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[21]This form for S_{ph} follows from the exact self-consistent dielectric function remembering that V_{ph} is screened by the square of the dielectric function and neglecting the energy dependence of $N(\xi)$ for $\xi \lesssim \frac{1}{2}E_d$. We have

$$\alpha \sim \frac{4\pi e^2}{Q^2}\sum_{n'}\sum_{\vec{G}}|\langle n|\rho_{\vec{Q}+\vec{G}}|n'\rangle|^2 < \frac{4\pi e^2}{Q^2},$$

where Q is a typical phonon wave number, and the state n is on the Fermi surface.

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ISOTOPE EFFECT IN SUPERCONDUCTIVITY

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The transition temperature T_c of a superconductor depends upon the average atomic mass M of its constituents:

$$T_c \propto M^{-z} = M^{-0.5(1-\zeta)}. \qquad (1)$$

Although the existence of this isotope effect has played an important role in the development of the theory of superconductivity, the experimentally observed values of ζ have never been properly explained. Here we present calculated values of ζ in agreement with experiment and show the observed qualitative difference between the reduced isotope effect ($\zeta \geq 0.3$) of the transition metals and the nearly complete isotope effect ($\zeta \sim 0.1$) of the simple[1] metals to follow from elementary ideas of band structure.

We have assumed an isotropic free-electron model for the simple metals and a two-band model consisting of nearly free electronic states or-

thogonalized to tightly bound d states for the transition metals.[2] We have already shown[2] that the experimentally observed properties of the transition metals must be described within the framework of the Anderson theory[3] of dirty superconductors. Thus, we describe the superconductivity of both the transition metals and the simple metals in terms of a single gap $\Delta(\xi)$ which is a function only of the renormalized normal-state energy,

$$\Delta(\xi) = -\int_{-\infty}^{\infty} d\xi' \,\mathrm{Re}[\Delta(\xi')]K(\xi,\xi')\tanh\frac{(E'/2k_BT)}{E'}, \quad (2)$$

where ξ is measured relative to the Fermi level and where

$$E' = \mathrm{Re}\{[\xi'^2 + \Delta^2(\xi')]^{1/2}\} \quad (3)$$

is the superconducting quasi-particle energy.[4] We assume the existence of only two contributions to the kernel of Eq. (2), a Coulomb contribution K_C and a contribution K_{ph} arising from the virtual exchange of phonons[5]:

$$K(\xi,\xi';M) = K_C(\xi,\xi') + K_{ph}(x,x'), \quad (4)$$

where $x = \xi/k_B\theta_D$ is measured in units of the M-dependent Debye energy.

We first discuss the general properties of the gap solutions $\Delta(\xi)$ in order to understand qualitatively the difference between the observed isotope effect in the simple metals and in the transition metals. As the isotope effect arises solely from K_{ph} through the $M^{-1/2}$ dependence of θ_D, we clearly expect a significant deviation ζ from the ideal isotope effect if T_c depends strongly on the average magnitude of $K_C(\xi,\xi')$. In all superconductors, the real part of $\Delta(\xi)$ changes sign at an energy very nearly equal to any energy at which the kernel $K(0,\xi)$ changes sign.[6] Thus, the product $\mathrm{Re}[\Delta(\xi)]K(0,\xi)$ is negative for essentially all energies ξ {assuming $\mathrm{Re}[\Delta(0)]K(0,0)<0$}, so that the contribution of $K_C(0,\xi_>)$ in the region $\xi_> > k_B\theta_D$ reduces the effect of $K_C(0,\xi_<)$ in the region $\xi_< < k_B\theta_D$.[7]

We find that in the simple metals $K_C(0,\xi)$ remains large up to energies $\xi > 10$ eV. On the other hand, we expect $K_C(0,\xi)/K_C(0,0)$ to be very small for $|\xi|$ greater than half a d-band width (~1 eV) for the case of the transition metals. Our explicit calculations have shown the effective cutoff energy ξ_c for $K_C(0,\xi)$ actually to be of the order of half a d-subband width $\frac{1}{2}E_d < 1$ eV for this case.[2,8] Therefore, we expect the contribution of $K_C(0,\xi_>)$ more nearly to cancel the effect of $K_C(0,\xi_<)$ in the simple metals than in the transition metals, leading to a smaller deviation ζ from the ideal isotope effect in the simple metals.

In order to obtain simple quantitative formulas for ζ, we must investigate the approximate form of the kernel $K(\xi,\xi')$. We find that $K_{ph}(x,x')$ depends strongly on $x-x'$ and approaches zero for $|x-x'| \gg 1$, but that the explicit dependence on $x+x'$ is weak. We also find that $K_C(\xi,\xi')$ is very nearly constant over any range in energy of order $k_B\theta_D$ (at least for the simple metals). We are thus led to assume the existence of a phonon cutoff parameter $x_c \gtrsim 1$ such that $K_{ph}(x-x')$ may be neglected whenever $|x-x'| > x_c$ and such that both the explicit $\xi+\xi'$ dependence of $K_{ph}(x,x')$ and the ξ and ξ' dependence of $K_C(\xi,\xi')$ over any range in energy less than $x_c k_B\theta_D$ may be neglected.

We consider as a zero-order approximation the simple two-square-well model of Tolmachev[9] and of Morel and Anderson[10]:

$$K_{ph}^{0}(x,x') = K_{ph}(0,0) \text{ for both } |x| \text{ and } |x'| < x_c = 1,$$
$$= 0 \text{ otherwise;}$$
$$K_C^{0}(\xi,\xi') = K_C(0,0) \text{ for both } |\xi| \text{ and } |\xi'| < \xi_c,$$
$$= 0 \text{ otherwise.}$$

This model yields the simple formula

$$\zeta = \zeta^0 = (K_C^*/K_{eff})^2. \quad (5)$$

The experimentally determined quantity $K_{eff} = 1/[2\ln(T_c/1.14\,\theta_D)]$ corresponds to the parameter $-N(0)V$ of Bardeen, Cooper, and Schrieffer (BCS),[11] and K_C^* is given by

$$K_C^* = K_C(0,0)/[1 + K_C(0,0)\ln(\xi_c/k_B\theta_D)]. \quad (6)$$

As K_{eff} may be expressed as the sum of an average phonon contribution $\langle K_{ph}\rangle$ plus the net Coulomb contribution K_C^*, Eqs. (5)-(7) clearly support our contention that the deviation ζ from the ideal isotope effect is significant only if the net Coulomb contribution K_C^* is of the same order as the phonon contribution $\langle K_{ph}\rangle$.

An integral equation for the variation $\delta\varphi(\xi)$ of the normalized energy gap

$$\varphi(\xi) = \mathrm{Re}\left\{\lim_{T\to T_c}\frac{\Delta(\xi)}{\Delta(0)}\right\}$$

with respect to small changes in T_c and θ_D follows immediately from Eqs. (2) and (3) without any square-well approximations, given our as-

sumption of a phonon cutoff parameter x_c:

$$\delta\varphi(\xi) = 2[\bar{K}_{ph}(x) - \bar{K}_{ph}(0)][\delta \ln(T_c) - \delta \ln(\theta_D)] + 2[\bar{K}_C(\xi) - \bar{K}_C(0)]\delta \ln(T_c) - \int_{-\infty}^{\infty} \frac{d\xi'}{\xi'} \tanh\left(\frac{\xi'}{2k_B T_c}\right) \times [K(\xi, \xi') - K(0, \xi')]\delta\varphi(\xi'), \quad (7)$$

where

$$\bar{K}(x) = \mathrm{Re}\left\{\frac{\theta_D}{4T_c}\int_{x-x_c}^{x+x_c} dx' K(x,x')\varphi(x') \times \mathrm{sech}^2\left(\frac{x'\theta_D}{2T_c}\right)\right\} \simeq K(x,0).$$

However, in order to solve Eqs. (2) and (7) numerically and thus calculate ζ, we have employed the square-well approximation $K_{ph}(x,x') = K_{ph}^{0}(x, x')$ which we justify after a discussion of our treatment of the Coulomb contribution $K_C(\xi, \xi')$ to the kernel.

Our isotropic free-electron model for the simple metals yields a Coulomb contribution $K_C(\xi, \xi')$ which may be written in the form $K_C(0,0)K_C^{n}(y, y'; E_F)$, where $y = \xi/E_F$ is measured in units of the Fermi energy and where the explicit dependence of K_C^{n} upon E_F is very weak. Therefore, we may write ζ in the form given by Eqs. (5) and (6) and calculate the ratio of the effective Coulomb cutoff energy to the Fermi energy, ξ_c/E_F ($\approx$4 for all of the superconducting simple metals), simply by calculating $K_C(\xi, \xi')$ numerically[5] and solving Eqs. (2) and (7) for any given simple metal.

Our lack of knowledge of the detailed band structure of the transition metals leads us to choose a simple two-square-well model for $K_C(\xi, \xi')$ in the transition metals:

$K_C(\xi, \xi') = K_C$ for $|\xi|$ and $|\xi'|$ both $< \xi_c'$,

$= K_C^{ss}$ for either $|\xi|$ or $|\xi'| > \xi_c'$ and both $|\xi|$ and $|\xi'| < \xi_c''$,

$= 0$ otherwise.

Here the cutoff ξ_c' corresponds roughly to half a d-subband width $\frac{1}{2}E_d$ (<1 eV),[12] and the cutoff ξ_c'' is of the order of 10 eV; K_C is the total Coulomb contribution to $K(0,0)$, and K_C^{ss} is the small contribution arising from matrix elements of the Coulomb interaction between the s-like parts of the electronic wave functions.[2] We again write ζ in the form given by Eqs. (5) and (6), determining the effective Coulomb cutoff energy ξ_c numerically for each transition metal. As the ratio K_C^{ss}/K_C is much less than unity, ξ_c is only slightly greater than ξ_c'. Although our lack of knowledge of the band structure of the transition metals introduces a large probable error into our calculation of ξ_c, the weak dependence of K_C^{*} upon ξ_c makes this error relatively unimportant.[13] The largest error in our calculations for the transition metals arises from the uncertainty in our calculation of $K_C(0,0)$, which depends both on the relative importance of umklapp processes and on the position of the Fermi surface in k space.

In order to justify the use of the square-well approximation $K_{ph}(x,x') = K_{ph}^{0}(x,x')$, we derive an equation for ζ valid for any physical $K_{ph}(x,x')$ and show that the ratio ζ/ζ^0 is approximately unity. From Eq. (7) we derive the equation

$$\partial\varphi(x)/\partial \ln(T_c) = (1+t)[\bar{K}(x) - \bar{K}(0)], \quad (8)$$

where $0 < t < 1$, and see that $\varphi'(x) = \partial\varphi(x)/\partial \ln(T_c) + \partial\varphi(x)/\partial \ln(\theta_D)$ is very nearly zero for $|x| < x_c$. Then, the deviation ζ from the ideal isotope effect is given by

$$\zeta = \zeta^0\left\{1 + \frac{\langle K_{ph}\rangle - \bar{K}_{ph}(0)}{\bar{K}_{ph}(0) + K_C^{*}} + \frac{(1+t)[K_C^{*}/2\langle K_{ph}\rangle]}{K_C - K_C^{*}[\langle K_{ph}\rangle - \bar{K}_{ph}(0)]} \times \int_{-x_c}^{x_c}\frac{dx}{x}K(0,x)[\bar{K}(x) - \bar{K}(0)]\tanh\left(\frac{x\theta_D}{2T_c}\right) + O\left(\left[\frac{\langle K_{ph}\rangle - \bar{K}_{ph}(0)}{K_{eff}}\right]^2\right)\right\}, \quad (9)$$

where the average phonon contribution is given by

$$\langle K_{ph}\rangle = -K_{eff}\,\mathrm{Re}\left\{\int_{-x_c}^{x_c}\frac{dx}{x}K_{ph}(0,x)\varphi(x) \times \tanh\left(\frac{x\theta_D}{2T_c}\right)\right\} = K_{eff} - K_C^{*}.$$

As numerical calculations indicate that the inequality

$$|\bar{K}_{ph}(0)/\langle K_{ph}\rangle - 1| \lesssim |K_{eff}|$$

should hold for all metals, we find that Eq. (9) shows our square-well approximation $K_{ph}(x,x') = K_{ph}^{0}(x,x')$ to lead to an error of less than or approximately equal to 25% in the calculation of ζ. We estimate the over-all probable error in our calculation of ζ to be less than or approximately equal to 30% for the simple metals and 40% for the transition metals.

Our calculated values of ζ and our estimated range of probable error are compared in Table I with the results of Bardeen, Cooper, and Schrieffer (BCS), Swihart (Swi),[14] and Morel and Anderson (MA), as well as with experiment.[15-23] The great improvement embodied in our results follows from (1) the recognition of the importance of band structure effects in the transition metals, and (2) a more exact treatment of the Coulomb contribution $K_C(\xi,\xi')$ than has previously been attempted. For the simple metals, when warranted by improved experimental determinations of ζ, our formalism can be extended through lengthy numerical calculations to include the effect of the detailed structure of the kernel $K(\xi,\xi')$.

In many recent articles,[24] it has been suggested that the superconductivity of the transition metals arises primarily from some interaction other than the electron-phonon interaction. However, the excellent agreement between our calculated values of ζ and the few available experimental values clearly demonstrates that one need not infer this notion from the reduced isotope effect of the transition metals. Indeed, the observed vanishing of the isotope effect in ruthenium can even be used as the basis for an argument against the existence of any important attractive interaction between electrons in the transition metals other than the interaction $V_{ph}(x,x')$ arising from the virtual exchange of phonons. Even if we disregard our explicit numerical calculations, we see that the large partial isotope effect observed in molybdenum and Mo_3Ir (Table I) implies a ratio $\langle K_{ph}\rangle/\langle K_C\rangle$ nearly as great as that in the simple metals. The assumption that the superconductivity of ruthenium arises from some interaction other than the electron-phonon interaction, coupled with its observed zero isotope effect, then implies that the ratio $\langle K_{ph}\rangle/\langle K_C\rangle$ is an or-

Table I. Deviations ζ from the ideal isotope effect.

Material	z (exp)	ζ (exp)	Experiment reference	ζ (BCS)	ζ (Swi)	ζ (MA)	ζ (Present calculation)
Zn	0.45± 0.05	0.10± 0.10	17, 18, 24	0.0	0.6	0.35	0.20± 0.06
Cd	0.50± 0.10	0.0 ± 0.2	19	0.0	0.6	0.32	0.27± 0.08
Sn	0.47± 0.02	0.06± 0.04	20	0.0	0.4[a]	0.16	0.12± 0.04
Hg	0.50± 0.03	0.00± 0.06	20	0.0	0.2[a]	0.08	0.07± 0.02
Pb	0.48± 0.01	0.04± 0.02	21	0.0	0.2[a]	0.06	0.06± 0.02
Tl	0.50± 0.10	0.0 ± 0.2	20, 22	0.0	0.4[a]	0.14	0.11± 0.03
Al				0.0	0.6[a]	0.32	0.31± 0.09
Ru	0.00± 0.05	1.0 ± 0.10	23	0.0	1.0	0.5[b]	1.0 ± 0.4
Os	0.10± 0.10	0.8 ± 0.2	17	0.0	0.8	0.5[b]	0.8 ± 0.4
Mo	0.37± 0.07	0.25± 0.15	24	0.0	0.7[a]	0.4[b]	0.3 ± 0.15
Ir				0.0		0.6[b]	1.4 ± 0.5
Hf				0.0		0.5	0.4 ± 0.2
V				0.0		0.18	0.7 ± 0.3
Ti				0.0		0.50	0.6 ± 0.3
Zr				0.0		0.40	0.3 ± 0.15
Ta				0.0		0.16[b]	0.3 ± 0.15
Re				0.0		0.18[b]	0.4 ± 0.2
Nb_3Sn	0.08± 0.02	0.84± 0.04	25	0.0		0.10[b]	0.6 ± 0.25
Mo_3Ir	0.33± 0.03	0.34± 0.06	24	0.0		0.18[b]	0.35± 0.15
V_3Ge				0.0		0.20[b]	0.7 ± 0.3
V_3Ga				0.0		0.10[b]	1.3 ± 0.5
V_3Si				0.0		0.10[b]	1.0 ± 0.4

[a]These values are calculated from the model used by Swihart,[14] but were not published by Swihart.
[b]These values are calculated from the formulas of Morel and Anderson,[10] but were not published by Morel and Anderson.

der of magnitude smaller in ruthenium than in molybdenum. This great fluctuation in the ratio $\langle K_{ph}\rangle/\langle K_C\rangle$ from one transition metal to another seems unreasonable. By contrast, our calculations indicate only a small variation in the ratio $\langle K_{ph}\rangle/\langle K_C\rangle$ as a function of position in the periodic table.[2]

The pressure dependence of the transition temperature T_c is also susceptible to an analysis similar to that given above. It is found experimentally[25] that the pressure dependence of T_c in the simple metals is an order of magnitude greater than in the transition metals. This experimentally observed qualitative difference between the pressure dependence of T_c in the case of the transition metals and in the case of the simple metals is consistent with our calculations.[26] However, we find that in both cases the pressure dependence arises almost entirely from the pressure dependence of $\langle K_{ph}\rangle$, which is extremely sensitive to the exact form of the pseudopotential in the simple metals and to the effective nuclear charge felt by a d electron at the Fermi surface in the transition metals. This sensitivity was too great in both cases to allow us to claim anything more than a fortuitous, qualitative agreement with experiment for the pressure dependence of the transition temperature.

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[1]By simple metals, we mean those metals which are not transition metals, rare earths, or actinides.

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[4]As was first pointed out by Eliashberg {G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. 38, 966 (1960) [translation: Soviet Phys. - JETP 11, 696 (1960)]}. Eqs. (2) and (3) are not strictly correct for temperatures below T_c. However, Eqs. (2) and (3) contain lifetime effects and are equivalent in the limit $T \to T_c$ to a finite-temperature generalization of the Green's function equations of Schrieffer, Scalapino, and Wilkins [J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters 10, 336 (1963)]. Although our calculations apply only to the isotope effect as defined by Eq. (1), not to the isotopic mass dependence of the critical magnetic field, $H_{cr} \propto M^{0.5(1-\xi')}$, it may be shown that ξ and ξ' are very nearly equal, even in the strong-coupling case of lead.

[5]Formulas for the calculation of $K_C(\xi,\xi')$ valid for both the transition metals and the simple metals are given in reference 2.

[6]This statement is not necessarily true of the s-band gap $\Delta_s(\xi)$ in the case of a clean transition metal discussed in reference 2, but is true in all cases thus far experimentally observed.

[7]The reader may easily verify the above arguments for the simple two-square-well model of Tolmachev (see reference 9).

[8]This result follows from the relative importance of small-q matrix elements and the fact that small-q matrix elements between different subbands vanish.

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[12]ξ_c' is roughly proportional to the inverse of the density of states $N(0)$ at the Fermi surface and is only weakly dependent upon valence z. The detailed calculation of ξ_c' depends upon a complicated model (to be published).

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[23]G. E. Devlin and E. Corenzwit, Phys. Rev. 120, 1964 (1960).
[24]See references 1-5 of the preceding Letter.
[25]E. Bucher and J. L. Olsen, Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962 (to be published).
[26]Our calculations also explain the fact that the anomalous pressure dependence of the density of states $\partial N(0)/\partial p$ at the Fermi surface observed in many simple metals does not greatly affect $\partial T_c/\partial p$. The insensitivity of $\partial T_c/\partial p$ to $\partial N(0)/\partial p$ follows from the fact that the anomalous pressure dependence of the density of states is confined to a thin shell about the surface of the first Brillouin zone and from the very small value of $K(x,x')$ for $|x-x'| \ll 1$. Thus, in the BCS terminology, although $\partial N(0)/\partial p$ is large, $\partial[N(0)V]/\partial p = \partial\langle N(\xi)V(0,\xi)\rangle/\partial p$ is not.

MAGNETIC FIELD AND PHASE TRANSITION IN THIN FILM SUPERCONDUCTORS*

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The behavior of superconducting specimens in a magnetic field at temperatures close to the critical temperature has been successfully treated by means of the Ginzberg-Landau-Gorkov (GLG) theory.[1-3] At lower temperatures down to zero, on the other hand, the theory seems to be in a confused state at present, a number of papers claiming conflicting results.[4-7] We would like to consider here a thin film of superconductor (thickness $L \lesssim 10^{-5}$ cm) allowing essentially complete penetration of the magnetic field which runs parallel to the film surfaces. Adapting and extending our previous calculations[5] done for bulk material to this particular condition, we conclude as follows:

(a) The phase transition to the normal state due to the magnetic field should be of the second order at all temperatures.

(b) A simple scaling rule exists concerning the field and temperature dependence of the energy gap.

(c) The critical field H depends on thickness L and reduced temperature t like $H_c \sim L^{-3/2}(\ln 1/t)^{1/2}$ for not too thin films ($L \gtrsim 0.5\times10^{-5}$ cm) and near $t=1$ in accordance with the GLG theory, but deviates from this behavior for very small thicknesses or at moderately low temperatures. We note in particular that the conclusion (a) is contrary to the calculations of Bardeen,[6] which predicts a first-order transition for thin films and $t \lesssim 0.3$.

The details of the calculations will be published elsewhere. We give here an outline of the arguments leading to the above results. Instead of treating the magnetic field as a perturbation on the standard BCS ground state, we first take the magnetic eigenstates $|n\rangle$ of single electrons and perform the pairing of these eigenstates. We may pair $|n\rangle$ and its spin- and space-reversed state $|\bar{n}\rangle$ as partners since our Hamiltonian in the London gauge and the boundary conditions are invariant under this operation. The energy gap equation at a temperature $T = 1/k\beta$ takes the form

$$\phi_n = \sum_m \frac{V_{nm}\phi_m}{2E_m}\tanh(\tfrac{1}{2}\beta E_m), \quad E_n = (\epsilon_n^2 + |\phi_n|^2)^{1/2}, \quad (1)$$

where ϕ_n is the gap parameter, ϵ_n the single electron energy, and V_{nm} the matrix element of the interaction. The result (a) follows immediately from this since the free energy of the superconductive state becomes always lower than that of the normal state, except when all $\phi_n \to 0$.

A closer examination of Eq. (1) shows that the effect of the magnetic field on ϕ_n appears mainly through the field dependence of the matrix element V_{nm}. This means that the suitably defined average $\varphi = \overline{\phi_n}$ depends on H only through a change in the effective coupling parameter $\rho(H) = N\overline{V}(H)$ characteristic of the BCS theory. We may thus