are proportional (except for the $\sqrt{E_F}$ factor) to the "single scatterer" density of states used in the original Gaspari-Gyorffy expression. For $l=0$, 1, and 4 these are monotonic in the interesting energy range. For $l=2$, τ_2 peaks somewhat below the d-band center due to the clear nonresonant form of δ_2 in Fig. 3(a). The sharp $l=3$ resonance results in a huge increase in τ_3 in the $4f$-band region. The effect of this resonance

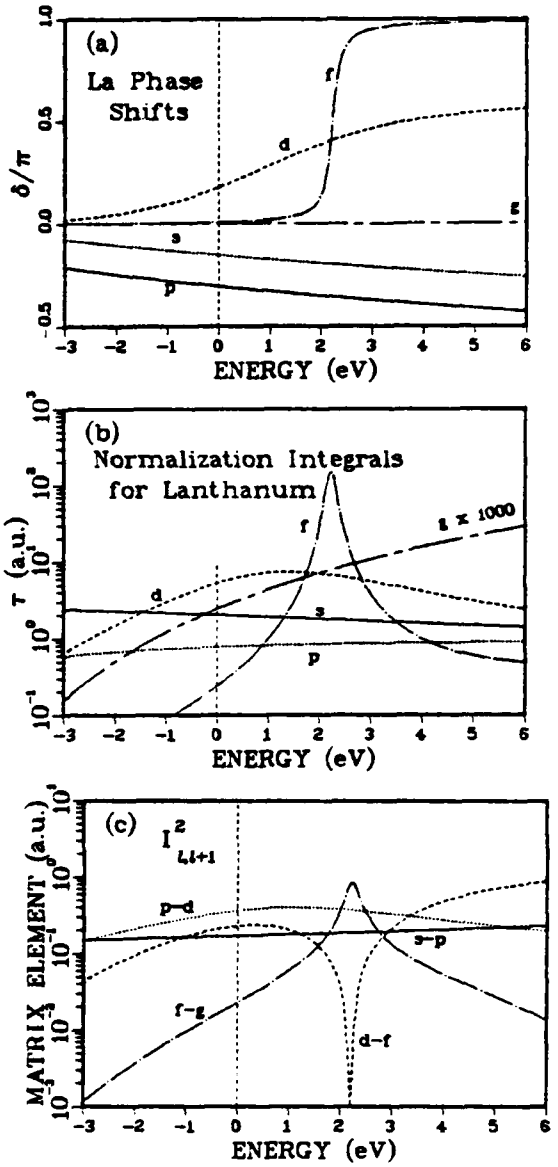

FIG. 3. La functions entering the RMTA expression for η. (a) Phase shifts δ_l relative to π. (b) Semilog plot of the normalization integrals τ_l. (c) Semilog plot of the single-channel matrix elements $I^2_{l,l+1}$. Note the zero of $I^2_{2,3}$ at the point where $\delta_2 = \delta_3$.

on $I^2_{l,l+1}$ is evident in Fig. 3(c), where $I^2_{2,3}$ drops by over an order of magnitude in this region; in addition, $I^2_{2,3}$ vanishes where $\delta_2 = \delta_3$. However, in the absence of the $4f$ bands, $I^2_{l,l+1}$ are smooth over the entire d-band region.

III. TRANSFERABILITY OF $I^2_{l,l+1}$

In this section we investigate the degree to which the matrix elements $I^2_{l,l+1}$ represent atomic-

like, transferable quantities. For this purpose we focus on Nb and V, for which Papaconstantopoulos, Klein, and Boyer (Refs. 3, 6, 9, 11, and 12) have carried out self-consistent band-structure determinations and calculations of η for the elemental metals, several $A15$-structure compounds, and two Nb-based NaCl-structure metals. These compounds are listed in Table I.

A feature which was not mentioned in the previous section is the dependence of the various quantities on the sphere radius R_S. As far as the RMTA itself is concerned, R_S should be fixed at the radius which most nearly reproduces the actual scattering properties. However, theoretical ambiguities can arise if spheres from distinct atoms overlap, and in the NRL calculations which will be used here, maximal nonoverlapping spheres have been used. Each of the quantities δ_l, N_l, and $N_l^{(1)}$ depend on R_S, but the ratio $\nu_l = N_l/N_l^{(1)}$ is independent of R_S to lowest order and the R_S dependence of δ_l is often weak. The resulting weak dependence of η on R_S is central to the usefulness of the RMTA in that it provides a relatively unambiguous result to compare with experiment.

The quantities f_l and $I^2_{l,l-1}$, the intermediate quantities in the interpretation of RMTA being proposed here, are separately dependent on R_S. For a comparison of these quantities in various systems, renormalization to a common radius $\bar{R}_S$ must be carried out first. This has been done as follows. For $l=0$, 1, and 2 the radial wave functions are varying slowly near R_S and the normalization correction $\Delta\tau_l^2$ is approximated by

$$\Delta\tau_l^2 = \int_{R_S}^{\bar{R}_S} r^2 dr\, R_l^2(r) \approx R_l^2(R_S)(\bar{R}_S^3 - R_S^3)/3 . \tag{10}$$

In addition the radial function R_l itself is renormalized to the appropriate value at the new radius $\bar{R}_S$. Explicitly,

$$\tau_l^2(\bar{R}_S) \cong [\tau_l^2(R_S) + \Delta\tau_l^2] \left| \frac{j_l(\kappa_F \bar{R}_S)\cos\delta_l - n_l(\kappa_F \bar{R}_S)\sin\delta_l}{j_l(\kappa_F R_S)\cos\delta_l - n_l(\kappa_F R_S)\sin\delta_l} \right|^2 . \tag{11}$$

For $l=3$ the fact that $R_3(r) \approx j_3(\kappa_F r)$ (inside as well as outside the sphere) was used to recalculate $\tau_3^2(\bar{R}_S)$ directly. No correction to the phase shifts has been considered.

The radius $\bar{R}_S$ was chosen to be midway between the elemental value of R_S and the mean of the $A15$-structure values given in Table I; these were taken as $\bar{R}_S = 2.57$ and 2.37 a.u. for Nb and V, respectively. The resulting values of $\tau_l^2(\bar{R}_S)$ in the $A15$ compounds were 5–20 % increases over

TABLE I. Sphere radius R_S (a.u.), Fermi energy E_F (Ry), density of states *per metal atom* per spin $N^A(E_F)$ (Ry^{-1}), phase shifts δ_l (radians) and density-of-states ratios f_l, and enhancements ν_l, for Nb- and V-based compounds discussed in the test.

	R_S	E_F	$N^A(E_F)$	δ_0	δ_1	δ_2	δ_3	f_0	f_1	f_2	f_3	ν_0	ν_1	ν_2	ν_3
NbC	2.313	0.869	4.76	−1.11	−0.51	1.30	0.0107	0.0086	0.0123	0.383	0.0288	0.193	0.150	0.361	2.571
NbN	2.308	0.849	6.43	−1.01	−0.47	1.72	0.0111	0.0057	0.0034	0.412	0.0234	0.161	0.056	0.613	2.945
Nb_3Al	2.450	0.837	16.60	−1.13	−0.50	0.86	0.0076	0.0115	0.0613	0.530	0.0123	0.965	3.257	1.707	4.248
Nb_3Ga	2.443	0.851	15.98	−1.14	−0.50	0.90	0.0082	0.0110	0.0668	0.529	0.0121	0.887	3.341	1.608	3.827
Nb_3Si	2.457	0.832	6.97	−1.12	−0.49	0.90	0.0079	0.0069	0.0557	0.560	0.0120	0.242	1.241	0.721	1.747
Nb_3Ge	2.438	0.866	8.89	−1.15	−0.51	0.92	0.0086	0.0061	0.0583	0.563	0.0126	0.271	1.597	0.967	2.108
Nb_3Sn	2.495	0.833	13.22	−1.11	−0.49	0.94	0.0083	0.0047	0.0544	0.594	0.0102	0.306	2.367	1.367	2.731
Nb_3Sb	2.482	0.874	4.33	−1.15	−0.51	1.02	0.0094	0.0046	0.0502	0.594	0.0137	0.099	0.687	0.446	1.052
Nb	2.685	0.676	9.71	−0.93	−0.36	1.14	0.0074	0.0178	0.0746	0.724	0.0128	0.807	2.923	0.681	3.846
V	2.477	0.675	12.70	−0.69	−0.17	1.03	0.0027	0.0102	0.0638	0.846	0.0071	0.549	2.341	0.634	6.936
V_3Al	2.282	0.819	15.74	−0.88	−0.28	0.95	0.0026	0.0047	0.0543	0.638	0.0056	0.365	2.698	1.003	4.288
V_3Ga	2.276	0.827	24.63	−0.88	−0.28	1.02	0.0028	0.0037	0.0565	0.652	0.0044	0.445	4.333	1.539	5.173
V_3Si	2.231	0.889	16.68	−0.94	−0.31	0.98	0.0031	0.0030	0.0568	0.629	0.0063	0.254	2.795	1.224	4.130
V_3Ge	2.253	0.871	9.56	−0.92	−0.30	1.02	0.0031	0.0038	0.0415	0.656	0.0071	0.183	1.183	0.670	2.776
V_3Sn	2.355	0.803	10.25	−0.84	−0.26	1.07	0.0029	0.0028	0.0317	0.739	0.0052	0.133	1.048	0.617	2.665

$\tau_l^2(R_S)$ for $l=0$, 1, and 3 and 5–10% decreases for $l=2$. The corresponding changes in elemental Nb and V were of opposite sign in each case, since $\bar{R}_S < R_S$ in these cases. It is notable that these renormalizations resulted in bringing τ_l^2 for the $A15$ compounds closer to the corresponding elemental value only for $l=0$ and 1. For $l=2$ the renormalization worsened this "correspondence," while no clear trend appeared for $l=3$. In any case these results seem to reflect real similarities or differences between the Nb- and V-atom environments in the elements and the compounds.

In Tables I and II an extensive listing of the quantities which enter into the determination of Nb- or V- atom contributions to η is presented.[18] Both $N_l^{(1)}$ and N_l have been renormalized to $\bar{R}_S$ by multiplying by the ratio $\tau_l^2(\bar{R}_S)/\tau_l^2(R_S)$, hence η is *unaffected*. Although corrections to the phase shifts could have been incorporated, this would amount to investigating the (small) R_S dependence of η, which is not the purpose of this paper. It should be noted that the extrapolation from R_S to $\bar{R}_S$ is somewhat more uncertain in NbC and NbN than for the other cases, due to the interval $R_S - \bar{R}_S$ being twice as large.

The principal result here is the regularity in the values of $I_{l,l+1}^2$(Nb) and $I_{l,l+1}^2$(V) from system to system, greater than that of the numerator $\sin^2(\delta_l - \delta_{l+1})$ or denominator $\tau_l^2\tau_{l+1}^2$ separately, each of which is dependent on radial function normalization. The deviations of $I_{l,l+1}^2$ from perfect regularity within the $A15$ compounds are generally 5% or less, whereas $\sin^2(\delta_l - \delta_{l+1})$ and $\tau_l^2\tau_{l+1}^2$ may vary by more than 25%. Comparing the $A15$ compounds with Nb and V, it is evident that $I_{l,l+1}^2$ of the element is smaller (for $l=1$, by nearly a factor of 2) than that of the $A15$ compound. However, for the dominant $l=2$ channel, variations in $\sin^2(\delta_l - \delta_{l+1})$ and $\tau_l^2\tau_{l+1}^2$ partially cancel, leaving $I_{l,l+1}^2$ as the most transferable quantitity. The relative constancy of $\langle I^2 \rangle$ in $A15$ compounds, described in the form $\eta \propto N(E_F)$, has been pointed out previously.[12]

The situation for the $B1$ compounds is not as clear. As mentioned previously, the extrapolation to the radius $R_S = 2.57$ a.u. may be introducing some unphysical irregularities, so only a pair of compounds is not sufficient to allow an evaluation of constancy of $I_{l,l+1}^2$ within this class. It is clear, however, that $I_{2,3}^2$ is significantly larger than in the $A15$ compounds, which may lead to comparable values of η(Nb) in spite of a lower density of states. This is discussed further below and in Sec. IV C.

In addition to variations in $I_{l,l-1}^2$ two possibilities remain for producing a larger Nb or V contributon to η. The obvious possibility is to find a compound with a larger value of $N(E_F)$ per atom. This approach leads to a well-known instability toward formation of a material with a smaller value of $N(E_F)$. Rather than placing a very large number of electrons at the highest occupied energy, the compound will tend to (a) distort to a lower symmetry, thereby moving some electrons to lower en-

TABLE II. Normalization integrals τ_l^2 (a.u.), $\sin^2(\delta_l - \delta_{l+1}) \equiv S_{l,l+1}^2$, $I_{l,l+1}^2$ (eV/Å)^2, $\eta_{l,l+1}^4$ and η^4 (eV/Å)^2, and $\langle I^2 \rangle^4$ (eV/Å)^2. Note the definition $\eta^4 \equiv N(E_F)^4\langle I^2 \rangle^4$, with $N(E_F)^4$ defined in the caption to Table I.

	τ_0^2	τ_1^2	τ_2^2	τ_3^2	$S_{0,1}^2$	$S_{1,2}^2$	$S_{2,3}^2$	$I_{0,1}^2$	$I_{1,2}^2$	$I_{2,3}^2$	$\eta_{0,1}^4$	$\eta_{1,2}^4$	$\eta_{2,3}^4$	η^4	$\langle I^2 \rangle^4$
NbC	0.715	0.436	3.40	0.0257	0.32	0.95	0.92	675	421	7000	0.02	0.18	4.62	4.82	13.8
NbN	0.770	0.449	2.95	0.0249	0.26	0.67	0.98	505	333	8850	0.00	0.06	6.91	6.97	14.8
Nb_3Al	0.676	0.358	3.54	0.0235	0.35	0.95	0.56	966	498	4480	0.55	5.27	6.09	11.91	9.8
Nb_3Ga	0.677	0.363	3.58	0.0246	0.36	0.97	0.61	956	495	4580	0.55	5.48	5.90	11.93	10.2
Nb_3Si	0.688	0.359	3.73	0.0235	0.35	0.97	0.61	929	478	4570	0.12	2.04	2.69	4.85	9.5
Nb_3Ge	0.671	0.366	3.49	0.0256	0.36	0.98	0.62	959	508	4600	0.15	2.91	3.65	6.71	10.3
Nb_3Sn	0.694	0.349	3.98	0.0242	0.34	0.98	0.64	932	466	4400	0.15	3.91	4.44	8.50	8.7
Nb_3Sb	0.678	0.355	3.88	0.0271	0.35	1.00	0.72	963	480	4490	0.05	1.22	2.00	3.26	10.2
Nb	0.819	0.316	7.90	0.0176	0.29	1.00	0.82	743	262	3900	0.47	2.72	4.42	7.61	10.7
V	0.900	0.363	12.97	0.0071	0.25	0.87	0.73	495	122	5230	0.20	1.64	5.06	6.90	7.4
V_3Al	0.704	0.366	6.96	0.0101	0.32	0.89	0.66	822	231	6220	0.16	2.47	4.38	7.01	6.1
V_3Ga	0.706	0.370	7.21	0.0104	0.32	0.93	0.72	808	230	6400	0.20	4.09	5.72	10.02	5.5
V_3Si	0.658	0.376	5.71	0.0122	0.34	0.92	0.69	919	284	6500	0.13	3.32	5.45	8.90	7.3
V_3Ge	0.676	0.376	6.31	0.0117	0.33	0.94	0.73	869	262	6480	0.07	1.34	3.64	5.05	7.2
V_3Sn	0.746	0.362	8.62	0.0101	0.30	0.94	0.77	733	200	5840	0.03	0.94	2.92	3.90	5.2

ergy and lowering $N(E_F)$ (the band Jahn-Teller effect), (b) crystallize in an unrelated structure with a smaller value of $N(E_F)$, or (c) phase separate into distinct compounds with lower values of $N(E_F)$.

The alternative choice is to increase η by shifting the character of states at E_F, that is, altering the fractions f_l to maximize $\langle I^2 \rangle$. An extreme example of this effect is to shift (somehow) the s and p character (or an equal amount of d character) in Nb to f character, thereby taking advantage of the stronger d-f scattering described by $I^2_{2,3}$ in Table II, and in this particular example increasing $\langle I^2 \rangle$ by a factor of 8. It is not immediately clear how such a shift is to be accomplished, although a change of crystal structure and/or bonding character is probably required.

A possible example of this effect may be provided by the refractory compounds NbC and NbN, which are currently understood in terms of a much more covalent type of bonding[19,20] than the primarily metallic bcc elements and $A15$ compounds. As a result f_3 *is twice as large*, and f_1 much smaller for Nb in these compounds than in the other in Table I. Since Nb has no atomic f states, f_3 results primarily from the Nb-site decomposition of neighboring atom states,[4,13] and covalent bonding (i.e., strong overlap extending into the Nb sphere) with C or N p states evidently enhances the Nb $l=3$ character of states of E_F in these compounds. Of course, $\langle I^2 \rangle$ will be maximized if as much weight as possible is shifted into the channel $\bar{l}$ with maximum $I^2_{l,l+1}$ such that $f_l = f_{l+1}$, with other fractions f_l vanishing. However, such shifts may well lead to small values of $N(E_F)$, or if not, the resulting increase in the electron-phonon interaction can lead to a "covalent instability" as discussed previously.[21,22]

IV. DISCUSSION AND CONCLUSIONS

A. Elemental transition metals

Expressing $\eta = N(E_F)\langle I^2 \rangle$ with $\langle I^2 \rangle$ given by Eq. (8) leads to a simple understanding of the variation of T_c in transition metals and their alloys. Both $I^2_{l,l+1}$ and f_l vary smoothly with Fermi-level position (equivalent to the mean valence or alloy concentration in the rigid-band model), so rapid changes in T_c such as occur in the NbMo alloy system[23] result from variations in $N(E_F)$, with some contribution due to changes in $\langle \omega^2 \rangle$. On the larger scale, however, Butler[4] has found $\langle I^2 \rangle$ to vary by a factor of 40 within the 4d transition series, in large part due to the factor f_3. On this point there is little to add to his thorough discussion except to recall the interesting crystal-structure effects found in Ru. For Ru (which is actually hcp) Butler carrier out both bcc and fcc calculations, finding f_3 and $\langle I^2 \rangle$ to be about 20% larger in the fcc phase. However, $N(E_F)$ is smaller by 33%, leading to a smaller value of η in the fcc phase. The differences in f_3 between the two phases are no doubt related to the nearest-neighbor distances and coordination numbers, but such detailed relationships are not well understood at present.

The present picture provides a new viewpoint on the differences in the $l=3$ effects between V and Nb. In the important df channel $I^2_{2,3}$ is one-third larger in V than in Nb, with the smallness of τ^2_3 in V more than compensating for the less favorable values of τ^2_2 and $\sin^2(\delta_2 - \delta_3)$. The average matrix element $\langle I^2 \rangle$, however, is only two-thirds that of Nb. Although this is due partly to large values of $I^2_{0,1}$ and $I^2_{1,2}$ in Nb, it is the larger value of f_3 in Nb which is primarily responsible. This illustrates that the presence of a larger f_3 will be accompanied by a larger τ_3, and hence smaller $I^2_{2,3}$ and that the relative importance of these effects is not necessarily reflected in the crystalline enhancement ν_3 (which is nearly twice as large in V as in Nb).

B. $A15$ compounds

It can be noted from Table II that within each of the Nb_3X and V_3X classes, the values of $I^2_{l,l+1}$ are virtually constant. The Nb_3X class includes X atoms with valences of 3, 4, and 5 leading to differing positions of the Fermi level and variations of $N(E_F)$ by a factor of 4. Nb_3Sn and Nb_3Sb, with T_c's which differ by 2 orders of magnitude (18.2 and 0.2 K, respectively), illustrate dramatically how their differences in η arise solely from the differences in $N(E_F)$. More to the point of this study, however, is the *degree of regularity* of $I^2_{l,l+1}$ and f_l which is not apparent in the ν_l nor always in the factors of $\sin^2(\delta_l - \delta_{l+1})$ (see Tables I and II).

It has been established in several $A15$ compounds[24] that T_c is sensitive to the degree of disorder (as measured by the residual resistivity). The main effect of disorder in the low-disorder regime is to broaden the electron states ("lifetime effects"). The effect on η and on T_c if the electron-

phonon spectral function α^2F is not altered by the disorder, can be accounted for by using Lorentzian-broadened values of $N(E_F)$ and $\langle I^2 \rangle$. As was pointed out above, however, $\langle I^2(E) \rangle$ is a smooth function which will be insensitive to broadening. On the other hand, many unusual properties of $A15$ compounds have been interpreted in terms of sharp structure in $N(E)$ and such structure has been verified by band-structure calculations.[12,25] The present interpretation of the RMTA makes it clear that the extreme sensitivity of T_c to disorder must be reflecting the fine structure.

C. NbC AND NbN

These $B1$ (NaCl-structure) compounds differ from the $A15$ compounds in having a more strongly covalent (metal d state with nonmetal p state) and ionic (metal-to-nonmetal charge transfer of the order of one electron) bonding, rather than primarily metallic bonding. This difference is reflected in the Fermi energy falling nearer the d resonance ($\delta_2 = \pi/2$) and results in a value of $I^2_{2,3}$ that is 80–90% larger than in Nb and the Nb-based $A15$ compounds. Another apparent consequence (in this case) of the strong bonding is the low value of $N(E_F)$, which leads to a rather unimpressive value of η_{Nb} in spite of $\langle I^2 \rangle$ being 40–50% larger than in the $A15$ compounds. These compounds do illustrate, however, that a change in bonding character can lead to substantial increases in $\langle I^2 \rangle$ relative to those in $A15$ compounds, and there remains the possibility that compounds with larger values of η may be found.

The predominance of Nb-based compounds in high T_c materials is still not completely understood. It is clearly *not* due to $\langle I^2 \rangle_{Nb}$, since $\langle I^2 \rangle$ peaks strongly at Mo rather than at Nb in the $4d$ series.[4] The evidence suggests[25] this predominance is due instead to the tendency of Nb-based (and similar) compounds to form phases with strongly split bonding and antibonding d bands. For Nb, with its slightly less than half-filled d shell, the Fermi level is left in a favorable region for large values of $N(E_F)$. The half-filled d shell Mo instead leaves E_F in the low density-of-states "gap."

The bcc transition-metal alloys and the $A15$ compounds are prime examples of this behavior. This point of view suggests that Mo will only be useful in raising T_c if a d electron is transferred onto another atom, transforming Mo into "pseudo-Nb." Exactly this behavior occurs[26] in the Chevrel phase compounds $M\mathrm{Mo_6S_8}$ and $M\mathrm{Mo_6Se_8}$ (M = metal atom, e.g., Pb, Sn,...), for which d bonding between neighboring Mo atoms is strong. An electron is transferred from each Mo to the chalcogen atoms and E_F falls in a region of high density of states just below the bonding-antibonding gap. For $\mathrm{PbMo_6S_8}$, $T_c = 15$ K results.

This behavior is violated in Mo-chalcogen compounds in which $d-d$ bonding is less dominant, and such compounds tend toward semimetallic or semiconducting character. It is also violated in the $B1$-structure compounds such as those discussed above, where metal d, nonmetal p bonding dominates and no $d-d$ bonding-antibonding gap occurs. Approximately one electron is transferred[11] off the metal atom in the Nb-based compounds, and similar behavior is expected in their Mo-based counterparts, since Nb and Mo are expected to form good rigid-band systems. A rigid-band picture suggests $N(E_F)$ in MoC should be 10% *larger*[11] than in NbC, and the results of Butler[4] suggest $\langle I^2 \rangle_{Mo}$ will be somewhat larger than $\langle I^2 \rangle_{Nb}$ (as in the elements). Indeed, it is found that T_c is 30% larger in MoC (14.3 K versus ~11 K).

The same argument suggests T_c of MoN should be considerably larger than that of NbN ($T_c = 16$ K). Rigid-band behavior suggests a 20% increase[9(b)] in $N(E_f)$; however, $\langle I^2 \rangle_{Mo}$ may be slightly less in MoN since E_F already lies slightly above the d resonance in NbN (see Table I). The few studies of molybdenum nitrides reported in the literature[27] have not unambiguously established the existence of $B1$-structure MoN. Although negative results often go unreported, there are at least two reasons why an extensive search for this material may have not been undertaken. The first is the *apparent* dominance of Nb-based compounds in high T_c superconductors, as mentioned above, which makes the substitution of Mo for Nb in these compounds unappealing. The second reason is the electron-atom ratio of MoN ($e/a = 5.5$), which violates the "Matthias rule"[28] that high T_c materials cluster around $e/a = 4.75$ and 6.5 with a deep intermediate valley. The Matthias rule can be understood in terms of the structure in $N(E)$ in materials dominated by $d-d$ bonding, and it is of considerable interest to establish whether this guideline is violated in the $B1$ structure. Finally, the lack of stability of MoN itself is suggestive of a strong electron-phonon interaction in this compound. The phonon spectrum will also affect the

value of T_c but such considerations are beyond the scope of the present paper.

D. A caveat

Allen and Dynes[22] have noted that, although soft lattices may contribute somewhat to high values of T_c, known metals with high T_c achieve this primarily through a large value of η. Within the RMTA, higher values of η in transition-metal compounds thus seem to rely on a larger $N(E_F)$ or $I^2_{2,3}$ or on larger f_3 ratios. The $l=3$ character arises from tails of states on neighboring atoms, and an $l=3$ expansion of these tails requires (i) they behave approximately as $j_3(\kappa r)$ as seen from a neighboring atom, as pointed out previously by Butler,[4] and (ii) they are expandable in $l=3$ angular functions. These requirements might be expected to point the way to crystal structures and chemical configurations with larger values of f_3, and perhaps η. The NaCl-structure compounds, it should be noted, have Nb f_3 ratios *twice as large* as for the $A15$ compounds, much of which probably derives from C or N p states.

However, the contribution to η involving f_3 arises in real space from near the sphere boundary, where the RMTA model of the screened potential is most approximate. Indeed it has been noted[3] that T_c's of elemental metals seem to show better agreement with measured values if $\eta_{2,3}$ is (somewhat arbitrarily) divided by two.[29] It is at first glance surprising that this df contribution, from near R_S, is not sensitive to the value of R_S, although the present treatment of RMTA clarifies this point (neither f_3 nor $I^2_{2,3}$ is sensitive to R_S). We want merely to caution here that requirements (i) and (ii) above are necessary to maximize f_3 *within* RMTA, but that the RMTA is least certain here. It seems likely that the inclusion of the nonrigid potential[30] and the concomitant relaxing of the $l \Longleftrightarrow l+1$ selection rule in a more rigorous theory may be necessary to lead to a more fundamental understanding of the best mechanism by which to increase η.

For f-band metals with *atomic* contributions to the $l=3$ quantities, that is, rare earths and actinides, Butler[4] has suggested that the f bands may be useful in reaching large η values. Calculations[17,31,32] for La, Ce, and Th do not confirm these expectations, however, and the discussion of Sec. II shows why narrow f bands will not lead to large η's, in spite of extremely large densities of states.

Note added in proof. Calculations of T_c for NbN and NbC have been presented by W.E. Pickett, B.M. Klein, and D. A Papaconstantopoulos [Physica 107B, 667 (1981)].

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Effect of a varying density of states on superconductivity

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A microscopic treatment of the consequences for superconductivity of a nonconstant electronic density of states is presented. Generalized Eliashberg gap equations valid for a varying density of states are presented, from which the change of T_c with static or thermal disorder can be calculated. The temperature dependence of the effective mass is shown to be altered by disorder. Use of these results provides a possible experimental approach for deducing the energy variation of the density of states of superconductors.

I. INTRODUCTION

There is currently an active interest in the effects upon the electronic properties of metals when the density of states $N(E)$ cannot be assumed to be constant near the Fermi level E_F. Recent band-structure calculations, especially on the $A15$ compounds, confirm that in transition-metal compounds with several atoms per cell, sharp structure in $N(E)$, at least on the order of the Debye frequency $k\theta_D \sim 25$ meV, occurs in a region around E_F. Since there is no general agreement (nor will there be soon) among band-structure calculations on this scale, the general trend has been to attempt to fit experimental data with models of $N(E)$, usually with *ad hoc* phenomenological expressions or oversimplified theories. Since the phenomenological approach appears to be the only way at present to deduce the structure in $N(E)$ on this scale, it is evident that correct theoretical expressions are needed to allow a proper unfolding of the data.

The effect upon the critical temperature T_c, due to static disorder has been studied extensively in $A15$ compounds, where T_c may either decrease or increase with disorder.[1] Explanations of this phenomenon has postulated a smearing of structure[2] in $N(E)$, gap anisotropy,[3] changes in the phonon spectrum,[4] or the special type of defect[5] which is present, although not all of these could raise T_c. Unfortunately, there is a great deal of uncertainty in the literature about the form the energy smearing will take, with the only microscopic theory (Labbe and van Reuth, Ref. 2) being based on a special type of disorder and an oversimplified model of an $A15$ compound.

In this paper a more rigorous theoretical treatment than previously available is given for the superconducting properties of a metal with a nonconstant $N(E)$. The results will be confined primarily to the effect on T_c and the effective mass. Theoretically, the effect upon T_c has been considered in different approximations by Horsch and Rietschel[6] (HR) and Ho, Cohen, Pickett[7] (HCP), with apparently conflicting conclusions: HR suggested that the structure in $N(E)$ is responsible for the high T_c found in many $A15$ compounds, while HCP contended that structure in $N(E)$ is ultimately of no importance in raising T_c. Here it is shown that both situations are consistent with a full theory. In addition it is found that, for metals in which the spectral function α^2F is accurately known, the dependence of T_c on (nonmagnetic) impurity concentration n_i and the altered temperature dependence of the mass enhancement $[1+\lambda(T)]$ due to disorder may provide information on the variation of $N(E)$ in the region of E_F. The change in $\lambda(T)$ has apparently not been anticipated.

II. ELIASHBERG GAP EQUATIONS

The Eliashberg gap equations assume a particularly simple form when expressed on the imaginary-frequency axis. The complex frequency-dependent normal $[Z(\omega)]$ and anomalous $[\phi(\omega)]$ self-energies collapse to functions defined at discrete imaginary frequencies $i\omega_n = i2\pi nk_BT$. Unfortunately, in this representation there is no straightforward intuitive interpretation, and numerical results which are obtained with relative ease are not easily analytically continuable to the real axis. Since one aim here is a clear understanding of the effects of a varying $N(E)$, the real-frequency expressions will be developed and interpreted.

The irreducible self-energy $\Sigma = \Sigma_{ph} + \Sigma_c + \Sigma_i$ is to be determined self-consistently from contributions from phonon, electron, and impurity scattering. The latter usually is not treated explicitly, as it has only the effect of changing the reference-band structure, i.e., changing $N(0)$. The self-energy is expressed as

$$\Sigma(\vec{k},\omega) = \omega[1-Z(\vec{k},\omega)]\tau_0 + \chi(\vec{k},\omega)\tau_3 + \phi(\vec{k},\omega)\tau_1 \ , \qquad (1)$$

where τ_1 and τ_3 are the Pauli matrices, and τ_0 is the 2×2 identity. The phonon contribution is given (on

the imaginary-frequency axis) by[8]

$$\Sigma_{ph}(\vec{k},i\omega_n) = -\beta^{-1}\sum_{\vec{k}'n'}|\bar{g}_{\vec{k}-\vec{k}'}|^2\tau_3 G(\vec{k}',i\omega_{n'}) \times \tau_3 D(\vec{k}-\vec{k}',i\omega_n - i\omega_{n'}) \quad (2)$$

where G, D are the electron, phonon Green's functions, respectively, and $\bar{g}$ is the screened electron-phonon matrix element. In this approximation for Σ_{ph} it is assumed that Migdal's theorem is valid, i.e., that other diagrams give a contribution to Σ_{ph} which is smaller than Eq. (2) by the factor $(k\theta_D/E_F)$, which is of the order of (electron mass/ion mass)$^{1/2}$ in ordinary systems. Although Migdal's analysis no longer guarantees that other diagrams always give a negligible result when the system contains very narrow bands, there should remain an important regime where the following treatment of Eq. (2) will give the dominant contribution to Σ_{ph}.

To convert the wave-vector (k) dependence to energy (E) dependence,[9] define for any function $C(k)$

$$C(E)N(E) = \sum_{\vec{k}} C(\vec{k})\delta(E - E_{\vec{k}}) \quad . \quad (3)$$

It will be assumed that the replacement

$$\sum_{\vec{k}} C_1(\vec{k})C_2(\vec{k})\delta(E - E_{\vec{k}}) = C_1(E)C_2(E)N(E) \quad (4)$$

is valid. This amounts to ignoring anisotropy and contributions which are off-diagonal in the (suppressed) band index,[10] but allows us to retain the energy dependence, which is the point of interest in this paper. This allows Eq. (2) to be written

$$\Sigma_{ph}(E,i\omega_n) = -\beta^{-1}\sum_{n'}\int dE' \frac{N(E')}{N(0)}\int d\Omega \frac{2\Omega\alpha^2F(E,E';\Omega)}{(i\omega_n - i\omega_{n'})^2 - \Omega^2}\tau_3 G(E',i\omega_{n'})\tau_3 \quad , \quad (5)$$

where

$$N(E)N(E')\alpha^2F(E,E';\Omega) = N(0)\sum_{\vec{k}\vec{k}'}|\bar{g}_{\vec{k}-\vec{k}'}|^2 B(\vec{k}-\vec{k}';\Omega)\delta(E - E_{\vec{k}})\delta(E' - E_{\vec{k}'}) \quad . \quad (6)$$

The phonon spectral density is denoted by B, and $\alpha^2F(0,0;\Omega)$ is the usual electron-phonon spectral function α^2F.

From Eq. (5) it is evident that the E dependence of Σ arises from the E dependence of α^2F and the analogous Coulomb and impurity functions, a fact noted by HR. In systems where $N(E)$ varies appreciably, very little is known about this energy dependence. For clarity we make the approximation

$$\alpha^2F(E,E';\Omega) = \alpha^2F(0,0;\Omega) = \alpha^2F(\Omega) \quad ;$$

it should be kept in mind that this approximation is untested. The full energy dependence can be retained in the development which follows, but doing so complicates the expressions considerably.

What must be evaluated then is

$$\eta(\omega) = -\frac{1}{\pi}\int_{-\infty}^{\infty} dE\, N(E)G(E,\omega) \quad . \quad (7)$$

This can be done formally by introducing the continuation $\tilde{N}(\xi)$ of $N(E)$ off the real axis

$$\tilde{N}(\xi) = \frac{1}{i\pi}\int_{-\infty}^{\infty} dE\, N(E)/(E-\xi) \quad . \quad (8)$$

$\tilde{N}$ is analytic in both the upper and lower half-planes of ξ but has a discontinuity $2N(E)$ along the real axis. This property allows η to be written

$$\eta(\omega) = -\frac{1}{2\pi}\int_C d\xi\, \tilde{N}(\xi)G(\xi,\omega) \quad , \quad (9)$$

where the contour C encircles the real axis in the negative sense at a distance $\delta = 0^+$ above and below, and ξ is substituted for E in G. The contour can be removed to infinity, leaving only the contributions from the poles of G at

$$\xi = \pm Q(\omega), \quad Q(\omega) = [(\omega Z)^2 - \phi^2]^{1/2} \quad .$$

χ will be ignored, as its effect can be shown to be negligible in all except the most pathological cases.

The result is

$$\eta(\omega) = i\{[(\omega Z\tau_0 + \phi\tau_1)/Q]\tilde{N}_-(Q) + \tau_3\tilde{N}_+(Q)\} \quad , \quad (10)$$

with

$$\tilde{N}_\pm(Q) = [\tilde{N}(Q) \pm \tilde{N}(-Q)]/2 \quad . \quad (11)$$

In the limit of a constant density of states, $\tilde{N}_-(Q) \to N(0)$ and $\tilde{N}_+(Q) \to 0$. In general $\mathrm{Re}\,\tilde{N}_-$ is the dominant term, as discussed below. The other contributions [$\mathrm{Im}\,\tilde{N}_-$, $\mathrm{Re}\,\tilde{N}_+$, and $\mathrm{Im}\,\tilde{N}_+$] are much smaller, since cancellation is present in their definition and, being oscillatory about zero as a function of ω' through $Q(\omega')$, contributions to the ω' integral will tend to cancel. These factors will be neglected relative to $\tilde{N}_-$.

III. CONSEQUENCES OF ENERGY DEPENDENCE

It is straightforward to apply the same approximations to the Coulomb and impurity (or more generally any static-disorder) contributions and continue the resulting expressions to the real axis.[8] The equation for the gap $\Delta = \phi/Z = \Delta_{ph} + \Delta_c + \Delta_i$ is most easily derived using $\Delta_{ph} = \phi_{ph} + (1-Z)_{ph}\Delta$, etc., with the

result at $T = T_c$ becoming

$$\Delta(\omega) = \int_0^{\omega_c} d\omega' \hat{N}(\omega') \left\{ \frac{\Delta(\omega)}{\omega} [\kappa_-(\omega, \omega') f(-\omega) + \kappa_-(\omega, -\omega') f(\omega')] - \frac{\Delta(\omega')}{\omega'} [\kappa_+(\omega, \omega') f(-\omega') - \kappa_-(\omega, -\omega') f(\omega')] - U_c \tanh \frac{\beta\omega'}{2} \right\}$$
$$+ i\pi \int_0^{\infty} d\Omega\, \alpha^2 F(\Omega) n(\Omega) \sum_{s=\pm 1}^{1} \left[\frac{\Delta(\omega_s)}{\omega_s} - \frac{\Delta(\omega)}{\omega} \right] \hat{N}(\omega_s) \quad . \tag{12}$$

Here $\omega_s = \omega + (-)^s \Omega + i\delta$, U_c is the Coulomb pseudopotential, ω_c is the cutoff frequency,

$$\kappa_\pm(\omega, \omega') = \int d\Omega\, \alpha^2 F(\Omega) [T(\omega' + \omega + \Omega) \pm T^*(\omega' - \omega - \Omega)] \quad , \tag{13}$$

$$N(0)\hat{N}(\omega) = \mathrm{Re}\, \hat{N}_-[Q(\omega)] = \frac{\Gamma(\omega)}{2\pi} \int_{-\infty}^{\infty} \frac{dE}{E^2 - \Gamma^2(\omega)} \{N[E - \omega + M(\omega)] + N[E - \omega - M(\omega)]\} \quad . \tag{14}$$

$f(n)$ denotes the fermion (boson) thermal occupation function, $T(x) = (x + i\delta)^{-1}$, and $M(\omega) - i\Gamma(\omega) = \omega[1 - Z(\omega)]$ denotes the normal-state self-energy at $T \geq T_c$. Within the approximations outlined above, the sole change in the gap equation (12) is the replacement of $N(0)$ by $N(0)\hat{N}(\omega)$, given by Eq. (14). Physically $\hat{N}(\omega)$ is a dimensionless function (as defined here) which reflects the average of the density of states at the quasiparticle energies $\pm[\omega - M(\omega)]$, broadened by the quasiparticle damping $\Gamma(\omega)$. It should be noted that, for strong electron-phonon coupling and a varying $N(E)$ near E_F, neglecting the temperature dependence of the energy shift M may not be justified.

The first effect [averaging over $\pm(\omega - M)$] was studied in some detail by HR, who neglected the smearing and made the replacement $N(0) \to \frac{1}{2}[N(\omega - M) + N(-\omega + M)]$. Using a model density of states with an $E^{-1/2}$ singularity, numerical solutions indicated an enhancement of T_c, over the value for constant $N(0)$, for Fermi-level placements $E_F \simeq \frac{1}{2}(1 + \lambda)\omega_D$ relative to the singularity, while other placements gave a reduction of T_c (ω_D is the Debye frequency). This behavior was interpreted as a reduction of the repulsive part of the interaction resulting from the interplay of the energy dependence of $N(E)$ and the frequency dependence of the interaction. Part of the effect no doubt is due to the fact that $\frac{1}{2}[N(\omega - M) + N(-\omega + M)] > N(0)$ for the important frequencies for this placement of E_F. In a sense the effective value of the density of states is *increased*. Since the other parameters are fixed, this results in an increase in T_c. The treatment of HR is valid if the damping $\Gamma(\omega)$ is negligible; this approximation is close to breaking down at $T = T_c$ in high-T_c $A15$ compounds.[7]

The second effect, the smearing of $N(E)$ resulting from quasiparticle damping, has been considered by HCP, who argue that for strong-coupling (and high T_c) superconductors, peaks in $N(E)$ become ineffective in raising T_c. A large λ leads to a large damping $\Gamma(\omega)$ and thus a greater smearing of $N(E)$. It was argued that for large enough λ, the peaks in $N(E)$ will be smeared out at $T = T_c$, implying that large values of $N(0)$ (resulting from sharp structure in the $T = 0$ band structure) are ultimately useless in reaching *very high* T_c. Roughly speaking, the broadening effect, with peaks heights decreasing in proportion to λ, will dominate over the increase in T_c, (ultimately) proportional[11] to $\lambda^{1/2}$. By assuming that E_F lies near the center of a very narrow peak in $N(E)$, it was estimated that T_c could be reduced by ~ 2–4 K by this effect in high-T_c (~ 25 K) $A15$ compounds. The averaging of $N(E)$ over a range $\pm\omega_D$ was neglected by HCP, but in fact tends to strengthen their conclusions if E_F lies precisely at a peak in $N(E)$.

The normal self-energy at $T \geq T_c$ is

$$M(\omega) - i\Gamma(\omega) = \int_0^{\infty} d\omega' \hat{N}(\omega') [\kappa_-(\omega, \omega') f(-\omega') + \kappa_-(\omega, -\omega') f(\omega')]$$
$$- i\pi \int_0^{\infty} d\Omega\, \alpha^2 F(\Omega) n(\Omega) [\hat{N}(\omega + \Omega) + \hat{N}(\omega - \Omega)] + (1 - Z)_c \omega - i n_i N(0) |V'|^2 \hat{N}(\omega) \quad . \tag{15}$$

The Coulomb contribution $(1 - Z)_c\omega$ arises from high-frequency processes and is unchanged by structure in $N(E)$; the impurity contribution is obtained by the replacement $N(0) \to N(0)\hat{N}(\omega)$ and a small real part has been ignored. The impurities, with (constant) matrix elements $|V'|^2$, have been treated in the second Born approximation[12] and in the small impurity concentration limit $n_i \ll 1$. It is this self-energy which must be inserted in Eqs. (14) and (12) when solving for T_c. The impurities do not enter *explicitly* into the gap Eq. (12), a manifestation of Anderson's theorem.[13] [This appears *not* to be true if

the energy dependence of $\alpha^2F(E,E';\Omega)$ is important, in which case the gap is renormalized by the impurities!] The impurities, however, do add to the damping, and hence contribute to the smearing of $N(E)$ in Eq. (12). This implies a variation of T_c with impurity content which in principle can be used to provide information on the variation of $N(E)$.

The temperature dependence of the effective mass $(m^*/m) = 1 + \lambda(T)$ is also altered by a variation in $N(E)$. The phonon contribution is given by

$$\lambda(T) = 2\int_0^\infty d\omega\, \hat{N}(\omega) \times \int_0^\infty d\Omega\, \alpha^2F(\Omega)\left[\frac{f(-\omega)}{(\Omega+\omega)^2} + \frac{f(\omega)}{(\Omega-\omega)^2}\right]$$

a less than obvious generalization of the usual expression.[14] This relation generalizes the known result[15] that strong impurity scattering does not destroy the electron-phonon mass enhancement. Impurity scattering *does* enter into $\hat{N}$ and may lead to either an increase or decrease in λ.

IV. DISCUSSION

In previous treatments[2,7] a dc relaxation time τ, usually taken from the resistivity, together with the uncertainty relation $\Delta E = \hbar/\tau$, has been used to smear an assumed $N(E)$. The resulting effective density of states $N_{\text{eff}}(E_F)$, together with the assumption $\Delta\lambda \propto \Delta N(E_F)$, was used to estimate changes in T_c. The form of Eq. (12), as well as the analysis of HR, suggests that this procedure will give a reasonable approximation only if the scale of the important structure in $N(E)$ is much larger than ω_D, as in the case of large disorder (concentrated alloys, large impurity concentrations, or radiation damage). The present treatment of course is only strictly valid for small amounts of disorder.

A quantitative study of the usefulness of these results in empirically inferring structure in $N(E)$ will be discussed elsewhere. A few observations should be made here. Superficially Eq. (16) appears to be the more promising approach, since the relation between $N(E)$ and the measured quantity is more direct, and $\lambda(T)$ can be extended (in principle) to temperatures $T > T_c$ where the energy smearing is larger. Although light effective masses have been seen up to $T \sim 100$ K in de Haas-van Alphen oscillations,[16] the heavy masses which should be associated with structure in $N(E)$ most likely will be observable only over a much more limited range of T. Another point to consider is whether a given experiment will actually measure the T-dependent mass enhancement as given by Eq. (16). For example, the usual T dependence[14] of λ [i.e., when $N(E)$ can be considered constant] is measured by cyclotron resonance[17] but apparently not by the de Haas-van Alphen effect.[17,18] More theoretical work is necessary to determine the appropriate experiments to measure $\lambda(T)$ of Eq. (16).

In the case of the dependence of T_c on disorder, the difficulty is less with the observation than with the interpretation of the effect. The variation of T_c with large amounts of static disorder has been known for some time.[19] However, for large static disorder the variation of $\alpha^2F(\Omega)$,[20] as well as the variation of $\hat{N}(\omega)$, is important in Eq. (12) which determines T_c. Of course α^2F *should* be determined by inverting Eq. (12) rather than the usual, simpler $N(E) \to N(0)$ equation; there is a difference even at $T = 0$.

A different approach to these equations has been taken by Lie and Carbotte,[21] who have evaluated $\delta T_c/\delta N(E)$ for a number of superconductors. Their results allow an estimation of the change in T_c due to a change in $N(E)$ more directly than the procedure outlined in this paper. However, since their results are numerical, so far they have not provided much insight into the physical mechanisms which affect T_c.

In this paper a microscopic formulation of the manner in which a varying density of states affects the superconducting properties of a metal has been developed and discussed. It is shown that the temperature dependence of the effective mass reflects the energy variation, as does the T_c dependence on impurity concentration. Finally, it is suggested that the energy spectrum near the Fermi level may be inferred from a careful inversion of experimental data on $T_c(n_i)$ and $\lambda(T)$.

Note added in proof. Although the chemical potential has not been exhibited explicitly in this paper, its variation with temperature can be important and must be included in Eqs. (12)–(15). This point often has been neglected in previous work.

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INFLUENCE OF ELECTRONIC STRUCTURE ON SUPERCONDUCTING PROPERTIES OF COMPLEX CRYSTALS: THEORY AND APPLICATION TO Nb_3Sn

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A thermodynamic theory valid for complex crystalline superconductors is applied to Nb_3Sn. It is shown how the structure of the Eliashberg equation and the solution is altered by density of states fine structure. One important implication is that the current method of inversion of tunneling data can be only approximate.

1. Introduction

The anomalous temperature (T) dependence of normal state properties of A15 compounds[1] have often been supposed to arise from a variation in the electronic state density $N(E)$ near the Fermi energy E_F on the scale of the maximum phonon frequency Ω. That such structure should occur in crystals containing several transition-metal atoms per cell can be argued quite generally,[2] and recently several band structure studies[3] of A15 compounds have verified structure on this scale. Unfortunately the usual theory of strongly coupled electron-phonon systems is based on a constant density of states (CDOS) assumption and is not directly applicable in the more general case.

Since the early weak-coupling models of the critical temperature T_c due to Barisic and collaborators[4], only a few attempts[5] at a general strong coupling theory have been made. However, each of these makes unnecessary approximations and/or uses pathological density of states models which obscure the underlying principles. Recently one of the authors[6] has generalized Eliashberg strong-coupling theory, subject only to the isotropic approximation. In this paper we report the application of this theory to Nb_3Sn. We point out several novel implications of the theory, emphasizing that superconducting properties, and in particular the gap function $\Delta(\omega)$, will be affected significantly by even non-pathological structure in $N(E)$.

2. Formalism

The electron self-energy $\Sigma_n = \Sigma(k, i\omega_n)$ in the Nambu-Matsubara formalism is given in standard notation[7] by

$$\Sigma_n = i\omega_n(1 - Z_n) + \chi_n\tau_3 + \phi_n\tau_1. \tag{1}$$

In Eliashberg's approach Σ is determined self-consistently in terms of the renormalized Green's function, given by

$$G_n^{-1} = i\omega_n - (E_k - \zeta)\tau_3 - \Sigma_n, \tag{2}$$

where ζ is the chemical potential and $\omega_n = (2n+1)\pi k_B T$. In the isotropic approximation the wavevector (k) dependence of Σ is averaged over[6], leaving only a weak dependence of $\Sigma(E)$ on the energy E which can be disregarded. For a general state density the generalized gap equation at T_c can be written

$$\sum_{m=0}^{N_c}\left\{\tilde{\lambda}(n-m) + \tilde{\lambda}(n+m) - 2\tilde{\mu}^* - \delta_{nm}(2n+1)\frac{Z_n}{N_n}\right\} N_m\tilde{\Delta}_m = 0, \tag{3}$$

where $\tilde{\Delta}_m = \Delta_m/\omega_m$, $\Delta_m = \phi_m/Z_m$ and N_c is the cutoff integer. The normal self-energies $\omega_n Z_n$ and χ_n are given by

$$Z_n = 1 + \frac{1}{2n+1}\sum_{m=0}^{N_c}[\tilde{\lambda}(n-m) - \tilde{\lambda}(n+m)]N_m, \tag{4}$$

$$\chi_n = -\pi k_B T\sum_{m=0}^{N_c}[\tilde{\lambda}(n-m) + \tilde{\lambda}(n+m) - 2\tilde{\mu}^*]P_m. \tag{5}$$

The state density enters through the even and odd averages

$$\begin{Bmatrix} N_n \\ P_n \end{Bmatrix} = \frac{1}{\pi}\int\begin{Bmatrix} Z_n|\omega_n| \\ E - \zeta + \chi_n \end{Bmatrix}\frac{N(E)dE}{(E-\zeta+\chi_n)^2 + \omega_n^2 Z_n^2}. \tag{6}$$

It is notable that the normally ubiquitous factor $N(E_F)$ *nowhere appears in the theory.* Accordingly the CDOS quantities λ and μ^*, which are formally proportional to $N(E_F)$, are replaced by the corresponding *intensive* quantities $\tilde{\lambda}$ and $\tilde{\mu}^*$ which depend on the character of the wavefunctions, but not on the density of states, in the vicinity of E_F. In the limit of a slowly varying $N(E)$, $N(E_F)\tilde{\lambda} \to \lambda$ and $N(E_F)\tilde{\mu}^* \to \mu^*$. In the equations above, $\tilde{\lambda}(j)$ is given by

$$\tilde{\lambda}(j) = 2\int\omega\tilde{\alpha}^2F(\omega)\,d\omega/(\omega^2 + [2\pi jT]^2) \tag{7}$$

in terms of an intensive electron-phonon spectral function $\tilde{\alpha}^2F$.

Equations (3)-(6) and the relation[8] determining $\zeta(T)$ form a system of coupled non-linear matrix equations which must be solved to find T_c and the self-energies. In the CDOS limit N_n approaches $N(E_F)$, P_n vanishes and the gap equation reduces to the well-known form.[9] We show below, however, that for a *realistic* $N(E)$, N_n and P_n differ greatly from these limits for Nb_3Sn (and no doubt for other compounds). Before discussing the numerical results it is helpful to understand the implications of this new behavior.

The eigenvector components of the gap Eq. (3) are given by $N_m\tilde{\Delta}_m$, rather than by $\tilde{\Delta}_m$ as in the CDOS theory. The kernel is altered from the usual theory only by the changes in the diagonal term Z_n/N_n, with changes in Z_n tending to be cancelled by the denominator. If for the moment the correction to the kernel is ignored, T_c and the corresponding eigenvector is unchanged but the gap function Δ_n is altered by a fraction $1/N_n$. This leads to the conclusion that the gap function $\Delta(\omega)$, which is given by the analytic continuation of Δ_n to the real axis, is fundamentally altered by a non-constant $N(E)$. It then becomes evident that $\Delta(\omega)$ and hence $\alpha^2F(\omega)$ *will be different from that inferred from tunneling data using the* CDOS *inversion procedure.* It will be shown below that T_c in fact *is* altered appreciably by the corrections to the kernel diagonal.

3. Application to Nb_3Sn

We have solved the coupled equations[10] for Nb_3Sn using α^2F and μ^* deduced by Wolf *et al.*[11] and the calculated $N(E)$

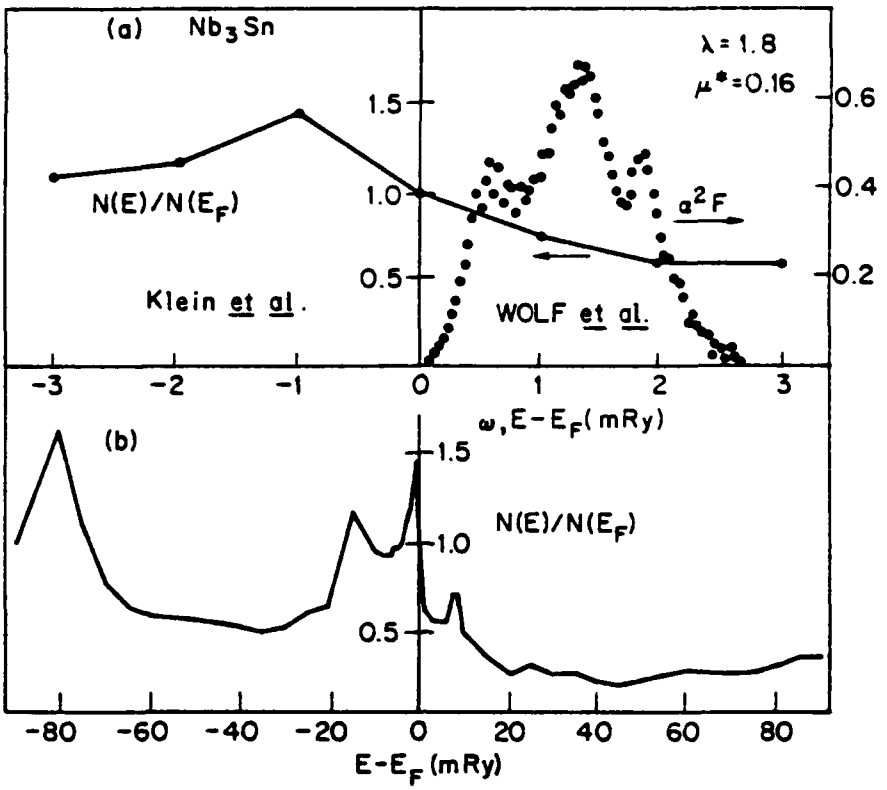

Fig. 1 — (a) The experimentally deduced spectral function $\alpha^2F(\omega)$ of Wolf *et al.* for Nb_3Sn (Ref. 11) for Nb_3Sn and the calculated function $N(E)$ of Klein *et al.* (Ref. 3) on the same scale as α^2F. (b) $N(E)$ shown on a larger scale to display its fine structure.

of Klein *et al.*[3] We make the somewhat arbitrary identification $\tilde{\alpha}^2F(\omega) = \alpha^2F(\omega)/N(E_F)$, and similarly for $\tilde{\mu}^*$, as the most reasonable choice available. The functions α^2F and $N(E)$ (the latter interpolated linearly between values on a 1 mRy grid) are shown in Figure 1 on the same scale to emphasize that, although N(E) has fine structure, it is utterly *non-pathological*, in contrast to those used previously[5] which had singularities and/or discontinuities. The general *behavior* we discuss is not critically dependent on the chosen functions $\alpha^2F(\omega)$ and $N(E)$. [It should be noted that we find that accurate numerical results cannot always be obtained if ζ and χ are disregarded. It is not appreciated generally that $\zeta(T)$ is strongly influenced by the electron-phonon interaction.]

In Figure 2a we show N_n and P_n for Nb_3Sn at $T_c = 18$ K. Clearly N_n differs greatly from $N(E_F)$ and P_n is strongly non-zero. Both vary rapidly for small n, reflecting the fine structure near E_F, before tending to saturate at larger values of n. As discussed above, the variation of N_n leads to corrections to Δ_n relative to the constant N_n approximation Δ_n^0. In Figure 2b this difference $\Delta_n - \Delta_n^0$ is displayed. The normalization $\Delta_0 = 1 = \Delta_0^0$ is used since the magnitude of Δ is arbitrary (infinitesmal) at T_c, but below T_c the *magnitude as well as the frequency dependence* of Δ will be altered. To learn the effect of $N(E)$ on the complex gap function $\Delta(\omega)$ the solution $\{\Delta_n\}$ of the (appropriately generalized[6]) equations at $T \leq T_c$ can be analytically continued to the real axis. Unfortunately we have found the Padé approximant approach[12] to be inadequate at $T_c = 18$ *K* due to having only 3-4 Matsubara frequencies in the region $\omega_n < \Omega$ where $\Delta(\omega)$ has sharp structure. However, Vidberg and Serene[12] have shown that this continuation to the *real axis can be performed reliably from* the first 100-200 values of Δ_n at low temperature. Since the shape of $\Delta(\omega, T)$ is nearly T-independent, the sensitivity of $\Delta(\omega)$ upon the values $\{\Delta_n\}$ found by Vidberg and Serene indicates important corrections to $\Delta(\omega)$ will result. Numerical solutions to Eqs. (3)-(6) at $T << T_c$ will be needed to study this effect more quantitatively.

Figure 2 indicates that corrections even from non-pathological DOS functions can be ~5% of $\Delta_0 \equiv \Delta(\omega = 0)$. However, to give a reliable picture of the structure in α^2F it is necessary[11] to invert tunneling data to a relative accuracy of $\sim 10^{-3}$. Here it is noteworthy that this has not been achieved in A15 compounds, although heretofore this deficiency has been ascribed solely to difficulties in preparing ideal junctions.

To illustrate the effect of DOS structure upon T_c we allow the assumed Fermi level E_F to vary over a range of 5 mRy near the calculated value $E_{F,o}$ of Klein *et al.* In Figure 3 it can be seen that T_c resulting from the CDOS theory, denoted T_c^o, varies from 10 to 26 K within 3 mRy, whereas T_c from Eq. (3) varies only from 13 to 18 K. Not least among the implications of this drastic smoothing of T_c is that band theory need not be absolutely accurate on a 1 mRy scale to provide reasonable values of T_c; conversely, T_c contains less straightforward information about $N(E)$ than usually assumed.

Currently there is considerable interest in obtaining approximate T_c values by using an appropriate average over $N(E)$ in the CDOS theory in the spirit of Nettel and Thomas.[5] Equation (3) suggests an average N_{eff} given by

$$N_{eff} = \sum_n N_n \bar{\Delta}_n \Big/ \sum_j \bar{\Delta}_j. \qquad (8)$$

The resulting critical temperature T_c^{eff} also is shown in Figure 3. Although T_c^{eff} is too large by a nearly constant amount (~1.5K), it reflects the trends in T_c quite well. Improvements upon this result will be investigated in a subsequent paper.

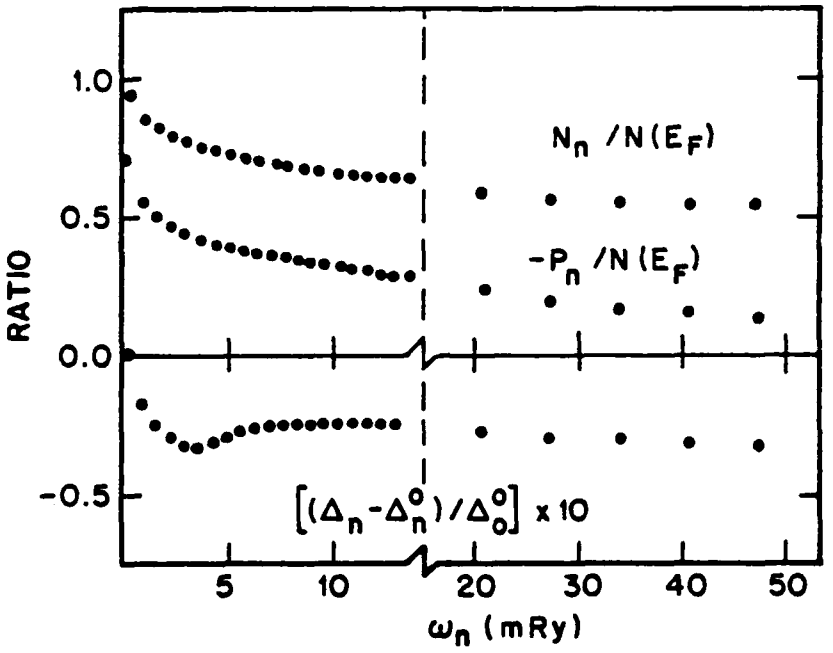

Fig. 2 — The even and odd density of states averages N_n and P_n respectively (for the calculated value $T_c = 16.6$ K for Nb_3Sn) plotted versus Matsubara frequency ω_n, and the correction to the gap function Δ_n due to the density of states shown in Figure 1. Note the change of scale at $n = 20$, above which only every tenth value is shown.

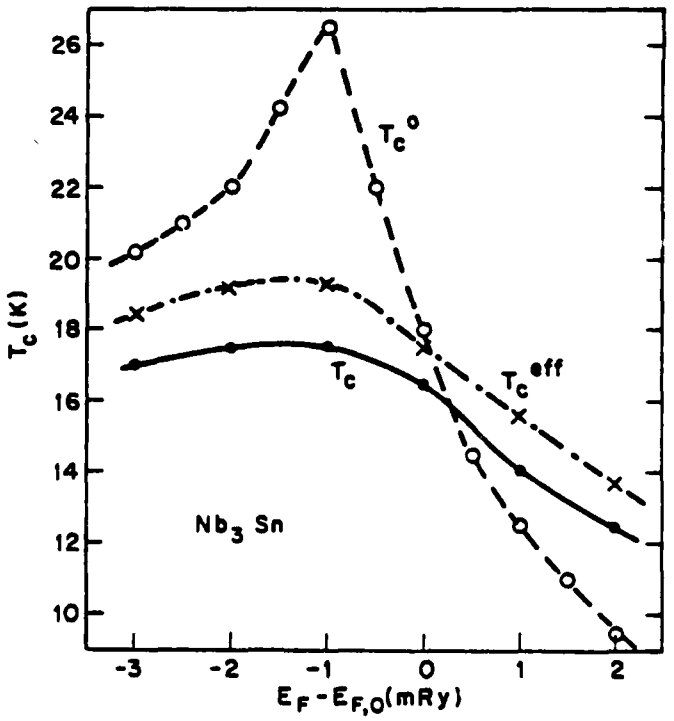

Fig. 3 — The behavior of the critical temperature versus the assumed position of E_F. Results of the general theory are denoted by T_c, those of the CDOS theory by T_c^0 and those of the average value of $N(E)$ suggested in the text by T_c^{eff}.

4. Discussion

We have shown that when fine structure in the electronic spectrum exists near E_F it is necessary to take it into account in the inversion of the tunneling data to obtain accurate values of Δ and $\tilde{\alpha}^2F$ as well as T_c. Our use in the calculations of $\tilde{\alpha}^2F(\omega) \propto \alpha^2F(\omega)$, with the latter deduced from the CDOS theory, was an expediency which will not be satisfied by a self-consistently determined $\tilde{\alpha}^2F$.

It should be emphasized that the present calculations have disregarded the disorder which is present in all Nb_3Sn samples. It is well known that disorder broadening of the DOS will tend to smooth fine structure and thereby reduce the effects discussed in this paper. The theory presented here recently has been extended to include the effects of disorder. Preliminary work indicates that for a resistivity ratio $\rho(300\ K)/\rho(20\ K) = 10$ (a "good" Nb_3Sn sample), the correction $(\Delta_n - \Delta_n^{(1)})/\Delta_n^{(1)}$ in Figure 2 is reduced by roughly a factor of 2. This should leave observable consequences of fine structure, which for more highly disordered material will become progressively weaker. As an experimental test of this effect, high quality Nb_3Sn tunnel junctions could be lightly irradiated thereby increasing the disorder in the Nb_3Sn, and the observed tunneling DOS monitored for alterations. A full discussion of the theory and further numerical results will be published elsewhere.[6]

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PARAMETER-FREE CALCULATION OF THE ENHANCED SPIN SUSCEPTIBILITY OF Nb_3Sn INCLUDING ELECTRON-PHONON EFFECTS

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A parameter-free calculation of the spin susceptibility $\chi_{sp}(T)$ of Nb_3Sn, which includes static and dynamic disorder as well as exchange-correlation enhancement, is presented. It is found that χ_{sp} is only 15% of the measured susceptibility, and its small temperature dependence cannot account for the experimental findings.

It is a well established fact that the anomalous variation[1] of the susceptibility $\chi(T)$ below room temperature in V- and Nb-based A15 compounds is directly correlated with the superconducting transition temperature T_c: $d \log \chi/dT$ is largest for the high T_c compounds. Attempts to explain the behavior of $\chi(T)$ have focussed on the spin susceptibility χ_{sp}, which is presumed to vary due to thermal repopulation of a narrow peak in the density of states N(E) near the Fermi level E_F. In this paper I present the results of a parameter-free calculation of χ_{sp} for Nb_3Sn which includes (1) the effects of both static and dynamic disorder and (2) electron-electron interactions through an ab initio Stoner enhancement. It is found that χ_{sp} is only 15% of the measured susceptibility,[2] and that $d\chi_{sp}/dT$ accounts for only 15% of the measured temperature variation.

A theory for the electron self-energy Σ has recently been developed[3] which accounts for cases where N(E) varies on the scale of a typical phonon frequency, such as often occurs in A15 compounds. Both defects and phonons are included in a self-consistent way. Calculation of Σ requires solving several nonlinear coupled matrix equations involving N(E) and the Green's function G. The input to the calculation of Σ is (1) the α^2F function derived from proximity effect tunneling on Nb_3Sn by Wolf et al.[4] which describes the electron-phonon interaction (EPI), (2) the N(E) function calculated for Nb_3Sn by Klein et al.[5] and (3) a Lorentzian defect broadening corresponding to 10 $\mu\Omega$cm of residual resistivity, typical of the best samples of Nb_3Sn.

The quasiparticle density of states is evaluated from the relation

$$n(\omega,T) = -\pi^{-1} \mathrm{Im}\ \mathrm{Tr}G(\omega), \qquad (1)$$

and therefore includes the effects of static and dynamic disorder. Σ is actually evaluated on the imaginary frequency axis, leading to the matrix equations mentioned above, and TrG is analytically continued to the real axis. From $\bar{n}$ the unenhanced spin susceptibility χ_{sp}^o is given by

$$\chi_{sp}^o(T) = \mu_B^2 \int d\omega \left|\frac{\partial f(\omega-\zeta)}{\partial \omega}\right| n(\omega,T) = \mu_B^2 \bar{n}(\zeta) \qquad (2)$$

where f denotes the Fermi distribution. A crucial feature of the present calculation is that the chemical potential ζ is retained explicitly.

Liu et al.[6] have shown that, with local density (LD) theory, exchange and correlation enhancement of χ_{sp}^o may be included at finite T through the Stoner-like relation

$$\chi_{sp}(T) = \mu_B^2 \bar{n}(\zeta) / \{1 - \bar{I}(\zeta)\bar{n}(\zeta)\}, \qquad (3)$$

where $\bar{I}(\zeta)$ is the thermal average around ζ of the LD Stoner parameter I, which can be evaluated from the band calculations of Klein et al.[5] Here it will be assumed that Eq. (3) holds when $\bar{n}(\zeta)$ includes the effects of disorder, a case which was not considered by Liu et al.

The calculated values of χ_{sp}^o and χ_{sp} are compared in Fig. 1 with the measured total susceptibility of Reywald et al.[2] Although $d \log \chi_{sp}/dT = -1 \times 10^{-3} K^{-1}$ is similar to the measured value of $d \log \chi/dT$, χ_{sp} accounts for only about 15% of χ. This last result is surprising,

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since Klein et al.[7] were able to fit $\chi(T)$ with only two parameters, $\bar{\Gamma}$ and a T-independent ("orbital") contribution $\bar{\chi}$, by ignoring disorder effects and including only thermal redistribution. The differences between this fit and the present calculation arise in two ways. First, the calculated value (only weakly T-dependent) of $\bar{\Gamma}(\zeta) = 2.3$ mRy is only about half the fitted value of 4.4 mRy. Both the Stoner enhancement $(1-\bar{\Gamma}\bar{n})^{-1}$ and its temperature variation are reduced (relative to the fit value) by more than a factor of two. Secondly, including disorder reduces $\bar{n}(\zeta)$, and thereby reduces χ_{sp}^{o} as well as further reducing the enhancement factor.

With regard to this second point, it is notable that $\bar{n}(\zeta)$ is reduced more by the variation of $\zeta(T)$ than by the explicit defect broadening. The effect of including broadening corresponding to 10 $\mu\Omega$ cm of residual resistivity is to displace $\zeta(0)$ upward by 2 mRy toward a region of lower N(E), and this effect alone leads to a value of $\bar{n}(\zeta)$ which is 85% of $N(E_F)$. Moreover, merely turning on the EPI further shifts electronic spectral weight out of the peak, shifting ζ upward by another 3 mRy (at 25K, the lowest temperature considered here) and resulting in a further decrease of $\bar{n}(\zeta)$ to 70% of $N(E_F)$. At 200K, the highest temperature considered thus far, I find ζ=10.5 mRy (relative to E_F) and $\bar{n}(\zeta)$=0.62 $N(E_F)$. The temperature variation of χ_{sp} shown in Fig. 1 results from this nearly linear decrease in $\bar{n}(\zeta)$ with temperature.

The results presented in Fig. 1 indicate that χ_{sp} cannot account for experimental data for Nb_3Sn. It should be noted that these results are not sensitive to details of the density of states which was used (the very fine structure is smoothed out by the disorder) as is the case when disorder is not included, and only the strength of α^2F (λ=1.8) is important in determining $\zeta(T)$ and $\bar{n}(\zeta)$. It now appears that the orbital susceptibility may be larger than χ_{sp} and may even show considerable temperature variation. A more detailed discussion of all aspects of this study will be published elsewhere.

The author wishes to acknowledge the use of unpublished results of the Nb_3Sn calculations (Ref. 5) as well as the discussions with D.A. Papaconstantopoulos and C.M. Soukoulis about disorder broadening and with B.M. Klein about the susceptibility fit described in Ref. 7.

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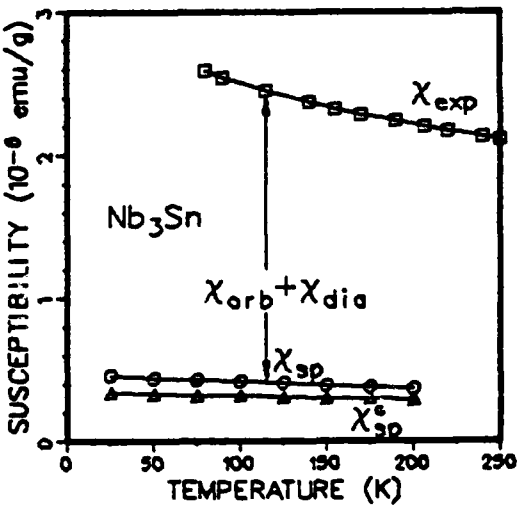

Figure 1. Susceptibility versus temperature as discussed in the text. χ_{exp} is from Ref. 2.

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Generalization of the theory of the electron-phonon interaction: Thermodynamic formulation of superconducting- and normal-state properties

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A thermodynamic formulation for the electron self-energy is given which is applicable when the electronic spectrum possesses structure on the scale of phonon frequencies, provided only that the ratio of phonon phase velocity to electron Fermi velocity is small. Electron-phonon, Coulomb, and electron-defect interactions are included on an equal footing and it is shown that their different frequency dependencies lead to specific effects on the Eliashberg self-energy: (a) The Coulomb interaction contributes nothing of essence to the normal-state self-energy (in this isotropic approximation) but retains its usual depairing effect upon the superconducting gap function, (b) defects affect superconducting properties primarily through a broadening of the electronic spectrum, and (c) phonons contribute a thermal shift and broadening as well as the mass enhancement. A generalization to *intensive* electron-phonon, electron-electron, and electron-defect interaction constants is necessary to redevelop an intuition into the effects of these interactions. The change in the structure of the Eliashberg equation due to a nonconstant density of states (DOS) and the consequent interplay between static and thermal disorder is analyzed in detail, with a central feature being the change in frequency dependence of the self-energy compared to a constant DOS solution. The effect of DOS structure on the superconducting transition temperature T_c, which is manifested in the defect dependence of T_c, is analyzed in detail. Further it is proposed that an extension of the self-consistent Eliashberg approach be extended above T_c to determine the normal-state self-energy and thereby the electronic contribution to thermodynamic quantities. Phonon broadening is shown to affect the spin susceptibility at finite temperature. Reinterpretation of several of the anomalous properties of $A15$ compounds in terms of the present theory is suggested. Several aspects of the theory are compared to experimental data for Nb_3Sn.

I. INTRODUCTION

Deeply ingrained in the formal theory of the interacting electron-phonon (e-ph) system in metals are two simplifying approximations. The first is an extension of the adiabatic, or Born-Oppenheimer approximation[1] in which the light electrons are considered to respond instantaneously to the heavy ions (of mass M). Central to the theory of e-ph systems is Migdal's theorem,[2] which demonstrates that nonadiabatic effects can be obtained accurately by low-order Feynman-Dyson perturbation theory, to lowest order in an expansion parameter of the order of $(m/M)^{1/2} \ll 1$. The second simplification is the assumption of a constant density of states (CDOS) over a region $\pm\bar{\Omega}$ around the Fermi energy E_F, where $\bar{\Omega}$ is a few times of the mean phonon frequency. This approximation allows the DOS function $N(E)$ to be approximated by $N(E_F)$ in certain energy integrals. The two approximations in fact are related, and it often seems to be assumed that Midgal's theorem is inapplicable if $N(E)$ is not constant [to within $(m/M)^{1/2}$] over a range $\pm\bar{\Omega}$ around E_F. As will be shown in this paper, however, there exists an important regime within which the CDOS approximation may be relaxed in a straightforward manner while retaining Migdal's simplification. The resulting generalizations of the CDOS expressions often are not intuitively obvious, and the consequences involve a reinterpretation of many of the properties of this class of materials.

That structure in the DOS on the scale of $\bar{\Omega}$ should be expected in crystals containing several transition-metal atoms per unit cell can be deduced from general considerations.[3] Elemental transition metals are known to have peak structure in their DOS which may be only a few tenths of an eV wide. A compound with (for example) ten atoms per unit cell will have 10 times the number of bands in the same overall bandwidth, leading to structure on the order of hundredths of an eV.

Recent band-structure calculations[4,5] on $A15$ compounds (eight atoms per unit cell) indeed have verified structure on this scale. DOS structure can be important even in elemental metals if the Fermi level E_F lies near a van Hove singularity, such as occurs in Pd and Pt.

The most intriguing consequence of the e-ph interaction, both theoretically and technologically, is superconductivity, and it has not been overlooked that the superconducting transition temperature T_c might be affected by DOS fine structure. An early study of $A15$ compounds was carried out by Barisič and co-workers[6] in the weak-coupling limit, where it was noted that the DOS within a region $\pm\bar{\Omega}$ around E_F contributes in the determination of T_c. Cohen, Cody, and Vieland[7] applied a strong-coupling version of the Koonce-Cohen[8] formalism to investigate the effect of model $A15$ DOS functions upon T_c.

In a model solution of the Eliashberg equation with non-CDOS effects included approximately Nettel and Thomas[9] suggested an average DOS given by

$$\bar{N}_{\rm NT}=\frac{1}{2}\int_{T_c}^{\Omega_c}\frac{d\omega}{\omega Z(\omega)} \times[N(\omega Z)+N(-\omega Z)]/\ln(\Omega_c/T_c) \tag{1.1}$$

as being most relevant in determining T_c. Here $Z(\omega)$ is the strong-coupling renormalization (real part), $\Omega_c\approx\bar{\Omega}$ is a cutoff frequency, and the DOS function will be taken with origin at E_F throughout this paper. It was evident to Nettel and Thomas that there is great utility in identifying, whenever possible, an effective value of $N(E_F)$ for use in the CDOS version of Eliashberg theory rather than having to deal always with the full energy dependence explicitly. This simplication will be explored further in this paper.

Horsch and Rietschel[10] obtained numerical solutions to the Eliashberg equation in the small $kT_c/\bar{\Omega}$ limit where the imaginary part of the self-energy can be neglected. They found an enhancement of T_c relative to the CDOS value T_c^0 for placements of a square root DOS peak near $E_F-\bar{\Omega}Z(0)$. This was interpreted as a reduction of the repulsive part of the e-ph interaction due to DOS variation. It could equally well be considered as an enhancement of the attractive part of the interaction (which occurs at $\omega<\bar{\Omega}$), with an approximate value of the enhancement given by $\bar{N}_{\rm NT}$.

A more general approach was taken by Lie and Carbotte,[11] who calculated a functional derivative $\delta T_c/\delta N(E)$ for several superconductors. Its shape was found to be quite insensitive to the metal considered, having a maximum at $E=E_F$, decreasing to half maximum at

$$|E-E_F|\approx 5-10T_c$$

and becoming negative (but remaining very small) above

$$|E-E_F|\approx 50-70T_c\ .$$

This (linear) approach leads to an average DOS

$$\bar{N}_{\rm LC}=\int dE\frac{\delta T_c}{\delta N(E)}N(E)\Big/\frac{dT_c}{dN(E_F)} \tag{1.2}$$

which is useful for estimating T_c from a CDOS theory. In Eq. (1.2) $dT_c/dN(E_F)$ is the integral over $\delta T_c/\delta N(E)$, and T_c is given by

$$T_c=T_c^0+[\bar{N}_{\rm LC}-N(E_F)]\frac{dT_c}{dN(E_F)}\ . \tag{1.3}$$

Written in this form $\bar{N}_{\rm LC}$ clearly has an interpretation as an effective value of $N(E_F)$. Since the important contributions to the integral in Eq. (1.2) come from the region $|E-E_F|<10T_c\sim\Omega_c$ (for strong coupling superconductors), for nonpathological DOS functions the averages $\bar{N}_{\rm NT}$ and $\bar{N}_{\rm LC}$ should be similar.

Whereas an average over the DOS may be sufficient for understanding T_c, for many properties of interest (e.g., the T dependence of the spin susceptibility χ_s) no such simplification will be possible. In this paper a general approach for obtaining the electronic self-energy, and thereby the thermodynamic properties, is described. Both static and dynamic disorder are included in a straightforward generalization[12] of the usual Eliashberg approach, and it is shown that each type of disorder contributes to the shift in chemical potential as well as to a shift and renormalization of the electronic spectrum. Although the emphasis here will be focused on the superconducting state, implications for normal-state properties also will be discussed. A preliminary report[13] of the application of this theory to Nb_3Sn has been published elsewhere.

The plan of the paper is as follows. Section II is devoted to the description of the system of interacting electrons, phonons, and defects which will be studied, and the approximations leading to our expression for the electronic self-energy are discussed and justified. The treatment of the energy dependence in the Eliashberg equation is given in Sec. III, where it is argued that the band-energy

dependence of the self-energy should be negligible in most cases. This leads in turn to a less formidable numerical procedure for solving for the self-energy. In Sec. IV the generalized Eliashberg system of equations is presented and the alterations arising from DOS structure are discussed. As a byproduct of retaining the band-energy dependence of the e-ph interaction in the equations, a better understanding of the Coulomb pseudopotential and of the role of impurity scattering is obtained. A discussion of several aspects of the theory at T_c is presented in Sec. V. In Sec. VI the spin susceptibility is discussed in terms of a self-energy determined from an Eliashberg-type equation at $T > T_c$. Unlike previous uses of Eliashberg-type equations,[14] which of necessity require an infinite summation of diagrams to describe appropriately the appearance of a gap (superconducting or spin-density-wave) in the spectrum, this novel application accomplishes more easily what could be accomplished (at least approximately) in some finite order of perturbation theory. It is suggested that this approach may be fruitful for studying other thermodynamic properties. Indeed, there has been little concern over non-CDOS corrections above T_c with the exception of the T dependence of χ_{sp} and the elastic constants, both of which show anomalous behavior in high-T_c $A15$ compounds.

II. GENERALIZATION OF THE ELIASHBERG SELF-ENERGY

The usual treatment of Eliashberg theory on the imaginary frequency axis is clearly set forward in the literature.[15] We will provide only the background necessary to clarify the generalizations we propose and the approximations which remain. The system we consider is described by the Hamiltonian

$$H = H_e + H_{ph} + H_{e\text{-}e} + H_{e\text{-}ph} + H_{imp} , \tag{2.1a}$$

where

$$H_e = \sum_k E_k \Psi_k^\dagger \tau_3 \Psi_k , \tag{2.1b}$$

$$H_{ph} = \sum_{Q\nu} \Omega_{Q\nu} b_{Q\nu}^\dagger b_{Q\nu} , \tag{2.1c}$$

$$H_{e\text{-}e} = \frac{1}{2} \sum_{kk'q} V(k,k';q) \Psi_{k-q}^\dagger \tau_3 \times \Psi_k \Psi_{k'+q}^\dagger \tau_3 \Psi_{k'} , \tag{2.1d}$$

$$H_{e\text{-}ph} = \sum_{k,k',\nu} g_{kk'\nu} (b_{k-k',\nu}^\dagger + b_{k'-k,\nu}) \times \Psi_{k'}^\dagger \tau_3 \Psi_k + \mathcal{T} , \tag{2.1e}$$

$$H_{imp} = \sum_{kk'} \sum_{j=1}^{n_i} V_{kk'}^{imp}(R_j) \Psi_k^\dagger \tau_3 \Psi_{k'} , \tag{2.1f}$$

where $\mathcal{T}$ denotes a second-order term. In the Nambu scheme the spin index is eliminated in favor of the two-component field operator

$$\Psi_k = \begin{pmatrix} c_{k\uparrow} \\ c_{-k\downarrow}^\dagger \end{pmatrix} \tag{2.2}$$

in terms of the electron annihilation operator $c_{k\sigma}$. The Pauli matrices are denoted by τ_1, τ_2, and τ_3. Electron-band and phonon-mode indices will not be exhibited explicitly except where necessary.

In this form of the Hamiltonian Ψ describes *band electrons*, for which the electron-static lattice and electron-electron interactions have been included in a mean-field sense. For the electron-lattice interaction the remaining coupling is given, to second order in the ion displacement, by the electron-phonon Hamiltonian $H_{e\text{-}ph}$. The second-order term, which has not been displayed explicitly, is required to keep the theory translationally invariant.[16] The residual Coulomb interaction between band electrons is assumed to be representable in the usual four-body form and is denoted by V in the electron-electron Hamiltonian $H_{e\text{-}e}$. The effect of this term on superconducting behavior is not understood in detail but fortunately an approximate treatment in terms of an empirical "Coulomb pseudopotential" (see below) seems sufficient for most purposes.

The "impurity" term H_{imp} represents[17] n_i identical, randomly distributed imperfections centered at positions R_j. The scattering potential V^{imp} represents the *difference* between the potential in the region of the imperfection and the perfect-crystal potential. The phonon Hamiltonian H_{ph} is expressed in terms of bare phonons (with creation operator $b_{Q\nu}^\dagger$) of frequency $\Omega_{Q\nu}$ which are dressed to the observed frequency $\omega_{Q\nu}$ by the band-electron polarization as described for example by Migdal.[2] In this paper we will *not* consider the effect of lattice imperfections on either the phonon spectrum or the electron-phonon coupling g, although the effect may become large for highly disordered materials.

The electron thermodynamic Green's funotion is given by

$$G(k,i\omega_n)^{-1}=i\omega_n-(E_k-\zeta)\tau_3-\Sigma(k,i\omega_n)\ , \tag{2.3}$$

where $\omega_n=(2n+1)\pi T$ and the self-energy Σ conventionally is given by[15]

$$\Sigma(k,i\omega_n)=i\omega_n[1-Z(k,i\omega_n)]+\chi(k,i\omega_n)\tau_3+\phi(k,i\omega_n)\tau_1\ . \tag{2.4}$$

For bulk superconducting properties the τ_2 term in Σ is proportional to ϕ and is assumed to be eliminated by the choice of phase. Two points should be noted here. First, the chemical potential ζ, which is determined by the relation

$$N_e=T\sum_{k,n}\mathrm{Tr}G(k,i\omega_n)e^{i\omega_n\epsilon} \tag{2.5}$$

in terms of the number of electrons N_e (ϵ is a positive infinitesimal quantity), will be retained explicitly. Second, we also retain the energy shift χ (not to be confused with the susceptibility) and find that although it does not reduce to a trivial shift in the chemical potential, its effects are usually of a secondary nature.

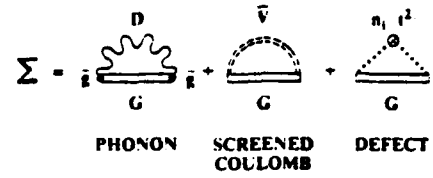

FIG. 1. Proposed phonon, Coulomb, and defect contributions to the electron self-energy Σ. The double lines indicate the renormalized Green's function $G(\Sigma)$, giving a self-consistent, infinite order relation for Σ.

The Eliashberg equation for the self-energy, represented diagramatically in Fig. 1 is[15]

$$\Sigma(k,i\omega_n)=-T\sum_{k',n'}\tau_3G(k',i\omega_{n'})\tau_3\left[\sum_\nu|\bar{g}_{kk'\nu}|^2D_\nu(k-k',i\omega_n-i\omega_{n'})+\bar{V}(k,k';i\omega_n-i\omega_{n'})+[n_i|t(k,k',i\omega_n)|^2/T]\delta_{nn'}\right]. \tag{2.6}$$

The first term results from coupling to phonon branch ν with renormalized phonon Green's function D_ν. The second term arises from the dynamically screened and Coulomb-vertex-corrected electron-electron interaction $\bar{V}$, which is discussed further below. The third term, which is usually not included, results from neglecting *correlated* multiple scattering between distinct static defects, but includes multiple scattering from a single defect by means of the t matrix[17] t. This treatment strictly applies to the dilute limit; however, the transport theory which results usually is found to be valid to rather large defect concentrations.

In writing the phonon contribution to Σ as in Eq. (6), Migdal's theorem[2] has been invoked. In its usual form this theorem states that, to within a quantity of order $(m/M)^{1/2}$, the electron-phonon vertex function $\Gamma_{e\text{-ph}}$ can be taken as unity (for the purpose of calculating the electron self-energy). Within simple metal language an equivalent expansion parameter is $\bar{\Omega}/E_f$. This had led to speculation that Migdal's theorem may not hold for systems which have DOS structure, and in some sense an effective degeneracy temperature (E_F) on the scale of $\bar{\Omega}$. As Scalapino[15(c)] has emphasized, however, the validity of the approximation rests on a small value of the ratio of phonon phase velocity ω_Q/Q to electron group velocity v_k. Even for $A15$ compounds with large $N(E_f)$ and low electron velocities the ratio of these quantities averaged over the Brillouin zone is $(2-3)\times10^{-2}$ (e.g.,[18] $\langle\omega_Q/Q\rangle\sim5\times10^5$ cm/sec and[5] $\langle v_k\rangle\simeq\langle v_k^2\rangle^{1/2}\equiv v_F=2\times10^7$ cm/sec for Nb_3Sn). The approximation $\Gamma_{e\text{-ph}}=1$ can break down in the *immediate* vicinity of a van Hove singularity $v_k=0$, but such a small number of electrons within $|E_k-E_f|<\bar{\Omega}$ have $v_k\lesssim\omega_Q/Q$ that the contribution to the Brillouin-zone sum in Eq. (2.6) will be negligible.

Recently Drozhov[19] has provided more insight into this problem. The situation Drozhov studied is that in which an M_1 van Hove critical point falls at E_F, which is one situation for which $v_k\lesssim\omega_Q/Q$. It was found that so much dispersion is introduced into the electronic states by the e-ph interaction that the corresponding quasiparticles are for the most part removed from the region of the critical point (and, of course, are highly damped). The quasiparticle velocities tend to diverge at the critical point. Thus, if the fully renormalized Green's function, rather than its bare counterpart, is used in Eq. (2.6) (as is done in Eliashberg theory and as it is shown in later sections must also be done in the normal state), it may well be the case that the criterion $V_k\geq\omega_Q/Q$

in terms of *renormalized velocities* V_k (if they can be defined) is satisfied even near critical points $v_k \to 0$ where Migdal's theorem as stated is unproven. Assuming this to be the case, the only remaining difficulty is with optic modes, for which near zone-center phase velocities ω_Q/Q diverge. It appears that a small enough number of modes are involved that the Brillouin-zone sum for Σ is unaffected.

Migdal[2] also demonstrated (for the normal state at $T=0$) that the renormalized Green's function G appearing on the right-hand side of Eq. (2.6) can be replaced, in the CDOS system he considered, by the unrenormalized Green's function, thus allowing a formal solution for low frequencies. No corresponding simplification is possible when variation in $N(E)$ is not negligible, as observed by Eliashberg[15(h)] for the superconducting state in which the opening of the gap gives a sharply varying density of quasiparticle states. A central point of this paper is that, when the energy variation of $N(E)$ occurs on the scale of phonon energies, Σ must be determined self-consistently from Eqs. (2.5) and (2.6) for the normal state as well.

The three contributions to Σ in Eq. (2.6) differ fundamentally in their frequency dependence. The phonon Green's function $D_\nu(i\omega_n)$ has its important frequency variation for $|\omega_n| \lesssim \bar{\Omega}$ and decreases as ω_n^{-2} for $|\omega_n| \gg \bar{\Omega}$. The Coulomb interaction $\bar{V}(i\omega_n)$ varies only on the scale of the electronic plasma frequency (peak in the energy-loss function) $\omega_{pl} \sim 10$ eV. The impurity contribution is energy conserving, with $(1/T)\delta_{n,n'}$ in Eq. (2.6) representing the δ function $\delta(\omega-\omega')$ in the thermodynamic formulation. For the phonon and impurity contributions the sum over $|\omega_{n'}|$ in Eq. (2.6) can be truncated at a cutoff frequency $\omega_c \sim 5-10\bar{\Omega}$ with negligible loss of accuracy. The practical necessity of using a minimal frequency range for solving for Σ has prompted the folding down of the Coulomb potential $\bar{V}$ into a pseudopotential $\bar{U}$ as described in detail elsewhere.[15,20] The treatment is generalized somewhat in Appendix A, with the result

$$1/\bar{U} = 1/\bar{V} + \bar{N}(\omega_{pl})\ln(\omega_{pl}/\omega_c) . \tag{2.7}$$

This relation, and the effective DOS $\bar{N}(\omega_{pl})$, will be discussed further in Sec. IV A. Using this pseudopotential and utilizing the evenness[15(b)] in frequency ω_n of the functions Z, χ, and ϕ, Eq. (2.6) can be reduced to an $N_c \times N_c$ matrix equation with $(2N_c-1)\pi T = \omega_c$ (i.e., $n = 0, 1, \ldots, N_c-1$).

III. TREATMENT OF THE ENERGY DEPENDENCE

In its most general form the Eliashberg equation is extremely difficult to solve even if the kernel in large parentheses in Eq. (2.6) is known. Besides the four-dimensional frequency-momentum variables which are summed over, G and Σ also are matrices in band index,[21] although this fact is nearly always ignored. To date little of a quantitative nature is known about the importance of off-diagonal (in band index) contributions to G; however, cases where these corrections seem to be necessary have been extremely rare (but see Chakraborty and Allen[21]). In the present paper all such "band-mixing" effects will be neglected. We will concentrate on including the energy dependence of the band density of states within an isotropic, band-diagonal approximation.

The isotropic average $A(E)$ of a wave-vector-dependent quantity $A(k)$ is defined by

$$A(E) = \sum_k A(k)\hat{\delta}(E-E_k) , \tag{3.1}$$

where to simplify notation we have introduced a dimensionless, normalized averaging function given by

$$\hat{\delta}(E-\epsilon) = \delta(E-\epsilon)/N(E) .$$

A further approximation necessary to reduce Eq. (2.6) is

$$\sum_{kk'} G(k',i\omega_{n'})B(k,k';i\omega_n - i\omega_{n'})\hat{\delta}(E-E_k)\hat{\delta}(E'-E_{k'}) = G(E',i\omega_{n'})B(E,E';i\omega_n - i\omega_{n'}) , \tag{3.2}$$

where[22]

$$G(E,i\omega_n)^{-1} \equiv i\omega_n - (E-\zeta)\tau_3 - \Sigma(E,i\omega_n) . \tag{3.3}$$

$B(k,k';i\omega_n - i\omega_{n'})$ is any of the three kernels in Eq. (2.6) and $B(E,E';i\omega_n - i\omega_{n'})$ is defined by Eq. (3.2). The self-energy becomes[15(a),15(c)]

$$\Sigma(E,i\omega_n) = T\sum_{|\omega_{n'}|<\omega_c} \int dE'\tau_3 G(E',i\omega_{n'})\tau_3 N(E')\{\tilde{\lambda}(E,E';i\omega_n - i\omega_{n'}) - \tilde{\mu}^*(E,E') - [\tilde{\Gamma}(E,E')/\pi T]\delta_{nn'}\} , \tag{3.4}$$

where

$$\tilde{\lambda}(E,E';i\omega_n)=-\sum_{kk'\nu}|\bar{g}_{kk'\nu}|^2 D_\nu(k-k',i\omega_n)\hat{\delta}(E-E_k)\hat{\delta}(E'-E_{k'}) , \tag{3.5}$$

$$\tilde{\mu}^*(E,E')=\sum_{kk'}\bar{U}(k,k';0)\hat{\delta}(E-E_k)\hat{\delta}(E'-E_{k'})\equiv\bar{U}(E,E';0) , \tag{3.6}$$

$$\tilde{\Gamma}(E,E')=\pi n_I\sum_{kk'}|t(k,k';0)|^2\hat{\delta}(E-E_k)\hat{\delta}(E'-E_{k'}) . \tag{3.7}$$

In the CDOS limit $N(E)\to N(E_F)$, the usual electron-phonon coupling constant λ, pseudopotential μ^*, and impurity width Γ are given by $N(E_F)\tilde{\lambda}(E_F,E_F;0)$, $N(E_F)\tilde{\mu}^*(E_F,E_F)$, and $N(E_F)\tilde{\Gamma}(E_F,E_F)$, respectively. It will become apparent, however, that the normally ubiquitous quantity $N(E_F)$ nowhere appears explicitly in this more general theory, although we will identify in Sec. V an effective average density of states which is useful in an approximate determination of T_c. The Coulomb pseudopotential $\tilde{\mu}^*$ is discussed further in Sec. IV A and in Appendix A.

The E dependence of Σ arises solely from the E dependence of the kernel

$$\tilde{\lambda}_{\rm eff}(E,E')\equiv\tilde{\lambda}(E,E')-\tilde{\mu}^*(E,E')-(1/\pi T)\tilde{\Gamma}(E,E') ,$$

which in turn is due to variation with energy of the *character of the wave functions and scattering properties but not the density of states.* In general we expect this variation to be small compared to DOS effects, although this question deserves further study. Information on the E dependence of $\tilde{\lambda}(E,E)$ can be gained by studying the E dependence of the mean-square electron-ion scattering matrix element $I^2(E)$ which enters $\tilde{\lambda}$. Using the calculated electronic structure and wave functions of Klein *et al.*[5] (to be used in the calculations described in Sec. V), it is found that $I^2(E)$ *varies by only 2%* in a 4-mRy region centered at E_F where $N(E)$ changes by a factor of 3. Neglecting this small energy dependence of the kernel gives

$$\Sigma_n=T\sum_{|\omega_{n'}|<\omega_c}\tilde{\lambda}_{\rm eff}(i\omega_n-i\omega_{n'})F_{n'} , \tag{3.8}$$

where $\Sigma_n\equiv\Sigma(i\omega_n)$, etc, and the density-of-states effects are confined to the factor

$$F_n=\int dE\,\tau_3 G(E,i\omega_n)\tau_3 N(E) . \tag{3.9}$$

Inverting G^{-1} in Eq. (3) leads to

$$\tau_3 G(E,i\omega_n)\tau_3=\frac{-i\omega_n Z_n-(E-\zeta+\chi_n)\tau_3}{C(E,i\omega_n)} , \tag{3.10}$$

with

$$C(E,i\omega_n)=(E-\zeta+\chi_n)^2+Z_n^2(\omega_n^2+\Delta_n^2) . \tag{3.11}$$

The gap function is given by $\Delta_n=\phi_n/Z_n$. Even and odd averages over $N(E)$ result, given by

$$\begin{Bmatrix}N_n\\P_n\end{Bmatrix}=\frac{1}{\pi}\int dE\frac{N(E)}{C(E,i\omega_n)}\times\begin{Bmatrix}Z_n(\omega_n^2+\Delta_n^2)^{1/2}\\E-\zeta+\chi_n\end{Bmatrix} , \tag{3.12}$$

with each average incorporating in the denominator $C(E,i\omega_n)$ an energy shift $\zeta-\chi_n$ and broadening half-width $Z_n(\omega_n^2+\Delta_n^2)^{1/2}$. Both functions are even in ω_n. The following sections describe the effects of a nonconstant $N(E)$ that are included in N_n and P_n, which for a constant density of states reduce to

$$\begin{Bmatrix}N_n\\P_n\end{Bmatrix}\to\begin{Bmatrix}N(E_f)\\0\end{Bmatrix} . \tag{3.13}$$

IV. GENERALIZED ELIASHBERG THEORY

The generalized equations for the Eliashberg self-energies are

$$\omega_n Z_n=\omega_n+\pi T\sum_{m=0}^{N_c}\tilde{\lambda}^{(-)}_{nm}N_m e_m+\tilde{\Gamma}N_n e_n\omega_n , \tag{4.1}$$

$$\chi_n=-\pi T\sum_{m=0}^{N_c}(\tilde{\lambda}^{(+)}_{nm}-2\tilde{\mu}^*)P_m e_m-\tilde{\Gamma}P_n e_n\omega_n , \tag{4.2}$$

$$(2n+1)\phi_n=\sum_{m=0}^{N_c}(\tilde{\lambda}^{(+)}_{nm}-2\tilde{\mu}^*)\frac{\omega_n}{\omega_m}N_m e_m\phi_m/Z_m+\tilde{\Gamma}N_n e_n\phi_n\omega_n/Z_n , \tag{4.3}$$

where $\tilde{\lambda}^{(\pm)}$ and the DOS "enhancement" e_n are defined by

$$\tilde{\lambda}^{(\pm)}_{nm} \equiv \tilde{\lambda}(i\omega_n - i\omega_m) \pm \tilde{\lambda}(i\omega_n + i\omega_m) , \tag{4.4}$$

$$e_n \equiv \omega_n / (\omega_n^2 + \Delta_n^2)^{1/2} . \tag{4.5}$$

A nonzero solution to Eq. (4.3) exists only for $T \le T_c$. However, Eqs. (4.1) and (4.2) may be useful at higher temperatures as well, a fact which is discussed in Sec. VI.

Converting Eq. (4.3) into an equation for the gap function leads to

$$\Delta_n = \pi T \sum_{m=0}^{N_c} \left[(\tilde{\lambda}^{(+)}_{nm} - 2\tilde{\mu}^*) N_m e_m - \delta_{nm} \sum_{l=0}^{N_c} \tilde{\lambda}^{(-)}_{nl} N_l e_l \right] \Delta_m / \omega_m . \tag{4.6}$$

Explicitly $\tilde{\lambda}$ is given by

$$\tilde{\lambda}(i\omega_n - i\omega_m) = 2 \int d\Omega \, \Omega \tilde{\alpha}^2 F(\Omega) / [\Omega^2 + (\omega_n - \omega_m)^2] \tag{4.7}$$

in terms of an *intensive* electron-phonon spectra function (i.e., coupling per electronic state)

$$\tilde{\alpha}^2 F(E,E';\Omega) = \sum_{k,k',\nu} |\tilde{g}_{k,k',\nu}|^2 \hat{\delta}(E - E_k) \times \hat{\delta}(E' - E_{k'}) \times \delta(\Omega - \omega_{k-k',\nu}) , \tag{4.8}$$

and

$$\tilde{\alpha}^2 F(\Omega) \approx \tilde{\alpha}^2 F(E,E';\Omega) \big|_{E \approx E' \approx E_F} .$$

Equations (2.5), (3.12), and (4.1)–(4.3) [or (4.3) replaced by (4.6)] form a system of coupled nonlinear matrix equations which must be solved iteratively for the self-energies at each temperature of interest. Their solution allows (at least in principle) the direct calculation[23] of electronic thermodynamic properties,[15(f)] such as T_c, specific heat, etc. Numerical solutions of these equations have been presented elsewhere[13] (and see below) but a number of effects, and their interpretation, resulting from a complex electronic structure will be discussed in this section. The care which must be exercised in any interpretation of the imaginary frequency equations is exemplified by the "enhancement" e_n defined by Eq. (4.5). Evidently e_n lies in the range $0 < |e_n| \le 1$. The designation "enhancement" is appropriate since, when continued to the real axis, the real part of this function gives the well-known DOS enhancement on the real axis

$$\mathrm{Re}e(\omega) = \mathrm{Re}\{\omega / [\omega^2 - \Delta^2(\omega)]^{1/2}\} . \tag{4.5'}$$

A. The Coulomb pseudopotential

From Eq. (4.2) it follows that the contribution to χ from the Coulomb interaction is independent of ω_n. This results in a constant shift χ_c in all quasiparticle energies and consequently a compensating shift $\zeta \to \zeta + \chi_c$ in the chemical potential. Therefore the Coulomb contribution to χ in Eq. (4.2) can be disregarded without loss of generality. On the other hand, phonon and impurity scattering give rise to nonconstant energy shifts χ_n which must be retained in an accurate theory.

The pseudopotential $\bar{U}$ in Eq. (3.6) is given as usual[20] as a solution to an integral equation describing the folding-down of high-frequency scattering processes included in $\bar{V}$. The zone-averaged pseudopotential $\tilde{\mu}^*$ satisfies the approximate relation (see Appendix A)

$$\frac{1}{\tilde{\mu}^*} = \frac{1}{\tilde{\mu}} + \bar{N}(\omega_{\mathrm{pl}}) \ln \left[\frac{\omega_{\mathrm{pl}}}{\omega_c} \right] , \tag{4.9}$$

where $\bar{N}(\omega)$ denotes an average over $N(E)$ on the scale of ω, and $\tilde{\mu}$ is given in terms of $\bar{V}$ by an equation analogous to (3.6). However, according to the gap equation (4.6) it is approximately the dimensionless quantity $\bar{N}(\omega_\Delta)\tilde{\mu}^*$ which enters into the determination of the gap function (and hence T_c). Here ω_Δ denotes the range of the average over $N(E)$ appropriate to the gap equation, which will be discussed further below. In the limit of a slowly varying DOS near E_F, $\bar{N}(\omega_\Delta) \to N(E_F)$ and

$$\frac{1}{\mu^*} = \frac{1}{\mu} + \frac{\bar{N}(\omega_{\mathrm{pl}})}{N(E_F)} \ln \left[\frac{\omega_{\mathrm{pl}}}{\omega_c} \right] . \tag{4.10}$$

This leads to a dependence of μ^* upon $N(E_F)$ similar in form to that of Bennemann and Garland,[24] who used $\mu = 0.26$ and $\bar{N}(\omega_{\mathrm{pl}}) \ln(\omega_{\mathrm{pl}}/\omega_c) = 3.85$ (eV atom)$^{-1}$ for transition metals. However, since μ in Eq. (4.10) is formally proportional to $N(E_F)$, which can vary widely within a given class of metals, Eq. (4.9) is the appropriate relation from which to determine $\tilde{\mu}^*$. The quantities $\tilde{\mu}$ and $\bar{N}(\omega_{\mathrm{pl}})$ vary slowly within a class of metals, with the dominant variation arising from scaling with bandwidth.

B. Impurity scattering and "Anderson's theorem"

In the CDOS limit $N_n \to N(E_F)$, $P_n \to 0$, χ_n vanishes, and the chemical potential is constant.

The gap equation (4.6) reduces to the usual form and, for $\Gamma \equiv N(E_F)\bar{\Gamma} \to 0$, the equation (4.1) for Z does likewise. For nonzero Γ the static impurities give a contribution to Z related to disorder broadening of the energy spectrum. Obviously this has no effect on the normal state, since (in the CDOS limit) there is no structure to broaden. The gap-induced structure in the superconducting state, where the quasiparticle DOS is

$$N(E_F)\mathrm{Re}\{\omega/[\omega^2-\Delta^2(\omega)]^{-1/2}\} ,$$

also is unaffected by the broadening since the equations for Z and Δ are uncoupled in this limit. This is a manifestation (indeed, a proof) of Anderson's theorem,[25] which states that superconducting properties (of CDOS systems) are unaffected by dilute nonmagnetic impurities.

The generalized Eliashberg equations above show that this statement of Anderson's theorem breaks down when structure is present in the DOS, due to the disorder broadening of the underlying electronic structure. Although Γ does not enter explicitly into the gap equation (4.6) (due to the energy-conserving nature of this interaction), disorder scattering can lead to important spectral broadening via Z, and conceivably to non-negligible spectral shifts $\chi_n - \zeta$. The effect on the gap and on T_c, is transmitted to the gap equation entirely through the resulting set $\{N_n\}$.

C. $T = T_c$

At $T = T_c$ ($\Delta_n \to 0$) the alteration of the quasiparticle density of states due to the gap vanishes,

$$\omega_n/(\omega_n^2+\Delta_n^2)^{1/2} \to \mathrm{sgn}\omega_n ,$$

and the expressions (4.1), (4.2), and (4.6) simplify somewhat. The equation for the (infinitesimal) gap becomes linear and decouples from the remaining equations, which still must be solved iteratively for N_n. The equation determining T_c can be written [Eq. (4.6) with $e_n \to 1$]

$$\sum_{m=0}^{N_c} \left[\tilde{\lambda}_{nm}^{(+)} - 2\tilde{\mu}^* - \delta_{nm} \left[\frac{2n+1}{N_n} + \sum_{l=0}^{N_c} \tilde{\lambda}_{nl}^{(-)} \frac{N_l}{N_n} \right] \right] N_m \bar{\Delta}_m = 0 , \tag{4.11}$$

where $\bar{\Delta}_m = \Delta_m/\omega_m$. Written in this form the T_c equation is a straightforward generalization of the CDOS expression, as given for example by Allen and Dynes.[26] Ignoring for the moment corrections to the kernel diagonal, the primary change is the replacement of the CDOS eigenvector $\bar{\Delta}_n$ by $N_n\bar{\Delta}_n$. This replacement has no effect upon either T_c or the eigenvector, whose components are now $N_n\bar{\Delta}_n$. This means that (at this level of approximation) Δ_n will be altered by DOS structure in proportion to N_n^{-1}. A similar correction to the gap occurs at $T < T_c$, and this indicates that the analytic continuation $\Delta(\omega)$ can be altered substantially[13,27] by energy dependence of the DOS.

The correction due to DOS structure to the phonon contribution to $Z_n - 1$, proportional to N_l in Eq. (4.11), *tends* to be canceled by N_n, while the factor N_n^{-1} multiplying $(2n+1)$ in the diagonal can be regarded as the self-consistent response of Δ_n to the DOS structure. It is this latter effect which gives rise to much of the correction to T_c compared to the CDOS limit. The structure of Eq. (4.11) will be clarified further in Sec. V where an approximate T_c equation is discussed.

V. DISCUSSION AND CALCULATIONAL RESULTS AT LOW TEMPERATURE

A. How much DOS variation?

The system of generalized Eliashberg equations has been applied to Nb_3Sn and Nb at $T = T_c$. Technical aspects of the numerical solution are discussed in Appendix B. For Nb_3Sn the corrections to the CDOS results are substantial, both for T_c and for the self-energies Δ_n, $\omega_n Z_n$, and χ_n. Crystalline Nb was checked as a possible fringe case, where corrections might be noticeable if not really important. The DOS of Nb is characterized by a large value of $N(E_F) \cong 10$ (Ry spin)$^{-1}$ with E_F lying 20 mRy above a peak, and the energy variation being described sufficiently well by a slope of -200 (Ry^2 spin)$^{-1}$ over a range of ± 20 mRy $= \pm 3 \times 10^3$ K around E_F. The correction to T_c was found to be 0.4% (downward), with correspondingly small corrections to the self-energies at T_c. Although this correction is well below the absolute accuracy of the Eliashberg equations as derived (keeping only certain classes of diagrams) and applied (especially the treatment of the Coulomb interaction), it nevertheless represents faithfully the accuracy of the CDOS approximation in Nb and in metals with similar or less DOS structure near E_F. A preliminary report of the Nb_3Sn calculations has been reported[13] and further results are discussed below.

B. Approximate relations for T_c

In the CDOS limit T_c is determined by α^2F and μ^*, or equivalently,

$$T_c = T_c[\lambda, g(\omega), \mu^*] , \tag{5.1}$$

where α^2F is described by a strength λ and shape function

$$g(\omega) = (2/\lambda\omega)\alpha^2F(\omega) .$$

Generalizing the pioneering work of McMillan,[28] Allen and Dynes[26] showed that, for widely varying strengths and shape functions, this *functional* of g can be replaced to high accuracy by a *function* involving only two moments $\omega_{\log}$ and ω_2 of g.

$$T_c \approx T_c^{\mathrm{AD}}(\lambda, \omega_{\log}, \omega_2, \mu^*) . \tag{5.2}$$

One of the most useful applications of such an approximate T_c equation is the extraction of λ from experimental data on T_c and reasonable estimates[29] of $\omega_{\log}$, ω_2, and μ^*.

In the previous sections it has been shown that the general functional form of T_c is

$$T_c = T_c[\tilde{\lambda}, \tilde{g}(\omega), \tilde{\mu}^*; N(E), \tilde{\Gamma}] , \tag{5.3}$$

where $\tilde{g}$ is defined analogously to g. The form of the gap equation (4.6), together with the work of Allen and Dynes, suggests an approximate T_c equation of the form

$$T_c = T_c(\tilde{\lambda}, \omega_{\log}, \omega_2, \tilde{\mu}^*; N_\lambda, N_\mu, N_\Delta, \tilde{\Gamma}) , \tag{5.4}$$

where N_λ, N_μ, and N_Δ are averages over $N(E)$. A few general features of these averages will be noted here.

The average denoted N_λ is that which should multiply $\tilde{\lambda}^{(-)}$ in the kernel diagonal in the approximation

$$\sum_{l=0}^{N_c} \tilde{\lambda}_{nl}^{(-)} N_l \to N_\lambda \sum_{l=0}^{N_c} \tilde{\lambda}_{nl}^{(-)} . \tag{5.5}$$

Since $\tilde{\lambda}$ decreases as ω_m^{-2} for $\omega_m \gg \tilde{\Omega}$, N_λ will correspond approximately to a Lorentzian average of $N(E)$ over a frequency half-width $\tilde{\Omega}$ around E_F (actually ζ).

In the off-diagonal terms the corresponding replacement is

$$\sum_{m=0}^{N_c} \tilde{\lambda}_{nm}^{(+)} N_m \bar{\Delta}_m \to N_\Delta \sum_{m=0}^{N_c} \tilde{\lambda}_{nm}^{(+)} \bar{\Delta}_m . \tag{5.6}$$

However, since $\bar{\Delta}_m$ decreases rapidly with increasing ω_m, even changing sign for $\omega_m \lesssim \tilde{\Omega}$, N_Δ averages over a smaller region than does N_λ, for example, on the order of $\tilde{\Omega}/2$.

The average N_μ multiplying $\tilde{\mu}^*$ is less straightforward, since $\tilde{\mu}^*$ has no frequency cutoff to make a partial sum coverage. Numerical solutions[30,31] show that Δ_n approaches a negative constant value Δ_∞ for large n (for nonvanishing $\tilde{\mu}^*$). Obviously N_n also approaches a constant average DOS value N_∞. If both N_n and Δ_n have approached their asymptotic value at $n = k < N_c$, it follows that N_μ, given by

$$N_\mu \equiv \sum_0^{N_c} N_n \bar{\Delta}_n \Big/ \sum_0^{N_c} \bar{\Delta}_n \cong \frac{\sum_0^{k-1} N_n \bar{\Delta}_n + \frac{1}{2} N_\infty \Delta_\infty \ln(N_c/k)}{\sum_0^{k-1} \bar{\Delta}_n + \frac{1}{2} \Delta_\infty \ln(N_c/k)} , \tag{5.7}$$

is weakly dependent on the cutoff N_c. This cutoff dependence is artificial and arises from the inconsistent treatment given to $\tilde{\mu}^*$ in folding $\tilde{\mu}$ down to $\tilde{\mu}^*$. The energy integral leading to Eq. (4.9) does not take into account the full variation of $N(E)$ whereas the "unfolding" to the cutoff N_c in Eq. (5.7) is taking this energy dependence into account. It is straightforward to correct this discrepancy by generalizing Eq. (4.9), that is, by using the relation (A5). However, the following approximation will suffice to illustrate some effects of DOS structure.

Owing to the rapid decrease of Δ_n with n and the $(2n+1)^{-1}$ factor in $\bar{\Delta}_n$, the DOS average,

$$N_\mu(M) \equiv \sum_{n=0}^{M} N_n \bar{\Delta}_n \Big/ \sum_{n=0}^{M} \bar{\Delta}_n , \tag{5.7'}$$

for small M "converges" (i.e., becomes stationary with respect to M) rapidly before the cutoff dependence mentioned above becomes a consideration and leads to the unwanted limit $N_\mu \to N_\infty$. In a preliminary report[13] of this work applied to Nb_3Sn (also see below) the first term alone

$$N_\mu(M=0) = \bar{N}(\pi T_c Z_0) \equiv N_{\mathrm{eff}}$$

was used in the CDOS theory, giving an approximate value T_c^{eff} which could be compared to numerical solutions of the full system of matrix equations for T_c. In essence T_c^{eff} is given by (for $\tilde{\Gamma} = 0$)

$$T_c^{\mathrm{eff}} = T_c^{\mathrm{AD}}(N_{\mathrm{eff}}\tilde{\lambda}, \omega_{\log}, \omega_2, N_{\mathrm{eff}}\tilde{\mu}^*) \tag{5.8}$$

(although numerical solutions to the CDOS equations were actually used rather than the Allen-Dynes equation). Note that

$$\pi T_c Z_0 \approx 0.85 - 0.90\omega_2 \approx \tilde{\Omega}/2$$

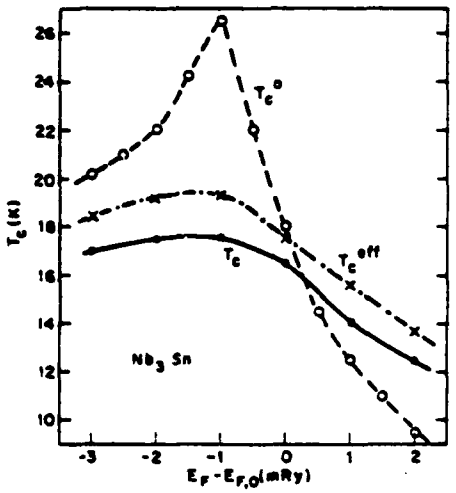

FIG. 2. Superconducting transition temperature T_c of Nb_3Sn vs Fermi-level position, calculated within different approximations. Full line, solution from full energy-dependent equations; dashed line, solution assuming CDOS $N(E)=N(E_F)$; dot-dash line, solution assuming CDOS $N(E)=N_{\text{eff}}$ (see text).

for Nb_3Sn ($T_c=18$ K, $Z_0=2.7$, $\omega_2=175$ K). The results of this approximation are shown in Fig. 2, where it is evident that T_c^{eff} reflects the trends of the numerical solution quite well as the assumed value of E_F is varied, although being ~ 1.5 K too large. The crude approximation T_c^0 resulting from the assumption $N(E)=N(E_F)$ is seen in Fig. 2 to give a much stronger $N(E_F)$ dependence than actually occurs.

For nonzero impurity scattering each DOS average N_n has its broadening half-width $\omega_n Z_n$ increased by $\tilde{\Gamma} N_n$ [see Eq. (4.1)]. A low-order approximation can include this by increasing by $\Gamma_{\text{eff}} \equiv N_\lambda \tilde{\Gamma}$ each of the widths which determine N_λ, N_Δ, and N_μ, of which the former must be calculated self-consistently (at least in principle). The calculations described below result from numerical solutions to the full energy-dependent equations, however.

The quantities N_λ, N_Δ, and N_μ offer a reasonable possibility of obtaining a realistic value of T_c without solving nonlinear coupled matrix equations. Unfortunately it is a monumental task to ascertain even an appropriate form of the approximate T_c equation envisioned in Eq. (5.4), as this would involve full solutions for a wide variety of shapes of $N(E)$ and $\tilde{g}(\omega)$ as well as coupling strengths $\tilde{\lambda}$, $\tilde{\mu}^*$, and $\tilde{\Gamma}$. Worse, it begins to appear hopeless to extract unambiguous information from an experimental value of T_c in the face of so many unknown parameters. The only compensation is that the behavior of T_c with the level of impurity scattering [$T_c(\tilde{\Gamma})$] can be incorporated into the analysis. A more realistic approach for interpreting experimental data is to use a single average N_{eff}, with $N_{\text{eff}}=N_\lambda$ being a good choice, in the CDOS expression of Allen and Dynes. This in effect is the usual practice, except that the value of $\lambda_{\text{eff}}=N_{\text{eff}}\tilde{\lambda}$ extracted in this manner may differ from the mass enhancement value derived from heat capacity or other measurements.

Although the DOS average appropriate for an approximate T_c equation given above differs in detail from that of Nettel and Thomas,[9] the spirit of the approximation is similar to theirs. The more rigorous, but linear, approach of Lie and Carbotte[11] for calculating $\delta T_c/\delta N(E)$ follows from the present formulation by calculating the correction ΔT_c arising from an infinitesimal variation of energy E from a constant DOS given by

$$\Delta N(E')=\epsilon\delta(E'-E) .$$

It could be of interest to study the effects of the supralinear terms for a particular DOS function using the present theory. However, the Lie-Carbotte results provide an important intuitive grasp of the general behavior of $\delta T_c/\delta N(E)$ as well as a first approximation for numerical calculations.

C. Defect dependence of T_c and $N(E_F)$

It was observed in Sec. V B that experimental data on $T_c[\tilde{\Gamma}]$ [i.e., T_c versus defect concentration n_i, since $\tilde{\Gamma}=\pi n_i |t^2|$ from Eq. (3.7)] provide

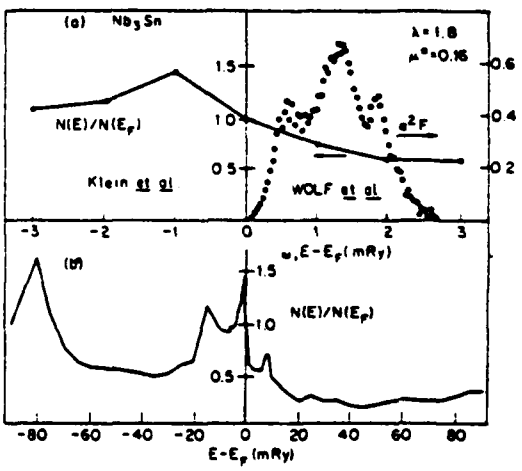

FIG. 3. Comparison of electron and phonon energy scales for Nb_3Sn. (a) $\alpha^2F(\omega)$ from tunneling data by Wolf *et al.* (Ref. 32) and $N(E)$ function calculated by Klein *et al.* (Ref. 5), shown on the same mRy scale. (b) Same $N(E)$ function on a scale of ~ 1 eV.

direct information on the energy variation of $\mathcal{N}(E)$. Calculation of $T_c(\bar{\Gamma})$ has been carried out for Nb_3Sn using the DOS function calculated by Klein *et al.*[5] For $\tilde{\alpha}^2F$ we have assumed

$$\alpha^2F(\omega)=\bar{\mathcal{N}}(\omega_{ph})\tilde{\alpha}^2F(\omega)\ , \tag{5.9}$$

$\omega_{ph}=300$ K, with $\alpha^2F(\omega)$ derived from tunneling data by Wolf *et al.*[32] Both $\mathcal{N}(E)$ and α^2F are shown in Fig. 3 on the same scale to allow an easy comparison of their energy variations. For $\tilde{\mu}^*$ the value $\mu^*=0.16$ determined by Wolf *et al.* has been used in the form $\mathcal{N}(E_F)\tilde{\mu}=0.16$.

To compare with experimental data the defect-broadening half-width Γ was related to the residual resistivity ρ_0 by

$$\rho_0=4\pi\Gamma/\Omega_p^2\ , \tag{5.10}$$

$$\Omega_p^2=(4\pi e^2/3)\mathcal{N}(E_F)v_F^2\ , \tag{5.11}$$

with[33] $\hbar\Omega_p=4.0$ eV. The experimental data on $\rho(T_c)\approx\rho(0)$ has been converted to the "true" residual resitivity ρ_0 by the use of the parallel resistor formula

$$\frac{1}{\rho(0)}=\frac{1}{\rho_0}+\frac{1}{\rho_{max}}\ , \tag{5.12}$$

$\rho_{max}=150\ \mu\Omega$ cm, since Weismann *et al.*[34] have found that ρ_0 given by this expression, and not $\rho(0)$, is approximately linear with damage-inducing radiation dose. The theoretical prediction is compared to four sets[35] of experimental data in Fig. 4. The calculation is consistent with experimental data for residual resistivities below 75 $\mu\Omega$ cm. For larger disorder the theoretical prediction approaches the asymptotic limit $T_c\simeq 9$ K whereas the experimental values saturate at $T_c\simeq 3$ K. This indicates that, for $\rho_0>75\ \mu\Omega$ cm, the disorder is decreasing the electron-phonon coupling $\tilde{\alpha}^2(\omega)$ and/or hardening the phonon spectrum $F(\omega)$, neither of which is included in the present theory which treats α^2F as independent of disorder.

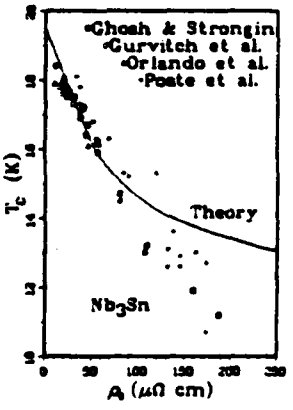

FIG. 4. Calculated T_c of Nb_3Sn (full curve) vs "true" residual resistivity ρ_0 (i.e., from parallel resistor formula) compared with experimental data (Ref. 35). The theory is not expected to be accurate for large defect concentration ($\rho_0>75\ \mu\Omega$ cm) since changes in $\tilde{\alpha}^2F$ are not included in the theory.

The correspondence between defect concentration and residual resistivity ($\bar{\Gamma}\leftrightarrow\rho_0$) is not as simple as Eq. (5.10) implies. It should be observed, for example, that Γ in Eq. (5.10) must be determined self-consistently from the relation

$$\Gamma=\bar{\mathcal{N}}(\Gamma)\bar{\Gamma}\ , \tag{5.13}$$

where, as will be shown below, the Γ dependence of $\bar{\mathcal{N}}(\Gamma)$ is strong. Therefore, although $\bar{\Gamma}$ increases linearly with disorder, Γ is distinctly sublinear. However, the factor Ω_p^2 in a suitably generalized version of Eq. (5.10) also contains the factor $\bar{\mathcal{N}}(\Gamma)$ so the DOS dependence of ρ_0 cancels. As a result the defect concentration dependence of ρ_0 *goes inversely with that of* v_F^2, a result analogous to an equivalent observation for the phonon-limited resistivity made previously by Allen.[36] This result can be written

$$\rho_0=3\bar{\Gamma}/e^2v_F^2[\Gamma(\bar{\Gamma})]\ . \tag{5.14}$$

We find by calculation, however, that $v_F^2(\Gamma)\propto 1/\bar{\mathcal{N}}(\Gamma)$ [since $\bar{\Omega}_p^2(\Gamma)$ is constant to within 2%], which makes Eq. (5.14) *numerically* equivalent to

$$\rho_0\leftrightarrow[4\pi/\Omega_p^2(E_F)]\bar{\mathcal{N}}(\Gamma)\bar{\Gamma}\ . \tag{5.14'}$$

Conceptually Eqs. (5.14) and (5.14') *are not at all equivalent* and the former relation gives the correct physical picture.

In Fig. 5 the effective defect broadening (or

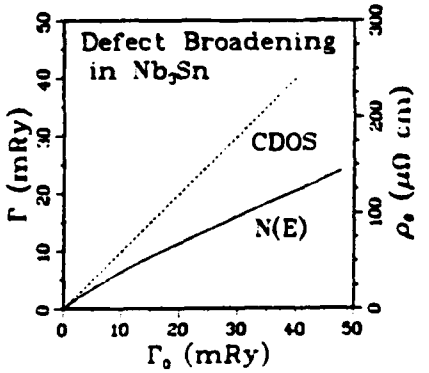

FIG. 5. Self-consistently determined defect broadening width Γ (equivalently residual resistivity ρ_0)—full line—vs disorder Γ_0, determined from $\mathcal{N}(E)$ shown in Fig. 3. The dashed line gives the CDOS approximation $\Gamma=\Gamma_0$.

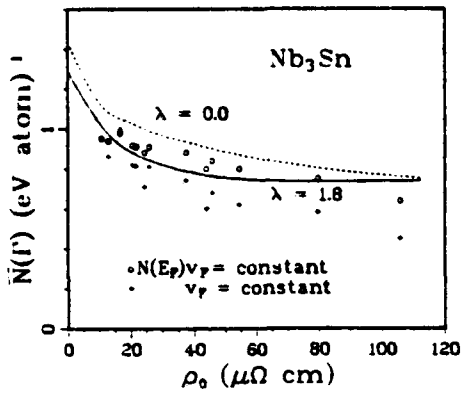

FIG. 6. Effective density of states $\bar{N}(\Gamma)$ vs residual resistivity ρ_0 for Nb_3Sn. Solid line: theory, including e-ph interaction with $\lambda = 1.8$. Dashed line: theory, no e-ph interaction. Symbols: experimentally inferred values (Ref. 38), assumed two different constraints on $N(E_F)v_F$ with varying disorder.

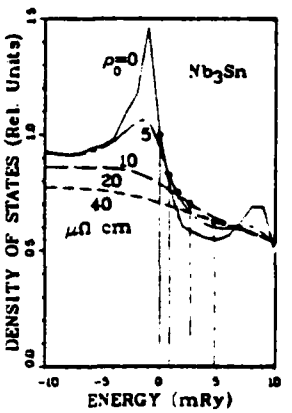

FIG. 7. Effect of defect broadening on the $N(E)$ function shown in Fig. 3. Vertical lines indicate the respective Fermi levels, determined from conservation of electrons. Circles denote $\bar{N}(\Gamma) = N(E_F)$. The best samples of Nb_3Sn have residual resistivities $\rho_0 \approx 10\ \mu\Omega$ cm, which precludes extreme energy variation of the density of states.

equivalently, ρ_0) is plotted versus

$$\Gamma_0 = N(E_F)\bar{\Gamma} = \pi n_i N(E_F)\,|\,t^2\,|\ .$$

Owing to broadening of the peak in $N(E)$ near E_F, Γ increases more slowly than that for a CDOS $N(E) \equiv N(E_F)$, shown by the dashed line. However, for $\rho_0 \geq 50\ \mu\Omega$ cm, Γ is *approximately* linear with defect concentration, just as the data of Weismann *et al.*[34] for ρ_0 are approximately linear with radiation fluence in this range.

The behavior of the factor of $N(E_F)$ in the linear specific-heat coefficient γ versus residual resistivity may provide more direct information on $N(E)$ than does $T_c(\rho_0)$, since only a straightforward Lorentzian broadening[37] of $N(E)$ is involved. In the few cases which have been studied systematically, however, γ has been inferred instead from the temperature dependence of the upper critical magnetic field,[38] which involves independent information (or assumptions) about the values of material constants such as λ, v_F, mean free path l, etc., as well as an assumption about the behavior of band-structure-related quantities with defect concentration. The resulting values of $\bar{N}(\Gamma)$ for Nb_3Sn obtained by Ghosh *et al.*,[38] resulting from the assumption that $N(E_F)v_F$, or secondly, v_F itself, remains constant with increasing disorder, are compared in Fig. 6 with that calculated from the DOS function in Fig. 3. Calculated values of $\bar{N}(\Gamma)$ are shown both for the (usually assumed) case where only defect broadening is taken into account (dashed line), and the more general case in which e-ph broadening is included (full line).

The calculated values including e-ph broadening are in slightly better agreement with the empirical values obtained assuming $N(E_F)v_F = \text{const}$ [however, the argument given above in the discussion of $T_c(\rho_0)$ indicates $N(E_F)v_F^2 = \text{const}$ would be the proper assumption]. The analysis of Ghosh *et al.* of course also needs generalizing along the lines of the present theory. It is clear from Fig. 6 that extrapolation from the existing data to obtain a "perfect crystal value" of $N(E_F)$ may not be valid, since a kink may occur at or below 10 $\mu\Omega$ cm. The degree of broadening of the full $N(E)$ curve is illustrated more clearly in Fig. 7. A peak of width 3–4 mRy or less is virtually lost for a residual resistivity of 10 $\mu\Omega$ cm, which corresponds to the highest quality samples of Nb_3Sn. Such a large perfect-crystal value of $N(E_F)$ implies a tendency toward defect formation, which serves to lower $N(E_F)$ and thereby decreases the number of electrons at high energy, resulting in a more stable material.

D. Defect dependence of T_c: Previous studies

There have been several previous applications of broadening to account for properties, especially T_c, of $A15$ compounds. Most of these have been phenomenological, as typified particularly by the work of Mattheiss and Testardi.[39,40] The studies of Aleksandrov, Elesin, and Kazeko,[41] and Huang, Chu, and Ting,[41] however, have used a more fundamental approach. Both groups studied T_c using

a weak-coupling formalism and model DOS functions to illustrate the effect of defect broadening of $N(E)$ upon T_c.

Aleksandrov *et al.*[41] purported to explain the saturation in Nb_3Sn of T_c at 3 K for high defect concentration solely in terms of DOS broadening. The present generalized theory and realistic DOS function shows saturation at $\sim 8-9$ K if only defect broadening is taken into account. In addition, this limit depends on the DOS function on only a large (~ 1 eV) scale, for which all band-structure calculations[4,5] give results similar (*modulo* $5-10\%$ bandwidth-type differences arisings from different exchange-correlation approximations, etc.) to those of Klein *et al.*[5] which were used here. A similar limit (~ 7 K) follows from the DOS broadening study of Soukoulis and Papaconstantopoulos,[42] if $T_c(10\ \mu\Omega\,\text{cm})$ is normalized to the experimental value of 18.6 K. To understand the 3-K saturation it is necessary to invoke a weakening in the strength of $\bar{\alpha}^2F$ by approximately a factor of 2. This weakening may result from weaker coupling or harder phonons. In fact, both of these effects have recently been observed in tunneling studies of Nb_3Al (Ref. 43) and Nb_3Ge (Ref. 44) with varying degrees of disorder.

Huang *et al.*[41] assumed a singular one-dimensional DOS and obtained results similar to those of Aleksandrov *et al.* and the present results. They concluded that, due to DOS variation near E_F, a high T_c compound can have a small value of $N(E_F)$. A look at Fig. 7 shows that this cannot be the case for $A15$ compounds with appreciable amounts of disorder, as in all samples of Nb_3Ge, Nb_3Al, or for that matter, Nb_3Sn. For $\rho_0=10$ $\mu\Omega$ cm, i.e., a clean Nb_3Sn sample, the broadening half-width Γ is 1.6 mRy=250 K, which is roughly equal to the maximum phonon frequency Ω. Thus $\bar{N}(\Omega)$, which determines T_c (see Sec. V B), cannot be much different from the value of $N(E)$ at E_F [$\bar{N}(\Gamma)$ in the present notation]. A *very low* ρ_0, high-T_c crystal may have a relatively low value of $N(E_F)$ if a large peak lies within $\sim\Omega$ of E_F, however.

Other mechanisms involving defect broadening have been proposed to account for the degradation of T_c by defects. Meisel and Cote[45] suggested that an assumed inability of phonons with wavelength longer than the electron mean free path to scatter electrons effectively (and hence bind Cooper pairs) could account for the defect dependence of high T_c compounds. This cannot explain the *increase* in T_c with ρ_0 in low-T_c materials,[46] however. Moreover, if this "phonon-ineffectiveness" concept is accepted it is very difficult to understand the rather large T_c and measured α^2F of highly disordered Mo (Kimhi and Geballe, Ref. 46). Ruvalds and Soukoulis[47] have attributed most of the high T_c (at least in Nb_3Ge and V_3Si) to an acoustic plasmon mechanism which decreases in strength as the electronic spectrum is broadened. However, there is strong evidence from tunneling measurements that the electron-phonon interaction itself is strong enough to account for the high T_c in V_3Ga (Ref. 48), Nb_3Sn (Ref. 32), Nb_3Al (Ref. 43), and Nb_3Ge (Ref. 44), so there is now little reason to except the acoustic plasmon mechanism to apply to any $A15$ compounds.

VI. NORMAL-STATE SPIN SUSCEPTIBILITY

In Sec. IV it was shown that in general T_c does not provide a measure of $N(E_F)$, but rather of an average of the DOS over a region $\pi T_c Z_0$ or larger. In this section we investigate what information about $N(E)$ is contained in the spin susceptibility χ_{sp}. For the sake of generality the full k dependence of the expressions will be retained as far as possible.

A. General considerations

The magnetization M is given by the difference in number of spin-up and spin-down electrons times the moment per electron,

$$M(\zeta,T)=\mu_B(N_{e,\uparrow}-N_{e,\downarrow}) =\mu_B\sum_\sigma \sigma N_{e,\sigma}\ , \tag{6.1}$$

with

$$N_{e,\sigma}=T\sum_{k,n} G_\sigma(k,i\omega_n)e^{i\omega_n\epsilon} \tag{6.2}$$

and

$$G_\sigma^{-1}(k,i\omega_n)=i\omega_n-(E_k-\zeta-\mu_B\sigma H) -\Sigma_\sigma(k,i\omega_n)\ , \tag{6.3}$$

where H is the magnetic field. Luttinger[49] has shown how this "self-evident" *exact* expression for M can be derived diagrammatically.

The measured zero-field susceptibility is given

by

$$\chi_{sp}=\left[\frac{\partial M}{\partial H}\right]_{T,N_e}\Bigg|_{H=0}=\left[\frac{\partial M}{\partial H}\right]_{T,\zeta}\Bigg|_{H=0,\zeta=\zeta(N_e)}$$

$$=\mu_B^2 T\sum_{k,n,\sigma}\sigma^2 G_\sigma^2(k,i\omega_n)e^{i\omega_n\epsilon}\left[-\frac{dG_\sigma^{-1}(k,i\omega_n)}{d(\mu_B\sigma H)}\right]_{H=0} \tag{6.4}$$

$$=-2\mu_B^2 T\sum_{k,n}G^2(k,i\omega_n)[1+\Sigma'(k,i\omega_n)]\,, \tag{6.5}$$

where we have used Eq. (6.3) and the expansion

$$\Sigma_\sigma(k,i\omega_n)=\Sigma(k,i\omega_n)-\mu_B\sigma H\Sigma'(k,i\omega_n)+O(H^2)\,. \tag{6.6}$$

Equation (6.5) is an *exact* expression for χ_{sp} in terms of the renormalized Green's function and the field derivative of the self-energy. As can be seen from Wolff's[50] diagrammatic theory for χ_{sp}, the G^2 term in Eq. (6.5) arises from the simple, but renormalized, bubble diagram in Fig. 8(a), whereas the $G^2\Sigma'$ term arises from all vertex corrections (i.e., diagrams with other than self-energy insertions to G). With Σ given by the diagrams of Fig. 1, we can write, introducing $J_\sigma=-dG_\sigma^{-1}/d(\mu_B\sigma H)\,|_{H=0}=J_{-\sigma}=J$,

$$J(k,i\omega_n)=1-\frac{d}{d(\mu_B\sigma H)}T\sum_{k'n'}\bar{\lambda}_{\rm eff}(k,k';i\omega_n-i\omega_{n'})G_\sigma(k',i\omega_{n'}) \tag{6.7}$$

$$=1+T\sum_{k'n'}\bar{\lambda}_{\rm eff}(k,k';i\omega_n-i\omega_{n'})G^2(k',i\omega_{n'})J(k',i\omega_{n'})$$

$$-T\sum_{k'n'}\left[\frac{d}{d(\mu_B\sigma H)}\bar{\lambda}_{\rm eff}(k,k';i\omega_n-i\omega_{n'})\right]_{H=0}G(k',i\omega_{n'})\,. \tag{6.7'}$$

The second term in Eq. (6.7') describes "ladder-type" vertex corrections (see below), with a typical graph shown in Fig. 8(b). The third term represents field corrections to the effective electron-electron interaction, with the lowest-order phonon contribution shown in Fig. 8(c). There is of course a large class of diagrams for χ_{sp} which are not included in Eq. (6.7) by virtue of the approximation for Σ from which this equation is derived.

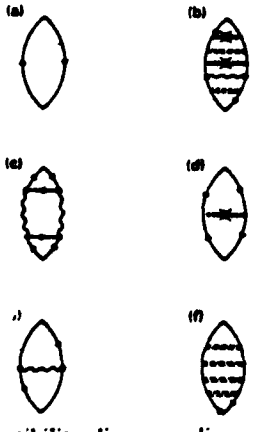

FIG. 8. Susceptibility diagrams discussed in the text. For simplicity the *renormalized Green's function is denoted by single full lines* rather than double lines as in Fig. 1. Other notation is as in Fig. 1.

For $T\to 0$ Luttinger[49] has shown that, as long as $\gamma(\omega)$ $[\Sigma(\omega)\equiv m(\omega)-i\gamma(\omega)]$ vanishes as fast as ω^2 as $\omega\to 0$, M is given by

$$M=\mu_B\sum_{k\sigma}\sigma\Theta(\zeta-\mathscr{E}_{k\sigma}) \tag{6.8}$$

where Θ is the unit step function and $\mathscr{E}_{k\sigma}$ is the renormalized energy given by

$$\mathscr{E}_{k\sigma}=E_{k\sigma}-m_\sigma(k,\mathscr{E}_{k\sigma}-\zeta)\,. \tag{6.9}$$

The susceptibility is given by

$$\chi_{sp}(T=0)=2\mu_B\sum_{k\sigma}\left[-\frac{d\mathscr{E}_{k\sigma}}{dH}\right]\delta(\zeta-\mathscr{E}_{k\sigma})\,. \tag{6.10}$$

The derivatives

$$\vec{\nabla}_k\mathscr{E}_{k\sigma}=\vec{\nabla}_k E_{k\sigma}-\vec{\partial}_k m_\sigma(k,\mathscr{E}_{k\sigma}-\zeta)$$
$$-\partial_\omega m(k,\omega)\,|_{\omega=\mathscr{E}_{k\sigma}-\zeta}\vec{\nabla}_k\mathscr{E}_{k\sigma}\,. \tag{6.11}$$

$$\frac{d\delta_{k\sigma}}{dH}=\frac{dE_{k\sigma}}{dH}-\frac{\partial}{\partial H}m_\sigma(k,\delta_{k\sigma}-\zeta)$$
$$-\partial_\omega m(k,\omega)|_{\omega=\delta_{k\sigma}-\zeta}\frac{d\delta_{k\sigma}}{dH}\ , \tag{6.12}$$

at the Fermi surface $\delta_{k\sigma}=\zeta$ become

$$\vec{\nabla}_k\delta_{k\sigma}=[\vec{v}_k-\vec{\partial}_k m_\sigma(k,0)]/(1-\lambda_k)\ , \tag{6.13}$$
$$\frac{d\delta_{k\sigma}}{dH}=-\mu_B\left[\sigma+\frac{\partial m_\sigma(k,0)}{\partial(\mu_B H)}\right]\Big/(1+\lambda_k)\ , \tag{6.14}$$

where $\lambda_k=-\partial_\omega m(k,\omega)|_{\omega=0}$ is the usual mass renormalization. Equation (6.10) becomes

$$\chi_{sp}(T=0)=2\mu_B^2 N(\zeta)\left\langle\left[1+\frac{\partial m_\uparrow(k,0)}{\partial(\mu_B H)}\right]\Big/\ |\hat{v}_k-\vec{\nabla}_k m(k,0)/v_k|\right\rangle\ . \tag{6.15}$$

Here $v_k=|\vec{v}_k|$ and $\vec{v}_k=v_k\hat{v}_k$, and the angle brackets $\langle\ \rangle$ denote a Fermi-surface average.

Equation (6.10) expresses χ_{sp} in terms of a renormalized density of states, including mass enhancement from Eq. (6.9), and a susceptibility per state $-d\delta_{k\sigma}/dH$ which also includes a mass enhancement factor [Eq. (6.14)]. Equation (6.15) expresses χ_{sp} in terms of the bare factor $N(\zeta)$ in which the total mass enhancement cancels out. That the phonon mass enhancement cancels out was first recognized by Quinn and Ferrell,[51] who interpreted the cancellation as the result of each of the spin-split bands carrying its own mass renormalization with it rigidly.

Reverting to the isotropic approximation for G, the relation for the thermal distribution function

$$f(E-\zeta)=T\sum_n G(E,i\omega_n)e^{i\omega_n\epsilon} \tag{6.16}$$

can be differentiated to yield

$$-\frac{df(E-\zeta)}{dE}=-T\sum_n G^2(E,i\omega_n)\ , \tag{6.17}$$

the convergence factor being unnecessary here. Equation (6.5) for χ_{sp} can therefore be written

$$\chi_p(T)=2\mu_B^2\int dE\left[-\frac{df(E-\zeta)}{dE}\right]$$
$$\times N(E)[1+\Sigma'(E,T)]\ , \tag{6.18}$$

with $\Sigma'(E,T)$ being defined from Eq. (6.5) by this equation.

The crucial feature of this expression is that interactions can alter $f(E)$ drastically from its free-particle counterpart

$$f_0(E)=[\exp(E/T)+1]^{-1}\ .$$

The behavior of f has been presented elsewhere[52] for the case of electrons interacting with an Einstein phonon spectrum of strength λ, where it was found that, with increasing λ, $-df/dE$ becomes ever more long ranged, resulting in considerably increased averaging over $N(E)$ as well as a greater variation of $\zeta(T)$ given by the isotropic form of Eq. (6.2):

$$N_e=2\int dE\, f(E-\zeta)N(E)\ . \tag{6.2'}$$

For even moderate values of λ, of the order of 0.5, f differs significantly from f_0 and results in an enhanced temperature dependence of χ_{sp} in Eq. (6.18). Bhatt[53] has found previously that a low-temperature expression leads to an enhancement $(1+\lambda)$ of the T dependence of χ_{sp}.

Returning to the expression (6.7) for the enhancement J, neglect of the field dependence of the interaction leads to

$$J(i\omega_n)=1+T\sum_{n'}\tilde{\lambda}_{\rm eff}(i\omega_n-i\omega_{n'})$$
$$\times\int dE\,N(E)G^2(E,i\omega_{n'})J(i\omega_{n'}) \tag{6.19}$$

in the isotropic approximation. As was the case for the self-energy in Sec. III, the (assumed) independence of $\tilde{\lambda}_{\rm eff}$ on E_k and $E_{k'}$ leads to an E-independent J. Also as was found for Σ, the distinct frequency dependences of the Coulomb, phonon, and defect interactions lead to different characteristic behaviors for J.

B. Coulomb interaction

In the presence of only Coulomb interactions (in the approximation of Secs. II and III) f is essentially unchanged from f_0. In the range of interest in Eq. (6.18), of the order of πT, the frequency dependence of the screened exchange interaction,

which will be denoted as usual by I, can be neglected. Equation (6.19) becomes ($J_\uparrow = J_\downarrow = J$)

$$J = 1 + I \int dE \left[-\frac{df(E-\zeta)}{dE} \right] N(E) J$$

$$= 1/[1 - I N_{\rm eff}(\zeta)] , \tag{6.20}$$

where

$$N_{\rm eff}(\zeta) = \int dE \left[-\frac{df(E-\zeta)}{dE} \right] N(E) \tag{6.21}$$

is the effective density of states at ζ at temperature T. With the enhancement $J = 1 + \Sigma'$ given in Eq. (6.20), Eq. (6.18) becomes the usual Stoner-enhanced expression for χ_{sp}.

C. Interaction with defects

Defects drastically alter the occupation of *crystalline* eigenstates, even at $T = 0$. Assuming a constant density of states, it is straightforward to show that f is given (in the dilute limit) by the convolution of f_0 with a Lorentzian of width $\Gamma = N(E_F)\tilde{\Gamma}$:

$$f(E) = \int dE' f_0(E') \frac{(\Gamma/\pi)}{(E-E')^2 + \Gamma^2} . \tag{6.22}$$

If $N(E)$ varies on the scale of $N(E_F)\tilde{\Gamma}$, Γ must be determined self-consistently as discussed in Sec. V C.

Defects give rise to a susceptibility enhancement given by

$$J(i\omega_n) = 1 + (\tilde{\Gamma}/\pi) \int dE\, N(E) G^2(E, i\omega_n) J(i\omega_n) = 1/[1 - \bar{I}_i(i\omega_n)] , \tag{6.23}$$

where $\bar{I}_i$ is given, after partial integration, by

$$\bar{I}_i(i\omega_n) = -(\tilde{\Gamma}/\pi) \int dE \frac{dN(E)}{dE} G(E, i\omega_n) . \tag{6.24}$$

Clearly no enhancement occurs for a constant $N(E)$. To provide an estimate of the magnitude of this correction we evaluate the lowest order correction $\delta\chi_i^{(1)}$, pictured in Fig. 8(d),

$$\begin{aligned}
\delta\chi_i^{(1)} &= 2\mu_B^2 (\tilde{\Gamma}/\pi) T \sum_n \sum_{kk'} G(k, i\omega_n)^2 G(k', i\omega_n)^2 \\
&= 2\mu_B^2 (\tilde{\Gamma}/\pi) \sum_{kk'} \frac{d}{dE_k} \frac{d}{dE_{k'}} T \sum_n G(k, i\omega_n) G(k', i\omega_n) \\
&\cong 2\mu_B^2 (\tilde{\Gamma}/\pi) \sum_{kk'} \frac{d}{dE_k} \frac{d}{dE_{k'}} \frac{1}{E_{k'} - E_k} T \sum_n [G(k, i\omega_n) - G(k', i\omega_n)] e^{i\omega_n \epsilon} \\
&= 2\mu_B^2 (\tilde{\Gamma}/\pi) \sum_{kk'} \frac{d}{dE_k} \frac{d}{dE_{k'}} \frac{f(E_k) - f(E_{k'})}{E_{k'} - E_k} .
\end{aligned} \tag{6.25}$$

The k dependence of the self-energy has been neglected in writing the energy denominator as $E_{k'} - E_k$. Using the isotropic approximation and performing partial integration in each variable gives

$$\delta\chi_i^{(1)} = 2\mu_B^2 \frac{\tilde{\Gamma}}{\pi} \int dE\, N'(E) \times \int dE' N'(E') \frac{f(E) - f(E')}{E' - E} . \tag{6.26}$$

We consider first the case where $N'(E) = dN(E)/dE$ can be taken to be constant in the important range around E_F. Setting

$$N'(E) = A N(E_F)/W , \tag{6.27}$$

where A is a constant of order unity and W is the bandwidth, leads to the result

$$\delta\chi_i^{(1)} = 2\mu_B^2 N(E_F) A^2 \frac{\ln 2}{\pi} \frac{\Gamma}{W} . \tag{6.28}$$

Thus defects may lead to a nonvanishing but usually small contribution to the Stoner I. For compounds with several transition-metal atoms per cell, however, W may represent a subband width such that Γ/W is not small, in which case it is necessary to do the integral in Eq. (6.26) more carefully. Nevertheless, we expect this contribution to χ generally to be secondary to the change in $N(E_F)$ in the simple bubble term due to defect

broadening. Finally, it should be noted that this defect contribution to χ_{sp} need not always be positive as in Eq. (6.28). If E_F occurs at a peak, or a dip, in $N(E)$, in which case $N'(E)$ and $N'(E')$ in Eq. (6.26) have opposite signs in the important region of integration, the correction to χ_{sp} may be negative.

D. Interaction with phonons

It is not generally recognized that phonons can seriously alter the thermal occupation of crystalline eigenstates if the e-ph interaction is even moderately strong. It has been shown elsewhere[54] that e-ph interactions shift the spectral weight of low-energy electronic excitations drastically, and as a result the thermal occupation $f(E)$ broadens, corresponding to occupation of higher-energy bare electrons and holes. The resulting modification of the first term in Eq. (6.18) can be substantial. Since this effect of the e-ph interaction on $f(E)$, as well as many of its implications, is described elsewhere,[52] only phonon effects on the susceptibility will be addressed here.

Previous treatments[55,56] of the effect of e-ph interactions on the susceptibility have approached the problem from the viewpoint of a phonon contribution to the Stoner interaction parameter I. These treatments have all assumed a CDOS system, however, and in the general case it is not clear that this "Stoner I" viewpoint provides a useful approach. To see this, consider the Eq. (6.7') neglecting the field dependence of the interaction: The frequency dependence of $\tilde{\lambda}$ from the e-ph interaction is essential to the correct evaluation of this term and results in a *frequency-dependent enhancement* $J(i\omega_n)$. As a result J cannot be written in the simple (constant) form (6.20) as is the case for Coulomb interactions, nor even in the still simple (but frequency-dependent) form (6.23) as for defects.

We content ourselves here with studying briefly the first correction to χ_{sp} from e-ph interaction (beyond self-energy insertions to G). This correction is shown in Fig. 8(e) and is given by

$$\delta\chi^{(1)}_{e\text{-ph}} = 2\mu_B^2 T^2 \sum_{\substack{kn \\ k'n'}} G^2(k,i\omega_n)\tilde{\lambda}(k-k';i\omega_n - i\omega_{n'})G^2(k',i\omega_{n'}) \,. \tag{6.29}$$

In the isotropic approximation this becomes

$$\delta\chi^{(1)}_{e\text{-ph}} = 2\mu_B^2 T^2 \sum_{nn'} \tilde{\lambda}(i\omega_n - i\omega_{n'}) \int dE \int dE' \, N'(E)G(E,i\omega_n)N'(E')G(E',i\omega_{n'}) \,. \tag{6.30}$$

If $N(E)$ varies on the scale of Ω, no further simplification of this expression is possible. In particular, $\delta\chi^{(1)}_{e\text{-ph}}$ is not bounded in magnitude by any small parameter and it may be of either sign. Since this contribution to χ_{sp} is the first [Fig. 8(e)] in the e-ph ladder series leading to a generalized Stoner enhancement, the e-ph contribution to a "Stoner I" may be large and of either sign.

If $N'(E)$ can be approximated by a constant $N(E_F)/W$ over the range $E_F - W$ to $E_F + W$, and is negligible otherwise, Eq. (6.30) can be evaluated for an Einstein phonon spectrum $\tilde{\alpha}^2F(\omega) = (\tilde{\lambda}\Omega_E/2)\delta(\omega - \Omega_E)$. The energy integral gives

$$\int dE \, N'(E)G(E,i\omega_n) \rightarrow -i\pi[N(E_F)/W]\,\mathrm{sgn}\omega_n \,. \tag{6.31}$$

For $W \gg \Omega_E$ the frequency sums lead to the result

$$\delta\chi^{(1)}_{e\text{-ph}} \sim 2\mu_B^2 N(E_F)\left|\frac{\lambda\Omega_E}{4W}\ln\frac{W}{\Omega_E}\right| \,, \tag{6.32}$$

suggesting that a ladder summation of such contributions would lead to a contribution to the Stoner I given by

$$I_{e\text{-ph}} \approx \frac{\lambda\Omega_E}{4W}\ln\frac{W}{\Omega_E} \,. \tag{6.33}$$

Oscillation in $N'(E)$ in transition-metal compounds is likely to severely reduce the dependence of $I_{e\text{-ph}}$ on the cutoff W, so the net result is likely to be dominated by DOS structure near E_F.

It is notable that Eq. (6.33) is of exactly the same form deduced by Fay and Appel[55] from the same diagram without invoking the isotropic approximation used here. Fay and Appel also emphasized that other diagrams may give phonon contributions to χ_{sp} of the same order as that resulting from Eq. (6.33). Although the contribution (6.30) to χ_{sp} is not bounded by any small quantity like Ω/W, there is still no assurance that other di-

agrams will not give important contributions. However, Eq. (6.30) has the advantage that the electron Green's function is dressed by phonons, implicitly accounting for an infinite subset of diagrams for χ_{sp}.

Kim,[56] taking another point of view, has considered the magnetic field dependence of the phonon frequencies arising from changes in electronic screening of the ion-ion interaction. The change $\Delta\omega_Q$ depends on the spin polarization, which may be Stoner-enhanced by the Coulomb interaction. Kim finds the result that the phonon contribution to I may itself be enhanced by the same factor, thereby greatly increasing the importance of $I_{e\text{-}ph}$ for nearly magnetic metals. Figure 8(c) gives the lowest-order diagram which arises from field dependence of the phonon spectrum. Recently MacDonald and Taylor[57] have suggested that refinements of Kim's theory will not lead to corrections as large as were envisioned by Kim.

E. Combined effects of interactions

A realistic calculation of χ_{sp} requires that all three of the interactions discussed above be taken into account simultaneously. The ladder diagrams, e.g., Fig. 7(b), can only be fully included by a numerical solution of Eq. (6.19), and corrections beyond the ladder approximation present additional difficulties. It might be expected that a reasonable first approximation would be to retain only the Coulomb part of $\tilde{\lambda}_{eff}$ in Eq. (6.19) but include defect and phonon contributions to G. The set of diagrams included in this approach is typified by the Coulomb ladder diagram of Fig. 8(f), and the corresponding contribution to χ_{sp} is given by

$$\chi_{sp}=2\mu_B^2 N_{eff}(\zeta)/[1-IN_{eff}(\zeta)]\ , \qquad (6.34)$$

with N_{eff} given by Eq. (6.21).

The results of the application of this expression, with I calculated from local-density-functional theory, have been described elsewhere.[58] It was found that, although the temperature dependence was qualitatively similar to the data of Reywald *et al.*,[59] both the calculated absolute magnitude and T dependence were only $\sim 15\%$ of the experimental values. The orbital susceptibility can certainly account for much of the discrepancy in magnitude, as well as for some of the T dependence which arises from the variation of ζ with temperature. However, it seems likely that disorder contributions to χ_{sp} other than those entering Eq. (6.30) through N_{eff} will be necessary for a more quantitative theory.

VII. CONCLUSION

A generalized formulation of the Eliashberg approach to the electron self-energy has been developed which is valid for crystals for which the electronic spectrum varies on the scale of phonon frequencies. The formulation has been kept on the imaginary frequency axis where it is numerically tractable, and further numerical application of the theory to $A15$ compounds will be presented elsewhere. Although there is no difficulty in extending the formalism to the real axis,[12,60] the resulting calculational difficulties make this approach unattractive when detailed results are wanted.

The present generalization of Eliashberg theory proposes a system of equations for describing the superconducting onset at T_c as well as the gap and renormalization functions below T_c. Calculations at and below T_c have shown that tunneling spectra[13,27] as well as thermodynamic behavior[60] can be significantly altered by DOS structure. In addition, it is proposed that the self-consistent approach of Eliashberg be extended above T_c to determine the *normal-state electronic self-energy*. This theory lays the foundation for a more unified picture of the relationship between high-temperature superconductivity and the anomalous normal-state behavior of $A15$ compounds, as in the conclusion that the temperature dependence of the susceptibility is increased substantially by the strong electron-phonon interaction.

The satisfying agreement between the calculational results discussed in Sec. V and the experimental data indicates that (1) the present proposal for the self-energy (Fig. 1) is adequate at low temperature, and (2) the DOS for Nb_3Sn calculated by Klein *et al.* is realistic. The disagreement between the theoretical and experimental susceptibility is certainly too large to be ascribed to an incorrect theoretical DOS function. A conceivable source of this discrepancy is that this *ansatz* for the self-energy is inadequate for temperatures approaching the Debye frequency; it is known (see Allen, Ref. 21) that even in CDOS systems there are further adiabatic corrections to Σ which cannot be shown to be small. However, I consider it more likely that the expression (6.34) for χ_{sp} is insufficient.

An important area which has not been addressed in this paper is the normal-state specific heat C_v, which has been used often to extract empirical values of $N(E_F)$. Let us assume, as the simplest situation, that the specific heat can be divided into

electron and phonon contributions, as was shown to be the case for CDOS systems by Grimvall.[61] Generalizing Grimvall's general relation Eq. (A7) along the lines of the present theory leads to additional contributions to $C_{v,e}$ due to DOS variation, arising from the temperature variation of ζ and of $\gamma(\omega)$. Grimvall[61] has already concluded that $C_{v,e}$ is "far from linear at $T \simeq T_c$" for certain strong coupling superconductors. In addition, many $A15$ compounds are known to have highly anharmonic phonons, which complicates the identification of $C_{v,ph}$. Thus much theoretical work remains before the measured specific heat can be used to deduce detailed information about variation in $N(E)$.

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APPENDIX A

The usual expression[15,20] for the Coulomb pseudopotential $\bar{U}$ generalizes in the present case to

$$\bar{U}(k,k';0)=\bar{V}(k,k';0)+T\sum_{\omega_n,\,\omega_n>\omega_c}\sum_{k''}\frac{\bar{V}(k,k'';i\omega_n)\bar{U}(k'',k';0)}{[E_{k''}-\zeta+\chi(k'',i\omega_n)]^2+Z(k'',i\omega_n)^2[\omega_n^2+\Delta(k'',i\omega_n^2)]}\,. \tag{A1}$$

The treatment to this point ignores the possibility of spin fluctuation contributions and also assumes[15(c)] that $\bar{V}$ is essentially positive, eliminating the consideration of enhancement of superconductivity by plasmon or exciton mechanisms. In principle, the dynamically screened Coulomb interaction $\bar{V}$ includes Coulomb renormalization and Coulomb vertex corrections.

For the "frequencies" ω_n and energies $E_{k''}$ of interest in Eq. (A1) it suffices to ignore the self-energy corrections to the denominator. Performing the energy surface averages leads to

$$\bar{\mu}^*(E,E')=\bar{\mu}(E,E')+T\sum_{\omega_n,\,\omega_n>\omega_c}\int dE''\bar{\mu}(E,E'')\frac{N(E'')}{E''^2+\omega_n^2}\bar{\mu}^*(E'',E')\,. \tag{A2}$$

To make contact with later notation $\bar{\mu}^*(E,E') \equiv \bar{U}(E,E';0)$ and $\bar{\mu}(E,E')\equiv\bar{V}(E,E';0)$ have been introduced, and also the frequency dependence of $\bar{V}$ has been ignored.

Assuming further that

$$\bar{\mu}(E,E')=\begin{cases}\bar{\mu}, & |E|,|E'|<\omega_{pl}\\ 0 \quad \text{otherwise}\end{cases} \tag{A3}$$

and that $N(E)$ vanishes for $|E|>\omega_{pl}$, one finds

$$1/\bar{\mu}^*=1/\bar{\mu}+L(\omega_c,\omega_{pl})\,, \tag{A4}$$

where

$$L(\omega_c,\omega_{pl})\equiv T\sum_{\omega_n,\,\omega_n>\omega_c}\int_{-\omega_{pl}}^{\omega_{pl}}dE\frac{N(E)}{E^2+\omega_n^2}\,. \tag{A5}$$

For a specific model of $N(E)$, L can be evaluated explicitly. Given the level of approximation leading to Eq. (A4) however, it suffices to note that

$$L(\omega_c,\omega_{pl})\approx\bar{N}(\omega_{pl})I(\omega_c,\omega_{pl})\approx\bar{N}(\omega_{pl})\ln(\omega_{pl}/\omega_c)\,, \tag{A6}$$

where $\bar{N}(\omega_{pl})$ is the mean DOS over a region $E_F\pm\omega_{pl}$ and $I(\omega,\omega')$ (introduced by Allen[15(e)]) is the function $L(\omega,\omega')$ with $N(E)$ replaced by unity. In the (strict) CDOS limit $\bar{N}(\omega_{pl})\to N(E_F)$, the usual expression

$$1/\mu^*=1/\mu+\ln(\omega_{pl}/\omega_c) \tag{A7}$$

is recovered, where $\mu=N(E_F)\bar{\mu}$ and $\mu^*=N(E_F)\bar{\mu}^*$. However, the CDOS limit of Eliashberg theory applies if $N(E)$ is approximately constant over the range $E_F\pm\omega_c$, in which case a more precise expression for μ^* is given by

$$1/\mu^*=1/\mu+[\bar{N}(\omega_{pl})/N(E_F)]\ln(\omega_{pl}/\omega_c)\,. \tag{A8}$$

This relation is discussed further in the text.

APPENDIX B

The calculations described in this paper require the self-consistent solution of the $N_c \times N_c$ matrix equations (2.5), (3.12), and (4.1)–(4.3). Two techniques used in the present computations will be described briefly here.

These equations have the feature that the low-frequency (small $|\omega_n|$) rows and columns are in some sense more critical for obtaining convergence than those of larger frequency. It has been found that the technique used by Allen[62] of using the solution of the $m \times m$ subsystem as an approximate solution of a larger subsystem provides an efficient method of providing an iterative solution of the system of equations. The sequence $m = 1,2,4,8,\ldots,N_c$ used by Allen has been used here, with $N_c = 128$ for all calculations described in this paper.

The only arbitrary assignments in this procedure occur in setting initial values of N_n and P_n. The iteration is begun by setting $N_0 = N(E_F)$, $P_0 = 0$, then calculating Z_0, χ_0, Δ_0, and $\zeta^{(0)}(T)$, the first approximation to $\zeta(T)$ (see below). Then N_0 and P_0 are recalculated until self-consistency is obtained. In proceeding from the solutions of $m \times m$ subsystem to the $2m \times 2m$ subsystem, the assignment

$$\begin{Bmatrix} N_j \\ P_j \end{Bmatrix} = \begin{Bmatrix} N_m \\ P_m \end{Bmatrix}, \quad m < j \leq 2m \tag{B1}$$

was made. A search for more sophisticated extrapolations of these functions did not result in significantly more efficient solutions.

A crucial step in attaining reasonably accurate solutions to this system is finding a procedure for determining $\zeta(T)$ from Eq. (2.5). The free Green's function G_0, for instance, gives rise to the Fermi-Dirac distribution function f_0

$$f_0(E) = T \sum_n G_0(E, i\omega_n) e^{i\omega_n \epsilon} \tag{B2}$$

only after an *infinite summation;* truncation of the frequency sum in Eq. (B2) at any point leads to a function which is nonexponential. In the present calculation ζ has been evaluated as follows.

For the $m \times m$ subsystem, $m = 1,2,4,\ldots,N_c$, we make the definition

$$Z_j = \Delta_j = \chi_j = 0, \quad j > m \ . \tag{B3}$$

Then Eq. (2.5) can be written

$$\begin{aligned} N_e &= 2T \sum_{n \geq 0} \int dE\, N(E) \mathrm{Re} G(E, i\omega_n; \zeta) e^{i\omega_n \epsilon} \\ &= 2T\, \mathrm{Re} \int dE\, N(E) \sum_{n \geq 0} \{ G_0(E, i\omega_n; \zeta) + [G(E, i\omega; \zeta) - G_0(E, i\omega; \zeta)] \} \\ &= 2 \int dE\, f_0(E - \zeta) N(E) + 2T\, \mathrm{Re} \sum_{n=0}^{m} \int dE\, N(E) [G(E, i\omega_n; \zeta) - G_0(E, i\omega_n; \zeta)] \ . \end{aligned} \tag{B4}$$

The relation $G(E, -i\omega_n) = G(E, i\omega_n)^*$ has been used in writing the sums over $\omega_n > 0$ only. The dependence on ζ, the *interacting chemical potential,* has been displayed explicitly to emphasize that introducing $G_0(E, i\omega_n; \zeta)$ and $f_0(E - \zeta)$ is merely a mathematical method for evaluating the infinite summation. In particular,

$$2 \int dE\, f_0(E - \zeta) N(E) \neq N_e \ . \tag{B5}$$

Finally, *the noninteracting chemical potential* $\zeta_0(T)$, determined by

$$N_e = \int dE\, f_0(E - \zeta_0) N(E) \ , \tag{B6}$$

was used to write the equation determining ζ as

$$2T\, \mathrm{Re} \sum_{n=0}^{m} \int dE\, N(E) [G(E, i\omega_n; \zeta) - G_0(E, i\omega_n; \zeta)] = 2 \int dE\, [f_0(E - \zeta_0) - f_0(E - \zeta)] N(E) \ . \tag{B7}$$

This equation is solved iteratively for ζ at each step of the iteration of the system of equations.

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Renormalized Thermal Distribution Function in an Interacting Electron-Phonon System

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The electron-phonon interaction is used to demonstrate the important effect of interactions on the electronic distribution function at finite temperature. It is shown that the usual picture of "thermal (Fermi) smearing" is a greatly oversimplified one. The distribution function resulting from an Einstein spectrum with various coupling strengths is presented and interpreted, and an exact expression for the spin susceptibility is used to illustrate the utility of this novel viewpoint for thermodynamics.

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One of the primary characteristics of a metal at a finite temperature T is that the crystalline electronic eigenstates (labeled by index k) of energy E_k are occupied according to a thermal distribution $f(E_k)$. Almost universally in the theory of metals this distribution is taken to be that of *noninteracting* fermions, i.e., the Fermi-Dirac distribution $f_0(E_k)$. Typically this assumption appears as a thermal broadening ("Fermi smearing"), given by $-df_0(E)/dE$, of some quantity over a region around the Fermi energy E_F. The effect of interactions, if included at all, is not introduced into the occupation function. For systems where the density of states (DOS) function $N(E)$ varies sufficiently slowly near E_F thermal averaging is expected to be insensitive to the actual form of f. For varying DOS systems, however, of which the $A15$ class of compounds provides the canonical example,[1] the understanding of their anomalous thermal behavior may depend critically on the proper description of f and df/dE.

Two questions arise: What is the effect of interactions on the thermal distribution f, and is our understanding of thermodynamic properties clarified by a viewpoint which includes interactions in f? In this paper we use the example of the electron-phonon (EP) interaction to show that f, and thereby the interpretation of thermodynamic quantities, can be radically altered by interactions.

The distribution function $f(E_k)$ is defined as the thermal expectation of the number operator $\hat{n}_k$. For $T>0$, f is given in general in terms of the thermodynamic Green's function G by the relation[2]

$$f(E_k)=T\sum_{n=-\infty}^{\infty}G(k,i\omega_n)\exp i\omega_n\eta, \tag{1}$$

where $\omega_n=(2n+1)\pi T$ and η is a positive infinitesimal. (In our units $\hbar=k_B=1$, and for simplicity an isotropic approximation for electrons will be used.) It is easily verified that (i) in the absence of interactions, $f=f_0$, and (ii) by converting the sum to a contour integral f can be written

$$f(E_k)=\int_{-\infty}^{\infty}d\omega f_0(\omega)A(k,\omega) \tag{2}$$

in terms of the spectral density A. Evidently $f=f_0$ *if and only* if A is a δ function at $\omega=E_k$. When A is broadened by interactions, f can differ considerably from f_0 (a result not often stated in quantum statistical theory texts), as I now explicitly demonstrate.

For simplicity let us initially consider a constant-DOS electronic system interacting with an Einstein phonon spectrum with EP spectral function α^2F given by

$$\alpha^2F(\omega)=(\lambda\Omega/2)\delta(\omega-\Omega), \tag{3}$$

where Ω is the Einstein frequency and λ is the EP coupling constant. A straightforward calculation of the electronic self-energy $\Sigma=M-i\Gamma$ on the real axis gives, with energies measured relative to E_F,

$$M(\omega)=-(\lambda\Omega/2)\mathrm{Re}\left\{\psi\left(\frac{1}{2}+\frac{\omega+\Omega}{2\pi iT}\right)+\psi\left(\frac{1}{2}+\frac{\omega-\Omega}{2\pi iT}\right)\right\}, \tag{4}$$

$$\Gamma(\omega)=(\pi\lambda\Omega/2)\{f_0(\Omega-\omega)+f_0(\Omega+\omega)+2n_0(\Omega)\}\,\mathrm{sgn}(\omega). \tag{5}$$

Here ψ and n_0 denote the digamma and Bose-Einstein functions, respectively. The spectral density is

given simply by (ζ = chemical potential)

$$A(k,\omega)=\frac{1}{\pi}\left|\mathrm{Im}\,\frac{1}{\omega-(E_k-\zeta)-\Sigma(\omega)}\right|. \tag{6}$$

In Fig. 1 I display $M(\omega)$ and $\Gamma(\omega)$ for several values of T. Spectral functions at $T=0$ have been studied previously by Engelsberg and Schrieffer[3] and by Shimojima and Ichimura,[4] who find that, even for $|E_k-E_F|\lesssim\Omega$, spectral weight is spread over a region of *several times* Ω around E_F. At $T>0$ this spread is further increased because of the increasing width $\Gamma(\omega)$ (Fig. 1). Neither of the previous studies have noted the affect of EP interactions on the distribution function.

The change in f due to EP interaction is represented most easily in unitless differential form $-T df/dE \equiv -f'$. The results, for several values of T and λ, are presented in Fig. 2 for $E>\zeta\equiv 0$. [Note that $f'(E)=f'(-E)$.] At $T=\Omega$ Fig. 2(a) indicates that increasing λ leads to the displacement of weight in $-f'(E)$ (i.e., occupation of bare electron and hole states) from the region $|E-\zeta|\lesssim 2\Omega$ to the higher excitation energy tails. At $T=\Omega/2$ [Fig. 2(b)] the behavior is similar. However, as the frequency dependence of Σ becomes sharper at $T\ll\Omega$ (Fig. 1), qualitatively new behavior—negative weighting near ζ—can occur at low energy, as shown in Fig. 2(c) for $T=\Omega/4$. This unusual behavior is exaggerated by the Einstein spectrum used here, although similar behavior may occur even for a realistic spectrum at lower temperatures. General features of $-f'$ include these: (a) at high energy $|E-\zeta|>\Omega$ it decreases as a Lorentzian of width $\Gamma=(\pi\lambda\Omega/2)[1+2n_0(\Omega)]$ rather than exponentially as does $-f_0'$, (b) at high $T\gtrsim\Omega$, $-f'$ is essentially Lorentzian $[\Gamma\approx\pi\lambda\Omega n_0(\Omega)]$ everywhere, and (c) the behavior at $T=0$ is as given previously by Shimojima and Ichimura[4]: f possesses a discontinuity of $(1+\lambda)^{-1}$ at ζ, which indicates that the Fermi surface remains sharp, and $-f'$ has a δ-function contribution of corresponding amplitude, with the remaining weight $\lambda/(1+\lambda)$ displaced over the range

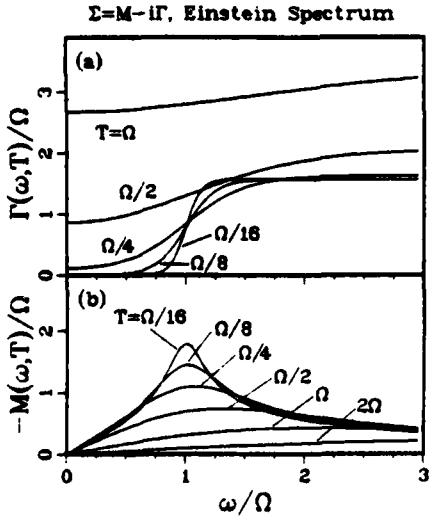

FIG. 1. Electron self-energy $\Sigma(\omega)=M(\omega)-i\Gamma(\omega)$ for an Einstein spectrum at energy Ω, for several temperatures T. The self-energies are proportional to λ and are shown for $\lambda=1$.

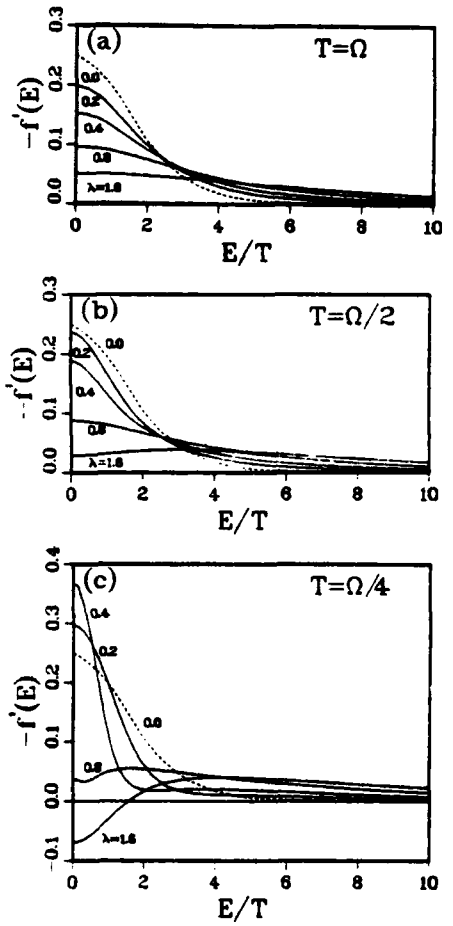

FIG. 2. The derivative $-f'(E)=-Tdf(E)/dE$ of the thermal distribution function f calculated from Eqs. (2) and (6) and the self-energies of Fig. 1, for several values of λ. The dashed line shows $-f'(=-f_0')$ in the absence of electron-phonon interaction ($\lambda=0$). Note that interactions broaden the thermal distribution considerably even for modest values of λ at all temperatures.

$|E - E_F| \sim \lambda\Omega$.

For systems in which the electronic spectrum varies on the scale of Ω, Σ becomes a functional[5] of $N(E)$ and the computation of f becomes correspondingly more involved. However, because of the substantial widths in the spectral density peaks for finite ω and/or T, the qualitative behavior of $-f'$ will generally reflect that of the constant-DOS model. The proper interpretation of thermodynamic properties, however, can be substantially altered in nonconstant-DOS systems, as will now be shown.

The case of the spin susceptibility χ_{sp} will be used to demonstrate that the renormalized thermal smearing function $-f'$, rather than $-f_0'$, often arises naturally in the formalism. That this should be the case is suggested by the relationship [Eq. (1)] between f and the (renormalized) Green's function G on the one hand, and the expansion of the thermodynamic potential, which is accomplished most concisely[6] in terms of G (rather than G_0), on the other. The conservation of electron number N_{el}, for example, is given naturally as the thermal redistribution of crystalline states:

$$N_{el} = 2\int dE\, f(E-\zeta)N(E), \tag{7}$$

although it can also be written

$$N_{el} = 2\int d\omega f_0(\omega-\zeta)\mathfrak{N}(\omega) \tag{7'}$$

in terms of a noninteracting electron distribution over a *broadened and renormalized* DOS[7] $\mathfrak{N}$ given by

$$\mathfrak{N}(\omega+\zeta) = \int dE\, N(E)A(E-\zeta,\omega). \tag{8}$$

This is simply a question of whether the ω or E integral is carried out first. However, from the magnetization $\mathfrak{M}$, given by[6]

$$\mathfrak{M} = \mu_B \sum_{\sigma=\pm} \sigma N_\sigma = \mu_B \sum_{\sigma=\pm} \sigma \int dE\, N(E) T\sum_n G_\sigma(E, i\omega_n)\exp i\omega_n\eta, \tag{9}$$

in terms of the number N_σ of spin σ electrons, χ_{sp} can be written *exactly* (within this isotropic treatment) as

$$\chi_{sp} = \frac{d\mathfrak{M}}{dH}\bigg|_{H=0} = -\mu_B \sum_{\sigma=\pm} \sigma \int dE\, N(E) T\sum_n G_\sigma^2(E, i\omega_n) \frac{dG_\sigma^{-1}(E, i\omega_n)}{dH}\exp i\omega_n\eta\bigg|_{H=0}$$

$$= 2\mu_B^2 \int dE\, N(E)\left[-\frac{df(E-\zeta)}{dE}\right][1+K(E,T)], \tag{10}$$

where $-df/dE$ is identified by differentiating Eq. (1) with $G_\sigma^{-1}(E, i\omega_n) = i\omega_n - (E - \zeta - \sigma\mu_B H) - \Sigma_\sigma(i\omega_n)$, and the thermal average K of the field derivative of the self-energy is defined by

$$K(E,T) = -T\sum_n G^2(E, i\omega_n)\frac{d\Sigma_\sigma(i\omega_n)}{d(\sigma\mu_B H)}\bigg|_{H=0}\left[T\sum_n G^2(E, i\omega_n)\right]^{-1}. \tag{11}$$

Equation (10) gives an interpretation of χ_{sp} as arising from the bare DOS, appropriately enhanced by $1+K$ and averaged around ζ according to the *interacting* thermal smearing function. Equation (10) gives directly an enhancement due to the EP interaction of the T dependence of χ_{sp} arising from a peak in $N(E)$, as surmised by Bhatt[8] for low temperature.

Essentially all other interpretations of $\chi_{sp}(T)$ have assumed a form like Eq. (10) with $f \to f_0$. By means of the standard analytic continuation[3] to express the frequency sum in Eq. (9) in terms of an integral over real frequencies, χ_{sp} can be written *in terms of* f_0 as two contributions $\chi_{sp}^{(0)} + \chi_{sp}^{(1)}$:

$$\chi_{sp}^{(0)} = 2\mu_B^2 \int d\omega \left(-\frac{\partial f_0}{\partial\omega}\right)\mathfrak{N}(\omega+\zeta), \tag{10'}$$

which is *reminiscent of but not identical* to the first (unenhanced) term in Eq. (10), and the "enhancement"

$$\chi_{sp}^{(1)} = -\frac{2\mu_B^2}{\pi}\,\mathrm{Im}\int_{-\infty}^{\infty} d\omega \int dE\, N(E) G^R(E,\omega)\frac{\partial}{\partial\omega}\left\{f_0(\omega)\frac{\Sigma_H' - \Sigma_\omega'}{1-\Sigma_\omega'}\right\}, \tag{10''}$$

where $\Sigma_H' = d\Sigma_\sigma^R/d(\sigma\mu_B H)|_{H=0}$ and $\Sigma_\omega' = \partial\Sigma^R/\partial\omega$ (superscript R denotes retarded functions).

The simplicity of Eq. (10), and a general knowledge of the behavior of $-\partial f/\partial E$ from Fig. 2, allows one to identify the underlying causes of thermal anomalies in exotic systems. In V_3X compounds, for example, the strong T dependence of χ correlates closely[10] with high superconducting T_c, and thus with large λ, exactly as Eq. (10), with a peak in $N(E)$ near ζ and broadening proportional to λ, suggests. It is also evident that the incluence of the lattice should lead to an isotope effect on the critical temperature for itinerant-electron magnetism distinct from that proposed by Hopfield.[11] Neither of these properties is evident in the form given in Eqs. (10′) and (10″).

In terms of the two questions posed at the outset, (1) the behavior of f is qualitatively as shown in Fig. 2 and is of itself useful and perhaps necessary in interpreting thermodynamic behavior, and (2) f has been shown to arise simply and naturally in the expression for χ_{sp}. In general, each thermodynamic quantity must be investigated individually for a useful expression involving f and/or f_0. It is encouraging that Lee and Yang[12] have shown that thermodynamics can be formulated *exactly* in terms of f, although the author is unaware of any application of their very formal approach to metals.

A contrast can be drawn between the present viewpoint and that of Fermi-liquid theory.[7] The latter approach describes the *low-temperature* thermodynamic properties in terms of *noninteracting* quasiparticles described by f_0 and a *renormalized* quasiparticle density of states $\mathcal{N}$. Typically $\mathcal{N}$ is a constant for excitations of interest, and this approach has been very successful for *phenomenological* descriptions. It is proposed here that viewing the interactions as distributing the excitations over the noninteracting spectrum will prove a more useful approach when variation of $N(E)$ is important. This formulation provides a *conceptual* basis as well as a *computational* approach for the detailed understanding of many classes of interesting compounds.

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THEORY OF THE NORMAL STATE HEAT CAPACITY OF Nb_3Sn

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The experimental α^2F of Wolf et al is applied to calculate the T-dependence of the electronic heat capacity. It is found that, if the phonon spectrum is Debye-like (which is not the case in Nb_3Sn), this T-dependence results in an extrapolated value of $N(E_F)(1+\lambda)$ which is overestimated by an amount which is proportional $N(E_F)\lambda$, equal to 13% for Nb_3Sn. It is further shown that the change in slope of C/T found by Stewart, Cort and Webb can be modeled by a combined Debye and Einstein spectrum with $\theta_D = 267$ K and having 1.5% of the acoustic modes at an Einstein frequency $\Omega = 40$ K.

I. INTRODUCTION

The specific heat of Nb_3Sn has long been an enigma. Vieland and Wicklund (1968) fit the normal state specific heat $C_n(T)$ above the superconducting transition temperature $T_c = 18$ K to the form

$$C_n/T = \gamma + \beta T^2.$$

However, the inferred normal state entropy $S_n(T_c)$ obtained by extrapolating this form below T_c was 14% larger than the measured entropy in the superconducting state $S_c(T_c)$, strongly violating the thermodynamic constraint $S_n(T_c) = S_c(T_c)$ for a second order phase transition. Thus, although C_n had assumed the "low temperature form" of Eq. (1) in the range of their measurements, it was evident that this form must change at still lower temperatures.

Recently Stewart, Cort and Webb (1981) (hereafter referred to as SCW) have resolved this particular enigma by measuring C in fields up to 18 T, which lowers T_c to around 6.5 K. The Vieland-Wicklund form was found to hold down to 12-13 K, whereupon the slope rapidly changed to give $\theta_D = 207$ K and an extrapolated $\gamma = 35 \pm 3$ mJ/mole K^2 at zero temperature compared to $\gamma = 96$ mJ/mole K^2 from above 13 K. Although this new extrapolation satisfies the entropy constraint, the interesting question arises as to what causes the rapid change in slope ("knee" or "kink") between 10 K and 12 K.

In this paper we initiate an investigation into this unusual and unexpected behavior. We assume at the outset, following the argument of Grimvall (1969), that even in systems in which the electron and phonon subsystems are strongly interacting, the specific heat nevertheless can be separated into two parts interpreted as due to renormalized electrons and renormalized phonons. It is not clear how this approach is to be reconciled with Allen and Hui's (1980) observation that the effects of electron-phonon (EP) interaction appear to be double-counted in such an approach. Furthermore, Grimvall's analysis does not take anharmonicity of the phonon system into account, while the phonons are known to show strong temperature variation in Nb_3Sn. For the present study, however, we shall proceed to investigate the heat capacity of Nb_3Sn in terms of the usual electron/phonon separation.

II. ELECTRONIC HEAT CAPACITY

Grimvall (1969) has shown how Prange and Kadanoff's (1964) generalized quasiparticle expression for the electronic heat capacity

$$C_{n,e}(T) = 2N(E_F)\int dE\, E\left\{\left[1 - \frac{\partial M(E,T)}{\partial E}\right]\frac{\partial f(E)}{\partial T} + \frac{\partial M(E,T)}{\partial T}\frac{\partial f(E)}{\partial E}\right\} \tag{1}$$

can be derived from field theoretical considerations. Here M is the real part of the electronic self-energy, f is the Fermi function and other quantities have their usual meanings. Using standard expressions for M this can be written explicitly as

$$C_{n,e}(T) = [\gamma_0 + \gamma_1(T)]T \equiv \gamma(T)T, \tag{2}$$

with

$$\gamma_0 = (2\pi^2/3)\, N(E_F)\, k_B^2 \tag{3}$$

and

$$\gamma_1(T)/\gamma_0 = \frac{3}{(\pi k_B T)^2}\int dE \int dE' \frac{\partial f(E)}{\partial E}\frac{\partial f(E')}{\partial E'}\int d\omega\, \alpha^2F(\omega)\frac{(E-E')^2}{E-E'+\omega}, \tag{4}$$

where α^2F is the electron-phonon spectral function.

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Equation (4) has been evaluated previously for an Einstein model (Grimvall 1968), for Pb and Hg (Grimvall 1969) and for amorphous Pb (Bergmann *et al* 1971). Here we use the α^2F function for Nb_3Sn obtained by the inversion of tunneling data by Wolf *et al* (1980) to evaluate Eq. (4). In Fig. 1 we show the result for $C_{n,e}/\gamma_0 T = 1 + \gamma_1(T)/\gamma_0$ in the range 0 to 200 K. The result is similar to those of Pb and Hg (scaled to the stiffer phonon spectrum of Nb_3Sn). At 9 K γ_1 peaks at a value 10% higher than its value $\lambda\gamma_0$ ($\lambda = 1.78$) at $T = 0$. Then γ_1/γ_0 decreases rapidly, reaching its minimum value of -0.24 at approximately 100 K.

This drop in $C_{n,e}$ *below* $\gamma_0 T$ has interesting implications. The thermal mass enhancement γ_1 is proportional to the magnitude of α^2F, i.e., λ, and its shape depends only on the shape of α^2F. As λ is increased, $C_{n,e}$ will vanish at the temperature at which γ_1 has its minimum for a critical value λ_c of λ, and will become negative for a range of temperatures when $\lambda > \lambda_c$. For α^2F having the Nb_3Sn shape $\lambda_c = 7.4$. For the Pb shape $\lambda_c = 8.2$ and the minimum in γ_1 occurs near 35 K. for an Einstein spectrum (which gives the sharpest structure possible) $\lambda_c = 3.7$ and the minimum occurs near $k_B T = \hbar\Omega_{Einstein}/2$. This negative "electronic" specific heat causes no obvious violation of thermodynamic principles, since increasing λ will lead to a softening of the phonon spectrum and thus an increase in the "lattice" contribution, which should keep the total heat capacity positive. (The condition $C \geq 0$ can be used to put a weak constraint on how hard the phonon spectrum can be.) Nevertheless, this behavior raises further questions into the separation of C into "electronic" and "lattice" contributions in strongly interacting EP systems.

It is now widely accepted that variation of $N(E)$ on the scale of phonon energies is a likely occurrence in high T_c A15 compounds, Nb_3Sn in particular. In such a case the expression for $C_{n,e}$ is altered in several ways. Following Grimvall's (1969) derivation of Eq. (1), variation of $N(E)$ near E_F results in an explicit dependence of $C_{n,e}$ on the imaginary part Γ of the electronic self-energy (also see Grimvall 1978); i.e., a breakdown of the generalized quasiparticle expression Eq. (1). This dependence will be neglected for reasons to be discussed below. Then Eq. (1) is modified by replacing $N(E_F)$ by $N(E)$ under the integral, with a similar replacement in the equation defining $M(E, T)$ (see Grimvall 1969). Finally one obtains

$$\gamma_1(T) \propto \frac{3}{(\pi k_B T)^2} \int dE\, N(E) \int dE'\, N(E')) \frac{\partial f(E)}{\partial E} \frac{\partial f(E')}{\partial E'} \int d\omega\, \alpha^2F(\omega)\, \frac{(E - E')^2}{E - E' + \omega}, \quad (5)$$

with the normalization $\gamma_1(0) = \lambda$. Equation (5) has been evaluated by Fradin (1975, 1977) for a model $N(E)$ function thought to be appropriate for V_3Ga, but no comparison with experiment was attempted.

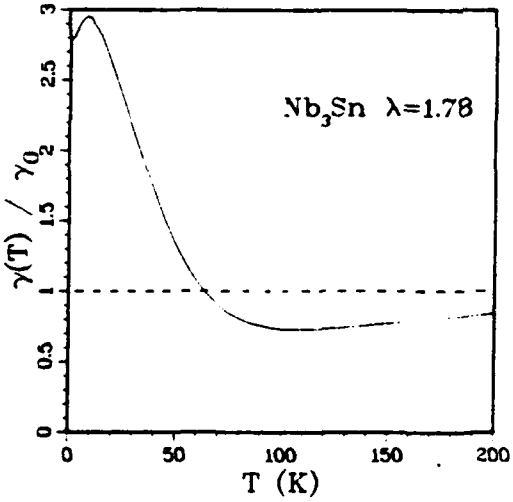

Fig. 1 — The variation of $\gamma/\gamma_0 = 1 + \gamma_1/\gamma_0$ with temperature in Nb_3Sn. The difference between this curve and unity is proportional to λ.

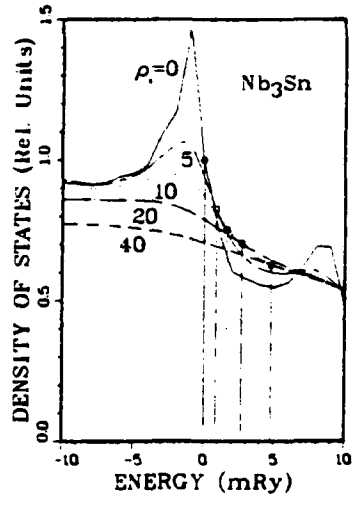

Fig. 2 — Density of states near $E_F = 0$ of Nb_3Sn (solid line) from Klein et al (1978). Also shown are the effects of defect scattering due to 5, 10, 20 and 40 $\mu\Omega$ cm of residual resistivity. Vertical lines denote the respective Fermi energies. The 10 $\mu\Omega$ cm curve is used for the calculations described in the text.

We have evaluated Eq. (5) for Nb_3Sn using the experimental data for α^2F and the $N(E)$ function calculated by Klein *et al* (1978). Since Nb_3Sn samples invariably have a residual resistivity of 10 $\mu\Omega$ cm (or more), we have broadened $N(E)$ accordingly (Pickett 1982). These $N(E)$ functions and the shift in E_f due to smearing are pictured in Fig. 2. It should be noted that $N(E)$ functions with even sharper structure than that calculated by Klein *et al* will not lead to broadened $N(E)$ functions with significantly more structure than the "10 $\mu\Omega$ cm" curve in Fig. 2.

In the range of interest here ($T \leqslant 30$ K) the temperature variation of the chemical potential is negligible. In this range γ_1 from Eq. (5) differs from that of Eq. (4) by less than 0.2%. This null correction results because $N(E)$ is essentially linear in the energy region sampled by Eq. (5) at these temperatures, and increased weighting at $E < E_F$ is cancelled by decreased weight at $E > E_F$. This is also why the contribution to $C_{n,e}$ from $\Gamma(E, T)$ (mentioned above) is negligible. This contribution arises only from *changes* due to the *energy variation* of $N(E)$, and for a linear variation these changes are vanishingly small. Even if E_F is artifically placed at the peak of the "10 $\mu\Omega$ cm" curve in Fig. 2, where the effect is largest, the correction is only 2% at 30 K.

It remains to determine the effect of the variation of γ_1 upon the interpretation of C_n. In Fig. 3 $\gamma(T) = C_{n,e}/T$ is plotted versus T^2 along with the normal state experimental data of SCW. On the scale shown the peak in $\gamma(T)$ is comparitively weak and has little to do with the knee in the data, despite the fact that both structures occur in the same temperature range. However, above 12 K the curve is approximately linear, with slope $\beta = -0.014$ mJ/mole K^4. Removing this linear contribution from the linear fit to the data above 12 K results in $\theta_D = 267$ K in this region, rather than the SCW value of 270 K.

The temperature variation of γ_1 can lead to a more significant correction to the extrapolated value of $\gamma_0(1 + \lambda)$. Assuming the lattice contribution $C_{n,e} = \beta T^3$ (i.e., extrapolates to zero), the approximately linear decrease in $\gamma_0 + \gamma_1$ vs T^2 above the peak in γ_1 leads to an overestimate of $\gamma(0) \sim N(E_F)(1 + \lambda)$ which is proportional to $N(E_F)\lambda$. For Nb_3Sn this overestimate is 13%. If $N(E_F)$ is known independently, the overestimate of λ is further leveraged by $(1 + \lambda)/\lambda$, equal to 20% for Nb_3Sn. Use of incorrect values of $N(E_F)$ can of course lead to worse empirical estimates of λ. This overestimate of $\lambda(0)$ in itself can lead to an apparent violation of the entropy constraint mentioned in the Introduction. For the actual data for Nb_3Sn above 12 K, where the phonon contribution does not extrapolate to zero, the overestimate of $\gamma_0(1 + \lambda)$ is 4.7 mJ/mole K^2, a rather small fraction of the difference (61 mJ/mole K^2) between the high and low temperature extrapolations of SCW.

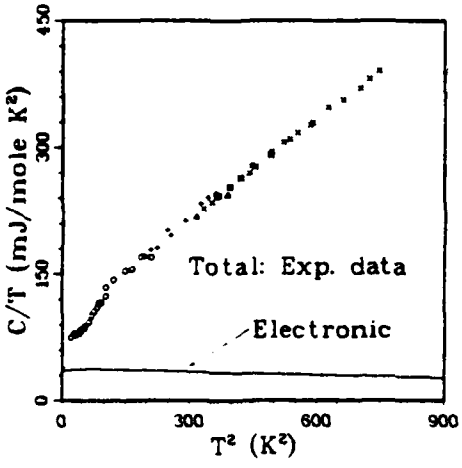

Fig. 3 — $C_{n,e}/T$ vs T^2 from 0 to 30 K. The calculated curve is normalized to 35 mJ/mole K^2 at $T = 0$. Data points (x, $H = 0$; +, 7 T; o, 18 T; Δ, 19 T) are normal state values at various magnetic fields (Stewart et al 1981). The lowest 6-7 data points reflect a broadened transition at $T_c = 6$ K in 18 T. The dotted line represents the extrapolation of Stewart et al (1981).

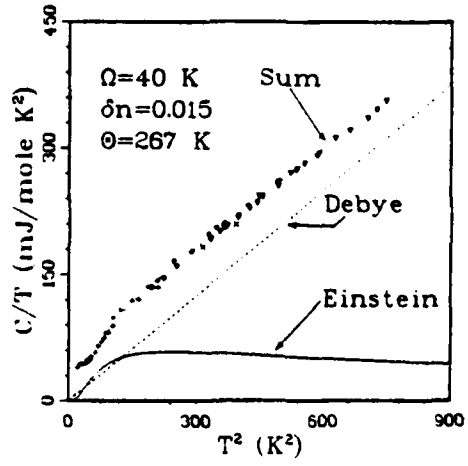

Fig. 4 — Normal state data points of Stewart et al (1981), with constant electronic contribution removed, compared with the Debye + Einstein model (plotted curves, see text).

III. LATTICE HEAT CAPACITY

The complexity of the lattice dynamics of Nb_3Sn makes a quantitative evaluation of the lattice heat capacity $C_l(T)$ impossible. "Good" samples—typically those with low residual resistivity—undergo a cubic-to-tetragonal transition at $T_m \sim 43$ - 51 K, as did the SCW sample. Definitive neutron scattering studies (Shirane and Axe 1971, 1978; Axe and Shirane 1973a,b) have uncovered a "soft mode" type of behavior of the $(\zeta,\zeta,0)$ T_1 branch: as T approaches T_m from above, the small ζ modes tend to disappear under a narrow central peak broadened by instrumental resolution, whereas for $T < T_m$ only broad scattering centered at zero energy transfer could be observed for $\zeta \leqslant 0.2$ (π/a). Thus the lattice dynamics are not only unknown but are also expected to be strongly anharmonic, at least near T_m.

We initially investigated two (spherically symmetric) acoustic phonon dispersion models with upward "kinks" in one TA branch, as found by Axe and Shirane (1973b) for $T > T_m$. In one of the models the branches were tied to the T-dependent sound velocities at $\zeta \to 0$. Both models displayed a smoothly increasing Debye temperature with temperature, qualitatively similar to the data, but neither could be fit even semiquantitatively to the data.

It is therefore surprising that the following, much simpler, model provides a *quantitative* fit to the SCW data above 8 K. We take a fraction δn of the acoustic modes to be modeled by an Einstein frequency Ω and assume the remaining $1 - \delta n$ to be characterized by a Debye temperature θ. The results for $\Omega = 40$ K $\simeq 3.5$ meV, $\delta n = 0.015$, $\theta = 267$ K are shown in Fig. 4 compared to the normal state data of SCW. (For this comparison we have neglected the small T-dependence of γ and subtracted out a constant electronic contribution of 35 mJ/mole K^2.) The model provides an excellent fit above $T^2 = 60$ K^2, with a possible small discrepancy in the range $100 \leqslant T^2 \leqslant 150$ K^2 where the data points are sparse. SCW concluded that an "abrupt change" occurs in this range, but a few more data points are needed to ascertain the abruptness. We emphasize that this model of the phonon spectrum should not be interpreted literally; it does not, for example, reproduce $\theta_D = 208$ K in the range $8 \leqslant T^2 \leqslant 20$ as is found from data taken in the superconducting state (Stewart *et al* 1981). Nevertheless it removes much of the mystery in the Nb_3Sn data by showing how an "excess" of soft modes can produce the observed behavior.

IV. FINAL POINTS

A question remains: why, SCW have asked, is the abrupt change in slope not observed in the superconducting state data? Again, the SCW data in the superconducting state are sparse in this range and it is the authors' opinion that structure in this region, where the electronic contribution is increasing rapidly, should not be ruled out. A definitive answer to this question will require a calculation of the electronic heat capacity in the superconducting state, as was done by Daams and Carbotte (1979) using earlier experimental data, in addition to more experimental data.

Finally we note that abrupt changes of slope of the C/T curve at low temperature are not uncommon; Nb shows such anomalies at 3 K and 9.5 K (see Leupold *et al* 1977 and references therein). Nb_3Sn is however unusual in the *magnitude* of the slope change.

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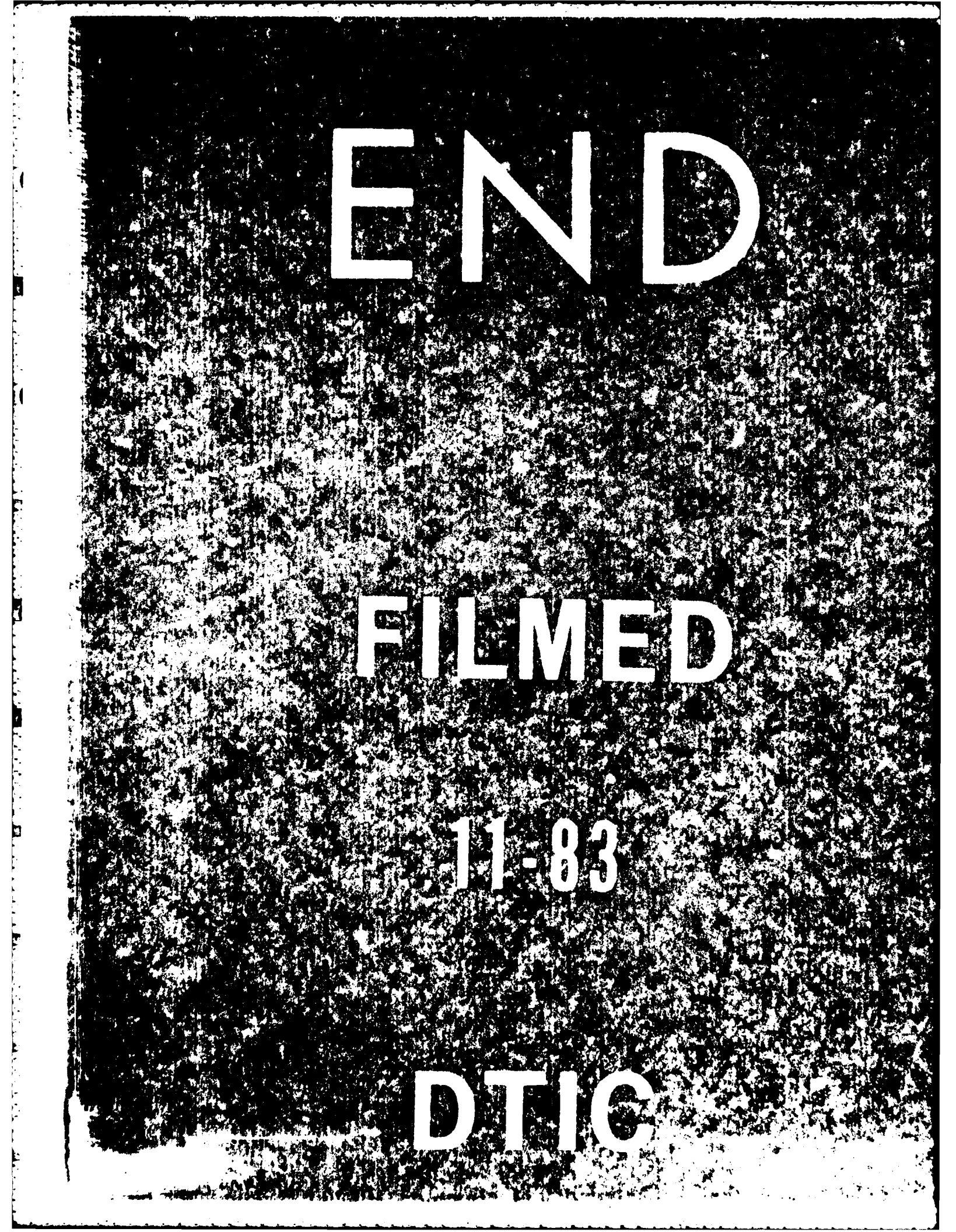
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