axis to be along the director $\hat{n}$, and Eq. (1) is consistent with the uniaxial symmetry of the liquid crystal. The condition $k_2^2 = k_1 k_3$ eliminates propagating shear modes, and the sound velocity is given by

$$c^2 = (1/\rho)[k_1 + (k_1 + k_3)\cos^2\theta], \tag{2}$$

which is of the form found experimentally in Fig. 2. However, the elastic constants must have an important frequency dependence, and as $\omega \to 0$ we would expect that $k_1 - k_3 \to 0$. If this were not the case, it would cost a finite energy to change the shape of a liquid crystal, the volume being kept constant. This is not consistent with our present ideas of the structure of a liquid crystal. The frequency dependence of the elastic constants could arise out of some structural relaxation process in the liquid crystal.[10] If we assume a single relaxation time τ_s for this process, then

$$k_3(\omega) - k_1(\omega) = k\omega^2\tau_s^2/(1+\omega^2\tau_s^2), \tag{3}$$

where k is a constant. It would be expected that $k\tau_s$ is of the order of a viscosity coefficient, i.e., 0.1 P.[10] The relative anisotropy in the velocity of sound is thus

$$\Delta = (k/2\rho c^2)\omega^2\tau_s^2/(1+\omega^2\tau_s^2). \tag{4}$$

Taking $k\tau_s \sim 0.1$ P, $\rho \sim 1$ g/cm^3, $c = 1.5\times10^5$ cm/sec, and $\omega/2\pi = 9$ MHz, we find that $\Delta \sim 10^{-4}\, \omega\tau_s/[1+(\omega\tau_s)^2]$. This is in rough agreement with experiment for $\omega\tau_s \sim 1$. This leads to a relaxation time $\tau_s \sim 2\times10^{-8}$ sec which is very much longer than that found in ordinary liquids. The experimental frequency dependence of Δ is only in rough agreement with (4) which might indicate a spectrum of relaxation times. Figure 3 indicates that τ_s increases with temperature by a factor of ~ 3 from $T = 30$ to 44.4°C.

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Electron-Phonon Interactions, *d* Resonances, and Superconductivity in Transition Metals

G. D. Gaspari*† and B. L. Gyorffy
H. H. Wills Physics Laboratory, Royal Fort, Bristol, United Kindom

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A simple theory is developed for calculating the electron-phonon coupling constant λ.

Both for weak- and for strong-coupling superconductors, the important parameter which determines the transition temperature T_c is the electron-phonon coupling constant[1] λ. For simple metals one can reliably estimate λ by using pseudopotentials.[2,3] However, no such first-principle understanding of λ exists in the case of transition metals. As is well known, a transition-metal ion, in a solid, must be represented as a resonant scatterer of electrons and therefore cannot be described by a weak pseudopotential. Consequently, to evaluate λ one must perform a full band-structure calculation for the Fermi surface and the wave functions. As such calculations are fraught with extreme difficulties none as yet has been attempted. Our main purpose here is to show how λ may be estimated without such elaborate effort.

From McMillan's strong coupling theory[1] we have that in the rigid-ion, one-electron approximation

$$\lambda = n(\epsilon_F)\langle I^2\rangle / M\langle \omega^2\rangle, \qquad (1)$$

where M is the atomic mass; $\langle\omega^2\rangle$ is the renormalized phonon frequency, squared and averaged according to the prescriptions given in Ref. 1; $n(\epsilon_F)$ is the density of states for one type of spin at the Fermi energy ϵ_F; and $\langle I^2\rangle$ is the square of the electron-phonon matrix element averaged over the Fermi surface. By determining λ from the experimentally measured T_c, and $\langle\omega^2\rangle$ from neutron scattering experiments, McMillan has evaluated $n(\epsilon_F)\langle I^2\rangle$ for most of the superconducting metals. The striking feature of the result is that while both $n(\epsilon_F)$ and $\langle I^2\rangle$ vary considerably from element to element, $n(\epsilon_F)\langle I^2\rangle$ remains approximately constant (~ 7 eV/Å^2) for all the bcc transition metals.

We explain this experimental fact by deriving a simple approximate expression for $n(\epsilon_F)\langle I^2\rangle$ in terms of quantities which should be available from a conventional band-structure calculation. We evaluate this expression for iron and tungsten. The agreement between our predictions and experiments indicate that the theory gives an accurate estimate for $n(\epsilon_F)\langle I^2\rangle$. Furthermore, we show that our simple model is also relevant to the noble metals by calculating λ for Cu.

The characteristic feature of transition metals is that the electron-ion interaction potential $v(\vec{r})$ has a d resonance above the muffin-tin zero. As is well known this resonance lies near the Fermi energy and is believed to be responsible for many of the most striking properties of transition metals. From this point of view, the present work is an attempt to clarify the role played by such resonances in determining the strength of the electron-phonon interaction.

For a resonant scatterer, an electron with energy close to the resonance spends a relatively long time in the vicinity of the scatterer [the Wigner delay time $2\hbar\delta_2'(\epsilon_F)$ is long]. Under these circumstances it is reasonable to suppose that local effects, like the extra scattering due to the displacement of an ion, are dominated by the local potential. It is this feature of the problem we want to exploit in constructing our theory.

The importance of the local environment in determining the electron-phonon coupling constant was first stressed by Hopfield.[4] We follow his lead and write $\langle I^2\rangle$ using a real space representation as

$$\langle I^2\rangle = \frac{V^2}{(2\pi)^6 n^2(\epsilon_F)} \int d^3k \int d^3k' \int d^3r \int d^3r' \, \nabla v(\vec{r})\cdot\nabla v(\vec{r}\,') \, \psi_{\vec{k}}^*(\vec{r})\psi_{\vec{k}'}(\vec{r})\psi_{\vec{k}'}^*(\vec{r}\,')\psi_{\vec{k}}(\vec{r}\,') \, \delta(\epsilon-\epsilon_{\vec{k}})\,\delta(\epsilon-\epsilon_{\vec{k}'}), \qquad (2)$$

where $\psi_{\vec{k}}(\vec{r})$ is the one-electron Bloch function and $\epsilon_{\vec{k}}$ is the corresponding eigenvalue. Clearly, we only need the wave function in the vicinity of the ion at the origin since the potential $v(\vec{r})$ vanishes outside the muffin-tin well. This suggests that for a spherically symmetric potential we should expand the Bloch function in the following angular-momentum representation about the origin:

$$\psi_{\vec{k}}(\vec{r}) = \sum_l \sum_{m=-l}^{l} a_{lm}(\vec{k}) R_l(r, \epsilon_{\vec{k}}) Y_l^m(\hat{r}), \qquad (3)$$

where $Y_l^m(\hat{r})$ is a spherical harmonic and $R_l(r, \epsilon_{\vec{k}})$ is the usual scattering solution of the radial Schrödinger equation such that for $r > a$, $R_l = j_l \cos\delta_l - n_l \sin\delta_l$, with the δ_l being the phase shifts and a the muffin-tin radius.

The effect of the ion at the origin is now mainly included in $R_l(r, \epsilon_{\vec{k}})$; this part of the problem we shall want to treat exactly, while the coefficient $a_{lm}(\vec{k})$ is mainly determined by the scattering properties of all other atoms and their relative positions, namely, the crystal structure. This we approximate by assuming that

$$a_{l,m}(\vec{k}) = a_l(\epsilon_{\vec{k}}) Y_l^m(\hat{k}). \qquad (4)$$

This is, no doubt, a severe approximation for it assumes that the bands are spherical. However, it is reasonable to suppose that it retains most of the nonstructural features of a real band structure. In any case, our present understanding of the electron-photon interactions in transition metals does not warrant efforts along more elaborate lines.

Substituting Eqs. (3) and (4) into Eq. (2) and performing all the angular integrations, we obtain

$$\langle I^2\rangle = \left(\frac{2m\epsilon_\mathrm{F}}{\hbar^2\pi^2}\right)\frac{1}{n^2(\epsilon_\mathrm{F})}\sum_l 2(l+1)\left|\int_0^{a_\mathrm{WS}} dr\, r^2 R_l \frac{dv}{dr} R_{l+1}\right|^2 \frac{n_l n_{l+1}}{n_l^{(1)} n_{l+1}^{(1)}}, \tag{5}$$

where a_WS is the Wigner-Seitz radius, n_l is the lth component of the density of states defined by the relations

$$n(\epsilon_\mathrm{F}) = \sum_l n_l = \frac{V}{(2\pi)^3}\sum_l \sum_{m=-l}^{l} \int_0^{a_\mathrm{WS}} dr\, r^2 R_l^2 \int d^3k\, \delta(\epsilon_\mathrm{F} - \epsilon_{\vec{k}}) a_{l,m}^*(\vec{k}) a_{l,m}(\vec{k}) \tag{6}$$

and $n_l = n_l^{(1)}$ in the case of a single scatterer.

Though Hopfield decomposed his wave function slightly differently, Eq. (5) is completely equivalent to the starting point of his discussion. Surprisingly enough, the matrix elements in Eq. (5) can be evaluated exactly[5]: They are equal to $\sin(\delta_{l+1} - \delta_l)$. Consequently,

$$n(\epsilon_\mathrm{F})\langle I^2\rangle = \frac{2m\epsilon_\mathrm{F}}{\hbar^2\pi^2}\frac{1}{n(\epsilon_\mathrm{F})}\sum_l \frac{2(l+1)\sin^2(\delta_{l+1} - \delta_l) n_l n_{l+1}}{n_l^{(1)} n_{l+1}^{(1)}}. \tag{7}$$

This is, then, the central result of our paper.

It is interesting to note that if we take $n_l = n_l^{(1)}$ and approximate $\sin^2(\delta_{l+1} - \delta_l)$ by $(\delta_{l+1} - \delta_l)^2$, then, we may write $\langle I^2\rangle = \frac{8}{9}k_\mathrm{F}^2\epsilon_\mathrm{F}^2\langle v_q^2\rangle$, where $\langle v_q^2\rangle$ is defined in Ref. 1. This is the pseudopotential result for the jellium model.

Let us now turn to our principal concern, the transition metals. In this case we assume that the s and p densities of states are not very different from their free-electron values and hence we take $n_l = n_l^{(1)}$ for $l \neq 2$. Also we neglect all phase shifts with $l > 2$. From Eq. (7) this yields

$$n(\epsilon_\mathrm{F})\langle I^2\rangle = \left(\frac{2m\epsilon_\mathrm{F}}{\hbar^2\pi^2}\right)\left[2\frac{\sin^2(\delta_1 - \delta_0)}{n(\epsilon_\mathrm{F})} + 4\frac{\sin^2(\delta_2 - \delta_1) n_2}{n_2^{(1)} n(\epsilon_\mathrm{F})} + 6\frac{\sin^2(\delta_2) n_2}{n_2^{(1)} n(\epsilon_\mathrm{F})}\right]. \tag{8}$$

The general discussion of this formula is greatly simplified in those cases where the density of states is very large, i.e., it is dominated by d-like contributions. This is indeed the case at the beginning and at the end of the first transition series, and to a lesser extent for Nb and Ta. Under this circumstance $n_2 \sim n(\epsilon_\mathrm{F})$ and $n_2^{(1)} \cong 5\delta_2'/\pi$.[6] Now, Eq. (8) takes the following simple form:

$$n(\epsilon_\mathrm{F})\langle I^2\rangle = 2(2m\epsilon_\mathrm{F}/\hbar^2\pi)\sin^2(\delta_2)/\delta_2'. \tag{9}$$

An interesting point to note about this formula is that one could have obtained it by evaluating Eq. (2) for a single resonant scatterer at the origin, neglecting the effects of all the other atoms. This indicates that it is the local potential which plays the most important role in determining the strength of the electron-phonon interaction for these materials. That this is indeed the case is also suggested by the fact that using just such a single-resonant-scatterer model allowed Evans, Greenwood, and Lloyd[7] to predict the resistivities of a number of liquid transition metals rather accurately.

Using the resonance formula $\tan\delta_2 = \Gamma/(\epsilon_d - \epsilon_\mathrm{F})$, where ϵ_d and 2Γ are the position and the width of the resonance, respectively, we obtain $\sin^2(\delta_2)/\delta_2' = \Gamma$. Since we do not expect Γ to vary strongly across the transition series, we are tempted to predict from Eq. (9) that $n(\epsilon_\mathrm{F})\langle I^2\rangle$ will also remain more or less constant. However, this would be incorrect since ϵ_F almost nowhere along the series is believed to fall within the resonant linewidth. In fact Γ is only the minimum value of $\sin^2(\delta_2)/\delta_2'$ which may be a factor of 2 or 3 larger depending on how far away the resonance is from the Fermi energy. This can be clearly seen in the case of Fe.[8] For Fe, as is indicated in Fig. 1, $\epsilon_\mathrm{F} - \epsilon_d \sim 2\Gamma$ and the calculated value of $\sin^2(\delta_2)/\delta_2' = 0.15$ Ry $\sim 2.5\Gamma$. Using these values

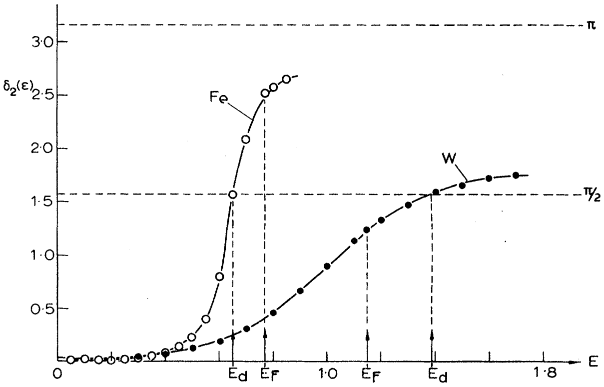

FIG. 1. d-wave phase shift as a function of energy for Fe and W.

TABLE I. The s, p, and d phase shifts, the derivative of the d phase shift with respect to energy, the density of states, and the calculated and experimental $n(\epsilon_F)\langle I^2\rangle$ for Fe, W, and Cu.

Element	δ_0	δ_1	δ_2	δ_2' (eV^{-1})	$n(\epsilon_F)$ (states/eV atom)	$n(\epsilon_F)\langle I^2\rangle$ (eV/Å^2)
Fe	−0.479	−0.071	2.52	0.17	1.75[a]	3.6 (4.2)[d]
W	−1.39	−0.711	1.23	0.14	0.15[b]	7.0 (6.3)[b]
Cu	−0.05	0.077	3.03	⋯	0.11[c]	0.42

[a] See Ref. 11.

[b] Experimental values, see Ref. 1.

[c] See Ref. 12.

[d] See Ref. 9.

and $\epsilon_F = 0.77$ Ry, Eq. (9) leads to $n(\epsilon_F)\langle I^2\rangle = 3.6$ eV/Å^2. This value is consistent with 4.2 eV/Å^2 estimated by Barisic, Labbe, and Friedel.[9]

Furthermore, for the group of transition metals considered by McMillan[1] the d contributions to the density of states at the Fermi energy is not always dominant, causing yet other complications. In fact for Mo and W, $n(\epsilon_F)$ is roughly a factor of 5 smaller than for Nb. Therefore, for these metals $n_2/n = 1$ is a bad approximation, and instead of our simple formula, Eq. (9), we must use the more accurate expression given by Eq. (8). Fortunately, this may be evaluated with relative ease.

In order to test Eq. (8) we shall now evaluate it for W using Mattheiss's[10] muffin-tin potential V_2 which yields band structures and densities of states in good agreement with experiments. Since n_2 is not given in a band-structure calculation, we adopt the point of view that there is a single electron in the s-p band and estimate n_2 as the difference between the band-structure density of states and the free-electron s-p density of states. If we take $n(\epsilon_F)$ from Mattheiss's calculation this procedure gives us $n_2/n \sim 0.3$. Using the phase shift listed in Table I from Eq. (9), we obtain $n(\epsilon_F)\langle I^2\rangle = 7.0$ eV/Å^2. This compares satisfactorily with the empirical value of 6.3 eV/Å^2. This agreement is particularly gratifying since our theory contains no adjustable parameters and, apparently, is fairly sensitive to the potential used.

Though there is no resonance in the strict sense of the word, $\delta_2(\epsilon)$ goes through $\pi/2$ and the energy at which this occurs may, nevertheless, be regarded as ϵ_d. Note then that while $\epsilon_F - \epsilon_d$ is about twice as large for W as for Fe, $\sin^2(\delta_2)/\delta_2'$ is 3 times as large. This suggests that $\sin^2(\delta 2)/\delta_2'$ is a sensitive function of the crystal potential or, roughly speaking, of the distance of the resonance from ϵ_F. Thus, it seems that the empirical trend observed by McMillan is the result of an interplay among several changing factors and does not have a single, physically interpretable origin.

To demonstrate that Eq. (8) predicts an $n(\epsilon_F)\langle I^2\rangle$ which is nevertheless almost the same for most of the bcc transition metals, the above calculation must be repeated for each one separately using reliable muffin-tin potentials. We hope to present a series of such calculations in a future publication.

Though we do not expect the theory to work as well for the noble metals as it does for the transition metals since in that case the d phase shift is no longer dominant, in Table I we also give $n(\epsilon_F)\langle I^2\rangle$ for Cu. As the contribution from the d resonance to the density of states at the Fermi energy is negligible for this calculation, we used Eq. (7) and set $n_l = n_l^{(1)}$ for all l. Estimating $(\langle\omega^2\rangle)^{1/2}$ from neutron scattering data[13] as 3.7×10^{13} rad/sec from Eq. (1), we find these approximations lead to $\lambda = 0.05$. This should be compared with $\lambda \leq 0.1$ suggested by Faulkner, Davis, and Joy[12] who used their band-structure calculation and the measured value of the specific heat to predict λ. Thus, the theory seems to give a good order-of-magnitude estimate even for the noble metals.

In summary, we would like to emphasize that Eq. (8) gives a coherent picture of the electron-phonon interaction constant λ for simple metals, noble metals, and transition metals in the sense that it yields good estimates of λ without any adjustable parameters. However, it is expected that it works best for the transition metals where a d resonance is the dominant feature.

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*Permanent address: University of California, Santa Cruz, Calif. 95000.

†Alfred P. Sloan Foundation Fellow.

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$$\int_0^R dr\, r^2 R_l \frac{dv}{dr} R_{l+1} \equiv \int_0^R dr\, u_l \frac{dv}{dr} u_{l+1}$$

can be simply evaluated by differentiating the Schrödinger equation for u_l, multiplying it by u_{l+1}, and integrating the result. The operation is repeated for u_{l+1} and the two results are added. After integration by parts the remaining integrals are evaluated again using the Schrödinger equation, yielding

$$\int_0^R dr\, r^2 R_l (dv/dr) R_{l+1}$$

$$= \tfrac{1}{2} [u_l u_{l+1}'' - 2u_l' u_{l+1}' + u_l'' u_{l+1}]_0^R$$

$$+ [(l+1)/R][u_l u_{l+1}' - u_l' u_{l+1}]_0^R.$$

For R greater than the range of the potential this gives $\sin(\delta_{l+1} - \delta_l)$ which was quoted in the text.

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Measurement of the Spin-Dependent Part of the Scattering Amplitude of Slow Neutrons on ^{19}F Using a Polarized Beam and a Polarized Target

A. Abragam, G. L. Bacchella, C. Long,* P. Meriel, J. Peisvaux, and M. Pinot
Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay,
91 Gif-sur-Yvette, France

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Using a polarized target of CaF$_2$, we have measured the spin-dependent part of the scattering amplitude of slow neutrons on ^{19}F. A value $\beta = a_+ - a_- = -0.135 \pm 0.002$ F was found, 10 times smaller than a recent theoretical estimate. A control experiment measuring $\beta = a_+ - a_-$ for the proton by Bragg scattering on a single crystal of LiH yielded the correct value within experimental error.

The scattering amplitude of a slow neutron on a nucleus of spin I can be written in operator form:

$$a = \bar{a} + \beta \vec{I} \cdot \vec{s}. \tag{1}$$

For ^{19}F, $\bar{a}$ is well known,[1]

$$\bar{a} = 5.74 \pm 0.03 \text{ F}. \tag{2}$$

The only existing information on β, obtained from the measurement of the total scattering cross section, is that $|\beta|$ is small:

$$\sigma_{\text{tot}}^{\text{sc}} = 4\pi(\bar{a}^2 + \tfrac{3}{16}\beta^2) = 4.0 \pm 0.3 \text{ b}, \tag{3}$$

whereas $4\pi\bar{a}^2 = 4.14 \pm 0.04$ b. It follows that $|\beta| \leq 3$ F and its sign is unknown.

A recent theoretical estimate is $\beta = -1.4$ F.[2] The Bragg scattering of a polarized neutron beam on a polarized target provides a method for obtaining the sign of β and also a much better accuracy for its magnitude when $|\beta|$ is small. With the assumption of a single nuclear species, the intensity of a Bragg-scattered beam is given by

$$\mathscr{I} = \bar{a}^2 + \beta I \bar{a} P p + \tfrac{1}{4}\beta^2 I^2 P^2, \tag{4}$$

where P and p are the respective nuclear and neutron polarizations counted positively along the applied magnetic field.

If $|\beta I P p| \ll |\bar{a}|$, the ratio of the intensities of scattered neutrons with spins up or down (with the above sign convention) is given with good accuracy by

$$\mathscr{I}_+/\mathscr{I}_- = 1 + 2\beta I P |p|/\bar{a}. \tag{5}$$

It is seen that in contrast to (3), (5) gives an ef-