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Superconductivity in the Periodic System

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The empirical regularities in the appearance of superconductivity in the periodic system discussed by Matthias are considered in the light of the microscopic theory of superconductivity proposed by Bardeen, Cooper, and Schrieffer. A simple model of electrons and ions interacting via screened Coulomb forces is used to describe the electron-lattice interaction. With the aid of this model, it is shown how the theory of Bardeen, Cooper, and Schrieffer provides both a satisfactory criterion for the appearance of superconductivity and a good qualitative account of the variation in transition temperature from one metal to another.

I. INTRODUCTION

MATTHIAS[1] has emphasized a number of interesting regularities in the appearance of superconductivity in the periodic system. These regularities hold for elements, compounds, and alloys and appear to be a property of only the average number of valence electrons Z and the electron density N_e in the solid. Some of the most important regularities are:

(1) Superconductivity is observed only for metals.

(2) Superconductivity is found only in elements for which $2 \leq Z \leq 8$. Essentially the same rule applies for compounds, though in the latter case one may find superconductors with Z slightly less than 2 or slightly greater than 8.

(3) No ferromagnetic or antiferromagnetic substances superconduct.

(4) Certain regularities are apparently connected with crystal structure. No superconductors have been found which do not possess a center of inversion. No superconductors have been found in certain space groups, notably that similar to Cd I.

(5) For a given Z the transition temperature T_c increases as a high power of the interelectron spacing r_s. This spacing r_s is defined by

$$r_s a_0 = (3/4\pi N_e)^{\frac{1}{3}}, \qquad (1)$$

where a_0 is the Bohr radius.

(6) No such regularities are observed for metals with $Z=2$ or $Z=8$.

(7) The variation of T_c with valency, Z, is that shown in Fig. 1. Note that the nontransition and the transition metals display a markedly different Z dependence.

Recently, Bardeen, Cooper, and Schrieffer[2] have proposed a microscopic theory for superconductivity which yields an energy gap of the right order of magnitude and reasonable values for other superconducting parameters (T_c, penetration depth, etc.) provided one fixes a certain parameter, V, which measures the average strength of the net interaction between electrons very close to the Fermi surface. Both the screened Coulomb repulsion between the electrons, and the phonon-induced electron-electron interaction (which is attractive for electrons sufficiently close to the Fermi surface) contribute to V. The criterion for superconductivity is that V be negative; i.e., the phonon-induced attractive interaction must predominate over the short-range Coulomb repulsion.

In the BCS theory,[2,3] the critical temperature, T_c, is given by

$$kT_c = 1.14 \langle \hbar\omega \rangle_{\text{Av}} \exp\{-1/[N(0)V]\}, \qquad (2)$$

where $\langle \hbar\omega \rangle_{\text{Av}}$ is the average energy of the phonons which scatter electrons at the Fermi surface, and $N(0)$ is the density in energy of electron states on that surface. Thus a knowledge of V will enable us to calculate T_c.

In this paper we consider the calculation of V from first principles. Our aim is to deduce the Matthias regularities from the BCS theory. Obviously, in the present stage of development of the theory of solids, such a deduction cannot be detailed and quantitative. Thus we cannot hope to obtain accurate values of T_c for all superconductors. [Everything else aside, the fact that T_c depends exponentially on $N(0)V$ puts such a goal beyond our grasp.] The best that we can hope for is a "microscopic qualitative" understanding of the Matthias regularities. By this we mean an understanding based on detailed quantitative calculations carried

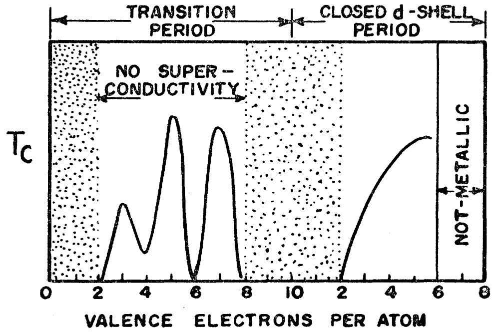

FIG. 1. The behavior of T_c as a function of Z (after Matthias[1]).

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[1] B. Matthias, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2.

[2] Bardeen, Cooper, and Schrieffer, Phys. Rev. **106**, 162 (1957).

[3] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957), hereafter referred to as BCS.

out with an oversimplified model for the interaction between electrons and ions in superconductors. Such a model may be regarded as adequate if (1) it yields the gross features of the occurrence of superconductivity in the periodic system, and (2) the known inadequacies of the model are consistent with the experimental observations.

The Matthias regularities furnish us with a useful hint in the choice of a model. Matthias finds that the properties of superconductors seem more closely linked to valency and interelectron spacing than to details associated with crystalline structure. We accordingly choose a model which is comparatively insensitive to the effects of lattice periodicity, *viz.*, a set of electrons and ions interacting via screened Coulomb forces, in which all relevant matrix elements are evaluated by treating the electrons as plane waves. We find the model leads to a criterion for superconductivity which distinguishes quite well between the superconducting and nonsuperconducting metals. Where the criterion fails, its failure may be attributed to the known inadequacies of the model. When we turn to the calculation of $N(0)V$, and hence T_c, we find that the model yields results which are qualitatively correct, but quantitatively in error. Again one can understand easily where the model is inadequate and its failings are in the right direction to explain the quantitative discrepancies. The difference in the behavior of T_c as a function of Z for the nontransition and the transition metals may be qualitatively understood, as may the variation in T_c with r_s for a fixed Z. Thus, we are able to achieve our aim of a microscopic qualitative understanding of the empirical regularities observed by Matthias.

In Sec. II we define and calculate V. We discuss in some detail the present knowledge of the matrix elements which enter into V before making our simple approximate calculation. Section III is devoted to a discussion of the criterion for superconductivity. In Sec. IV we consider the variation in T_c in the periodic system, while in Sec. V we summarize the conclusions to which we have been led in the course of these investigations.

II. CALCULATION OF V

Let us recall certain relevant aspects of the BCS theory. BCS begin their considerations with the effective Hamiltonian for electron interaction in a metal. The Hamiltonian may be written as [4,5]

$$H=H_{\mathrm{Coul}}+H_{\mathrm{ph}}, \tag{3}$$

where H_{Coul} represents the effective screened Coulomb interaction between the electrons and H_{ph} is the phonon-induced electron-electron interaction. If we follow BCS, and confine our attention to those interactions which scatter a pair of electrons of opposite momentum and spin $(k\uparrow, -k\downarrow)$ to another pair state $(k'\uparrow, -k'\downarrow)$, the interactions take the form

$$H_{\mathrm{Coul}}=\tfrac{1}{2}\sum_{kk'} U(\mathbf{k}-\mathbf{k}')C_{k'}{}^*C_{-k'}{}^*C_{-k}C_k, \tag{4}$$

$$H_{\mathrm{ph}}=\tfrac{1}{2}\sum_{kk'} \frac{2\hbar\omega M_q{}^2(\mathbf{k}-\mathbf{k}')C_{k'}{}^*C_{-k'}{}^*C_{-k}C_k}{(E_k-E_{k'})^2-\hbar^2\omega_{k-k'}{}^2}. \tag{5}$$

The C_k's are the creation and annihilation operators for electrons in Bloch states (the spin index being understood since we deal only with pairs of electrons of opposite spin). $U(\mathbf{k}-\mathbf{k}')$ is the matrix element for the Coulomb scattering of an electron from state $\mathbf{k}$ to $\mathbf{k}'$. $M_q(\mathbf{k}-\mathbf{k}')$ is the matrix element for scattering from $\mathbf{k}$ to $\mathbf{k}'$ (with emission of a phonon of wave vector $\mathbf{q}$) due to the electron-ion interaction; it is calculated for zero-point amplitude of the lattice vibration. E_k and $E_{k'}$ are the energies of the corresponding Bloch states, and $\omega_{k'-k}$ is the frequency of the phonon $\mathbf{q}$ which couples the states $\mathbf{k}$ and $\mathbf{k}'$.

BCS remark that (5) corresponds to an attractive interaction for electrons of sufficiently close energies. They work with variational wave functions designed to take maximum advantage of this attractive interaction, and they make the assumption (which later turns out to be self-consistent) that the important electronic states of interest are those very close to the Fermi surface, such that

$$E_k-E_{k'}\ll\hbar\omega_{k-k'}.$$

They are then able to introduce an averaged strength of the net electron-electron interaction at the Fermi surface,

$$-V=\left\langle -2\frac{M_q{}^2(\mathbf{k}'-\mathbf{k})}{\hbar\omega(k'-k)}+U(\mathbf{k}'-\mathbf{k})\right\rangle_{\mathrm{Av}}, \tag{6}$$

where the average is to be carried out over all electrons at the top of the Fermi distribution. With the aid of V and the foregoing approximations, the effective Hamiltonian, (3), may be written as

$$H=-\sum_{kk'}{}' VC_{k'}{}^*C_{-k'}{}^*C_{-k}C_k, \tag{7}$$

where the prime indicates the sum is to be carried out only over the electron *pair* states. The Hamiltonian (7) forms the starting point of the BCS theory. $-V$ is taken as an arbitrary parameter, and is assumed to be negative.

The calculation of V requires a knowledge of the actual electron-electron and electron-ion interactions for the electrons on the Fermi surface in the metal under consideration. The coupled system of electrons and ions in a metal displays the following general behavior. Because the ions are heavy and slow, when they move the conduction electrons respond quite well to their motion, cancelling out the great portion of the ionic field. Thus, the effective field seen by a given electron or another ion is that of the ion plus its associ-

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[4] H. Fröhlich, Proc. Roy. Soc. (London) **A215**, 291 (1952).

[5] J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

ated shielding electrons. In the same way, the effective interaction between electrons is a screened, short-range Coulomb interaction because an electron at a distance much greater than the individual electronic spacing sees not only a given electron but also its associated electronic shielding cloud. The validity of this general picture has been established in detail for the free-electron gas[6] and for the coupled electron-ion system.[5] It has recently been shown that in the nontransition metals periodicity will affect the response of the electrons to each other and to the ionic motion only very slightly.[7]

Consider the electrons at the Fermi surface. If we assume that all charged-particle interactions in the metal are pure Coulombic (a not unreasonable assumption), the direct interaction between the electrons is given by $e^2/|\mathbf{r}_i-\mathbf{r}_j|$. The electron-ion interaction is $Z^*e^2/|\mathbf{r}_i-\mathbf{R}_j|$, where Z^* is the effective ionic valency seen by the electron. If we approximate the electrons as plane waves, the matrix elements in which we are interested are given by

$$U^0(\mathbf{k}-\mathbf{k}')=\frac{4\pi e^2}{|\mathbf{k}-\mathbf{k}'|^2}, \tag{8}$$

$$M_q{}^0(\mathbf{k}-\mathbf{k}')=\frac{4\pi Z^*e^2 i}{|\mathbf{k}-\mathbf{k}'|}\left(\frac{N}{M}\right)^{\frac{1}{2}}\left(\frac{\hbar}{2sq}\right)^{\frac{1}{2}}, \tag{9}$$

where s is the longitudinal sound velocity and N and M are the ionic density and mass.

The electrons at the Fermi surface interact with the other electrons in the metal, and it is this interaction which shields out the field of a given electron within a distance of the order of the interelectronic spacing. The most complete calculation of the effect of this shielding on the matrix elements (8) and (9) has been given in a paper by Bardeen and the writer[5]; the results are

$$U(\mathbf{k}-\mathbf{k}')\cong\frac{4\pi e^2}{|\mathbf{k}-\mathbf{k}'|^2}\left\{\frac{(k-k')^4}{8m^2[\omega_P{}^2+(\mathbf{k}-\mathbf{k}')^2v_0{}^2(\frac{3}{5})]}\right\}, \quad |\mathbf{k}-\mathbf{k}'|<k_c, \tag{10a}$$

$$U(\mathbf{k}-\mathbf{k}')=U^0(\mathbf{k}-\mathbf{k}'), \quad |\mathbf{k}-\mathbf{k}'|>k_c \tag{10b}$$

$$M_q(\mathbf{k}-\mathbf{k}')=\frac{4\pi Z^*e^2 i}{|\mathbf{k}-\mathbf{k}'|\epsilon(|\mathbf{k}-\mathbf{k}'|)}\left(\frac{N}{M}\frac{\hbar}{2sq}\right)^{\frac{1}{2}}, \quad |\mathbf{k}-\mathbf{k}'|k_c \tag{11a}$$

$$M_q(\mathbf{k}-\mathbf{k}')=M_q{}^0(\mathbf{k}-\mathbf{k}'), \quad |\mathbf{k}-\mathbf{k}'|>k_c \tag{11b}$$

where k_c is the maximum plasmon wave vector, and v_0 is the velocity of an electron at the top of the Fermi distribution. The quantity $\epsilon(k)$ is the dielectric constant of the metal for wave vector k calculated in the free-electron approximation; it is given by

$$k^2\epsilon(k)=k^2+k_s{}^2\left\{\frac{1}{2}+\frac{4k_0{}^2-k^2}{8k_0k}\ln\left|\frac{2k_0+k}{2k_0-k}\right|\right\}, \tag{12}$$

$$\cong k^2+k_s{}^2$$

where k_s is the inverse Fermi-Thomas screening length, defined by

$$(k_s/k_0)=0.814r_s{}^{\frac{1}{2}}. \tag{13}$$

In the derivation of (10) and (11) the long-wavelength response ($k<k_c$) of the electrons to the motion of a given electron or ion is calculated quite accurately through the introduction of the plasmon modes; the short-wavelength response ($k>k_c$) is neglected. Bardeen[8] has calculated the short-wavelength response of the electrons to the ionic motion using the Hartree approximation, which begins to fail somewhat in this region. His result is identical with (11a), so that it extends (11a) into the short-wavelength region.

Further complications arise with the electron-electron interaction matrix elements. There are no calculations available for the short-wavelength response (although undoubtedly some screening persists), and the long-wavelength matrix element, (10), is altered somewhat by subsidiary conditions which act on the electronic wave functions. However, recently Nozières and the writer[9] have shown that when one can separate out a minority group of electrons at the Fermi surface, their effective interaction (for low-frequency excitations) may be written as

$$U(\mathbf{k}-\mathbf{k}')=\frac{4\pi e^2}{(\mathbf{k}-\mathbf{k}')^2\epsilon(|\mathbf{k}-\mathbf{k}'|)}, \tag{10a$'$}$$

where ϵ is defined by (12). In other words, the effect of the subsidiary conditions on (10a) is the slight alteration, (10a′). Again, (10a′) should not be regarded as completely reliable because of the complications which arise in separating out the electrons at the Fermi surface, as discussed in reference (9).

On the basis of the foregoing considerations, we believe that the following expressions for the relevant matrix elements,

$$U(\mathbf{k}-\mathbf{k}')=\frac{4\pi e^2}{(\mathbf{k}-\mathbf{k}')^2+k_s{}^2}, \tag{14}$$

$$M_q(\mathbf{k}-\mathbf{k}')=\frac{4\pi Z^*e^2 i|\mathbf{k}-\mathbf{k}'|}{(\mathbf{k}-\mathbf{k}')^2+k_s{}^2}\left(\frac{\hbar}{2sq}\frac{N}{M}\right)^{\frac{1}{2}}, \tag{15}$$

represent a simple, tolerable approximation for all values of $|\mathbf{k}'-\mathbf{k}|$. Of course we could have decided on (14) and (15) at the outset; the purpose of the discussion above was to compare this choice with the best available values for the matrix elements. As will be

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[6] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

[7] P. Nozières and D. Pines, Phys. Rev. (to be published).

[8] J. Bardeen, Phys. Rev. **52**, 688 (1937).

[9] P. Nozières and D. Pines, Phys. Rev. (to be published).

seen below, there is good reason to believe that the approximation made in our use of (14) and (15), rather than some other "plane wave" matrix elements, is the least of our difficulties.

Two cases arise for the electron-ion matrix element, (15). These correspond to the long-wavelength normal processes (N processes), for which $|\mathbf{k}'-\mathbf{k}|<k_D$, and $\mathbf{k}'-\mathbf{k}=\mathbf{q}$; and the *Umklapp* processes (U processes), for which $|\mathbf{k}'-\mathbf{k}|>k_D$, and $\mathbf{k}'-\mathbf{k}=\mathbf{q}+\mathbf{K}_N$, where K_N is a reciprocal lattice vector.[10] For the U processes we make the further approximation that $q\approx k_D$, an approximation which certainly underestimates the effectiveness of the U processes. Finally, we remark that within the spirit of the approximation which yields the expressions (14) and (15), we should take as the ion-ion interaction, $(Z^2e^2/|\mathbf{R}_i-\mathbf{R}_j|)\exp\{-k_s|\mathbf{R}_i-\mathbf{R}_j|\}$. This latter approximation leads to a sound velocity s, given by[5]

$$s^2=\frac{1}{3}\frac{m}{M}Z^*v_0^2. \tag{16}$$

For Z^*, the ion valency, which determines the effective number of electrons taking part in the screening processes and the state density at the Fermi surface ($N_e=Z^*N$), we shall take the number of electrons outside the last closed shell or the number of holes in the last shell, whichever is the smaller. In the case of a compound or alloy Z^* represents the average valency, defined according to this prescription. Evidence that this is a good approximation for the number of electrons free to take part in screening processes in the nontransition metals comes from the plasmon spectrum of solids.[11]

With the foregoing approximations, we find the following expressions for V:

(1) N processes

$$-V_N=\left\langle -\frac{4\pi N(Z^*)^2e^2}{M}\frac{4\pi e^2}{[(\mathbf{k}-\mathbf{k}')^2+k_s^2]^2}\frac{(\mathbf{k}-\mathbf{k}')^2}{s^2(\mathbf{k}-\mathbf{k}')^2}+\frac{4\pi e^2}{(\mathbf{k}-\mathbf{k}')^2+k_s^2}\right\rangle_{\mathrm{Av}}, \tag{17}$$

where the average is to be carried out over $|\mathbf{k}'-\mathbf{k}|<k_D$.

(2) U processes

$$-V_U=\left\langle -\frac{4\pi N(Z^*)^2e^2}{M}\frac{4\pi e^2}{[(\mathbf{k}-\mathbf{k}')^2+k_s^2]^2}\frac{(\mathbf{k}-\mathbf{k}')^2}{s^2k_D^2}+\frac{4\pi e^2}{(\mathbf{k}-\mathbf{k}')^2+k_s^2}\right\rangle_{\mathrm{Av}}, \tag{18}$$

where the average to be carried out over $|\mathbf{k}'-\mathbf{k}|>k_D$.

We first remark that $-V_N$ is always positive, so that N processes alone would never yield a sufficiently attractive phonon-induced electron interaction to give superconductivity. To see this, substitute (16) and (13) into (17); one finds

$$-V_N=\frac{\pi e^2}{k_0^2}\int_0^{1/(4Z^*)^{\frac{1}{3}}}dx\,2x\left\{\frac{1}{x^2+a^2}-\frac{a^2}{(x^2+a^2)^2}\right\}, \tag{19}$$

where we have made use of

$$|\mathbf{k}'-\mathbf{k}|=2k_0\sin(\theta/2)=2k_0x,$$

θ being the angle between $\mathbf{k}$ and $\mathbf{k}'$, and we define

$$a^2=(4/9\pi^4)^{\frac{1}{3}}r_s=r_s/6.02. \tag{20}$$

Since the maximum value of r_s is 5.57 (for Cs), it is clear that the integrand of (19) is always positive, so that $-V_N$ is always positive. On carrying out the indicated integrations, one finds for the parameter of direct interest in the BCS theory,

$$-N(0)V=a^2\left\{[1-(4Z^*)^{\frac{2}{3}}a^2]\ln\left(\frac{1+a^2}{a^2}\right)+(4Z^*)^{\frac{2}{3}}a^2\ln\overset{1}{-}\left(\frac{+(4Z^*)^{\frac{2}{3}}a^2}{(4Z^*)^{\frac{2}{3}}a^2}\right)+\frac{(4Z^*)^{\frac{2}{3}}a^2}{1+a^2}-1\right\}. \tag{21}$$

We have used the free-electron value of $N(0)$ in obtaining (21). We see that with our model, $N(0)V$ depends only on Z^* and on the interelectron spacing.

III. CRITERION FOR SUPERCONDUCTIVITY

The criterion for superconductivity in the BCS theory is that $-V$ be negative. In Fig. 2 we plot the relation $V=0$, derived from Eq. (21), as a function of Z^* and r_s. We thus have a smooth curve, which should accordingly distinguish between superconductors and nonsuperconductors (the superconductors should be found above the curve). For comparison we have indicated the positions of the various superconducting and nonsuperconducting elements which are metals. We have omitted those elements which are ferromagnetic, or antiferromagnetic, as well as the semimetals and semiconductors; we discuss these below.

We see that the requirement that our expression, (21) be negative furnishes a rather accurate criterion for the appearance of superconductivity in the periodic system. The reason that for a fixed r_s a larger Z^* favors superconductivity lies in the increased importance of the U processes, which enable the attractive interaction to play a more important role. For the same reason, for a fixed Z^* an increased value of r_s favors superconductivity.

We see that our criterion is in worst shape for $Z^*=2$; this is also the region for which Matthias observes no regularities. Such a situation is not surprising. It is for

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[10] As has been emphasized recently by H. Jones [Handbuch der Physik (Springer-Verlag, Berlin, 1956), Vol. 19, p. 227], the separation of scattering processes into U processes and N processes is somewhat arbitrary for polyvalent metals. However, this simple separation appears to be the only procedure we might adopt which, within the spirit of our general approach, has some chance of proving useful for a wide variety of metals.

[11] D. Pines, Rev. Modern Phys. 28, 184 (1956).

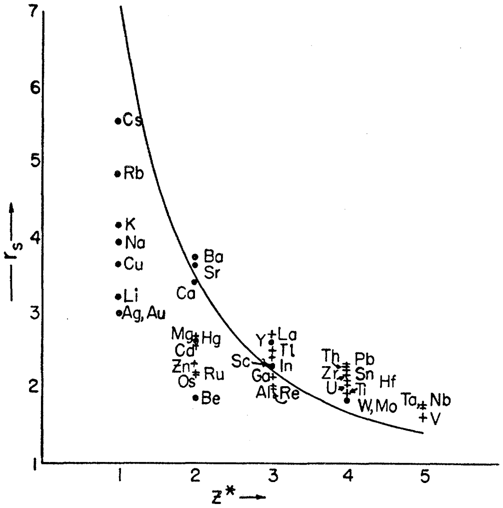

FIG. 2. The critical r_s for superconductivity as a function of Z^*. The superconducting elements are denoted by +; the nonsuperconducting elements by ●.

just this region that our major approximation, the neglect of periodicity in the evaluation of our matrix elements, may be expected to be at its worst. In the absence of band overlap, there are just enough electrons to fill the Brillouin zone. Of course there is overlap, so that elements with $Z^*=2$ are metals, but we may still expect the proximity of the Brillouin zone boundaries to alter markedly the electronic wave functions. Hence we may expect the failure of regularities which are insensitive to effects of periodicity, as are the Matthias rules, and predictions based on our result, (21). A similar situation should not occur for $Z^*=4$ or 6, because here the Brillouin zones are sufficiently complex, and overlap is sufficiently large, that periodicity plays a much less important role.

We do not predict superconductivity for the trivalent metals, Ga, Al, and Re. Again this result is not surprising, because in approximating V_U we have replaced $\hbar\omega$ by $k\theta_D$, an approximation which certainly underestimates the attractive contribution there. We accordingly expect our criterion to be somewhat on the pessimistic side, and it is. (On the other hand, in improving our estimate of V, we would not expect the monovalent elements to become superconductors, since the relative importance of the U processes increases with increasing Z^*.)

On the basis of these considerations, we expect the following metals to become superconducting: Sc, Y, Pa, Mo, and W. A similar conclusion has been reached by Matthias[1] on the basis of his empirical regularities.

It is also clear from Fig. 2 why semimetals are not superconducting: Z^* is far too small. In a metallic phase they are superconducting. Hence we expect that metallic As and Sb, if made, will be superconductors. A similar conclusion doubtless applies for the semiconductors, Se, and Te, though the case of degenerate semiconductors in general deserves further consideration.

Ferromagnetic and antiferromagnetic metals are not superconducting for a rather different reason. We remark that in Eq. (21) there is a near-cancellation between the contributions from the attractive phonon-induced interaction and the repulsive Coulomb interaction. Hence any factor which prevents the electrons from taking maximum advantage of the attractive part of the phonon-induced interaction will strongly inhibit superconductivity. As BCS have shown, the phonon-induced interaction is most attractive when we work with variational wave functions containing paired electrons of opposite spin and momentum. Such pairing is opposed by the exchange interactions between the electrons in those metals which display ferromagnetic or antiferromagnetic behavior; in fact the energy gain from the exchange-induced spin correlations is large compared to that achieved in a superconducting transition at absolute zero. Hence ferromagnetic or antiferromagnetic metals should not superconduct. The rare-earth metals should not be superconductors for a similar reason: the unpaired electron spins prevent the electrons from taking proper advantage of the phonon-induced electron interactions.

Let us now turn to the possible influence of crystalline structure on the appearance of superconductivity. Our expression (21) is, as we have remarked, not dependent on the crystalline structure. However, if we improve our treatment of the U processes, by taking $\mathbf{q}=\mathbf{k}'-\mathbf{k}+\mathbf{K}_n$ in the matrix elements deriving from (15) which appear there, a dependence on crystalline structure emerges. We have carried out preliminary calculations using an improved model for the U processes, that

TABLE I. $N(0)V$ for the superconducting elements. T_c and θ_d are taken from the American Institute of Physics Handbook; the values of r_s and θ_d indicated by an asterisk are estimated.

Metal	Z^*	r_s	T_c	θ_d	$N(0)V$
Al	3	2.06	1.20	375	0.193
Zn	2	2.30	0.93	235	0.200
Ga	3	2.18	1.10	240	0.206
Cd	2	2.58	0.56	165	0.196
In	3	2.40	3.37	109	0.345
Sn	4	2.21	3.74	195	0.296
Hg	2	2.66	4.16	69	0.446
Tl	3	2.48	2.39	100	0.316
Pb	4	2.28	7.22	96.3	0.493
Ti	4	1.92	0.39	430	0.155
V	5	1.61	4.89	338	0.274
Zr	4	2.14	0.55	265	0.178
Nb	5	1.78	8.8	252	0.357
Tc	3	2.12*	11.0	350*	0.345
Ru	2	2.20	0.47	350*	0.165
La	3	2.70	5.0	132	0.370
Hf	4	2.08	0.35	213	0.171
Ta	5	1.79	4.4	230	0.296
Re	3	1.98	1.7	210	0.236
Os	2	2.17	0.71	280*	0.185
Th	4	2.36	1.39	168	0.236
U	4	2.04	0.8	200	0.202

introduced by Jones[12] for the monovalent metals. The principal difficulty in carrying the calculations through arises from the large number of reciprocal lattice vectors which are of importance in the U processes. The use of the Jones model does bring in a slight dependence of T_c on lattice structure. Face-centered cubic and body-centered cubic metals of equivalent Z^* and r_s have negligibly different values of $N(0)V$, while hexagonal close-packed metals (again with the same Z^* and r_s) should show a slightly higher transition temperature than their cubic counterparts.

We believe that metals without a center of inversion fail to superconduct because the number of useful U processes available to the electrons is markedly reduced. In other words, the effects of crystalline symmetry (rather, here, the lack of it) are such as to prevent the electrons from taking maximum advantage of the phonon-induced attractive interaction. In general we expect crystalline symmetry to play a role through the U processes.*

Finally we remark that we expect the conclusions of this section apply equally well to superconducting compounds and alloys, an expectation which is certainly borne out by the Matthias regularities.

IV. VARIATION OF T_c AND $N(0)V$

In the BCS theory, T_c is given by Eq. (2). It may vary from one metal to another because $\langle\hbar\omega\rangle_{\mathrm{Av}}$ varies (and this variation yields the isotope effect), or because $N(0)V$ varies, the latter variation being the more important. We are primarily interested in the behavior of $N(0)V$, since it is this quantity which reflects the electronic behavior. [We remark that in searching for empirical regularities amongst the superconductors it would now seem more sensible to compare $T_c/\langle\hbar\omega\rangle_{\mathrm{Av}}$ for various superconductors, rather than T_c.] In Table I, we give our determination of $N(0)V$ for the superconducting elements, under the assumption that $\langle\hbar\omega\rangle_{\mathrm{Av}} = \theta_D/2$. The results are displayed in Figs. 3 and 4. We see that the regularities of Matthias still persist for $N(0)V$ (although of course in weakened form, since we have removed the exponential dependence):

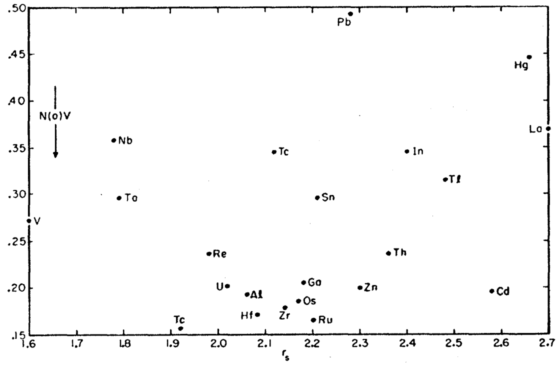

FIG. 3. $N(0)V$ for the superconducting elements as a function of r_s

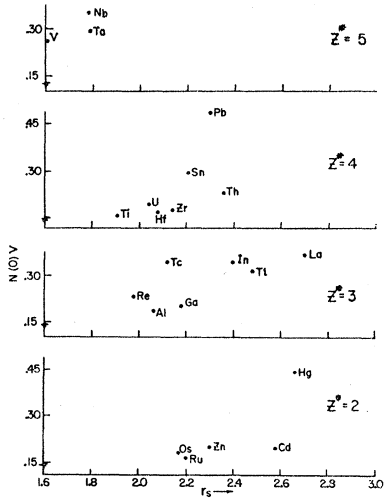

FIG. 4. $N(0)V$ for the superconducting elements as a function of r_s for different Z^*.

(1) For a given Z^* (aside from the divalent metals), $N(0)V$ increases with increasing r_s.

(2) For the nontransition elements, there is an increase of $N(0)V$ with increasing Z^*, for metals with approximately the same r_s.

(3) The variation of $N(0)V$ with Z^* is quite different for the transition elements; for roughly the same r_s, $N(0)V$ displays the same periodic variations (though correspondingly less marked) that T_c does in Fig. 1.

Similar results hold for the superconducting alloys and compounds.

We first remark that our calculated values of $N(0)V$ fall well below the experimental values. [For example, we obtain $N(0)V = 0.074$ for Sn.] Again, the reason we underestimate the attractive phonon-induced electron-electron interaction is our underestimate of V_U. In carrying out the calculations leading to (21) our two principal approximations tend to cancel one another. By neglecting the influence of the periodic potential on the electronic wave functions, we overestimate the matrix elements, $U(|\mathbf{k}'-\mathbf{k}|)$ and $M_q(|\mathbf{k}'-\mathbf{k}|)$, while our use of k_D for the U-process phonon wave vector leads to an underestimate of V_U. Qualitatively, it is clear that the net effect of improving both approximations will be in the right direction, since the periodicity correction will reduce both $M_q(|\mathbf{k}'-\mathbf{k}|)$ and $U(|\mathbf{k}'-\mathbf{k}|)$ by roughly the same amount, while an improved treatment of the U processes will increase only $M_q^2(\mathbf{k}'-\mathbf{k})/\hbar\omega$. Thus $N(0)V$ for all superconductors will be increased over the values predicted by (21).

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* H. Jones, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 227.

[13] For the purpose of this discussion we regard the behavior of the electrons in metals with $Z=2$ or 8, or the variation in state density in the d band in transition metals, as having origins elsewhere.

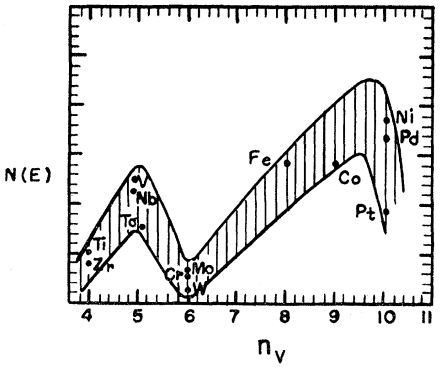

FIG. 5. Density of states in the $3d$ band (after Daunt[13]). The circles give the density of states, $N(E)$ at the Fermi level as deduced from the observed electronic specific heats for the metals as marked. The shaded path indicates the possible region in which the $N(E)$ values for the other, as yet unmeasured, transition metals may fall.

Despite our lack of quantitative accuracy in the calculation of $N(0)V$, we may still draw certain qualitative conclusions of interest concerning its variation throughout the periodic system from (21). We find that (21) yields results for $N(0)V$ which are consistent with regularities (1) and (2) above [or with the Matthias regularity (5) and that part of (7) applying to the nontransition elements]. These results are obvious from inspection of Fig. 2, which tells us that $-N(0)V$ becomes more negative with increasing r_s for a fixed Z^*, or with increasing Z^* for a fixed r_s.

The situation is quite different for the transition metals, a difference which we believe can be traced to the variation in the density of states in energy in the d band with valency. The close relationship between the variation in T_c and the d-band state density (see Fig. 5) has been pointed out by Daunt[13] and Matthias.[1] Let us see how it might follow from the BCS theory.[14]

In (21), the dependence of $N(0)V$ on the state density $N(0)$ is not particularly simple, since the state density in the free-electron theory is proportional to r_s^{-1}, and hence to $(1/a^2)$. The rather complicated dependence is due to the fact that the value of V, in (21), is quite sensitive to the value of the screening radius k_s^{-1} we assume. For our simple model, $k_s \propto [N(0)]^{-\frac{1}{2}}$, and the variation of V with k_s tends to counterbalance the appearance of $N(0)$ in the expression $N(0)V$. This conclusion appears to be valid for the nontransition metals. Let us now consider the transition metals.

The physical situation for the coupled electron-ion motion in the transition metals differs substantially from that obtaining in the nontransition metals. The overlap of the s and d bands, with their quite different state densities, leads to rather complex electronic behavior, which cannot be analyzed on the basis of the foregoing simple model. Consequently, we shall only endeavor to present a qualitative account of the electronic behavior, and the way in which it may account for the superconducting properties of the transition metals. The ideas which follow are intended to be suggestive of how an account of that behavior may be formulated, rather than representing the fruits of such a formulation.

The basic difference between the transition metals and the nontransition metals is that the effective screening wavevector, which so largely determines V, is not simply related to the state density $N(0)$. As a result $N(0)$ and V are more nearly decoupled in the transition metals. One therefore expects a transition temperature which varies more nearly as $\exp[-N(0)]$, where $N(0)$ is determined almost entirely by the "d"-band state density, that being much higher than the corresponding "s"-band density. Such a variation accounts quite well for the variation of T_c with Z^* in the transition elements, since the appearance of $N(0)$ in the exponential certainly emphasizes the role of the state density.

Let us consider the problem in more detail. We have both Coulomb repulsive and phonon-induced attractive interactions between d electrons, between d electrons and s electrons, and between s electrons. In the BCS theory, because it is a variational approach, only the "d–d" or "s–s" interactions will be of importance. Hence, the s–d interaction plays a role only as, in higher order, it modifies the "direct" "d–d" and "s–s" interactions. The s electrons are fairly mobile, and behave very much like the nontransition element electrons. Thus, their effective interaction, and their contribution to $N(0)V$, may be expected to go in much the same fashion. However, as we have mentioned, the d band is responsible for the major portion of the state density at the Fermi surface. As a result, we may expect that it is the d–d interactions which are of primary importance for superconductivity, and the role played by the "s–s" electron interaction may be neglected to a good degree of approximation.

For the short wavelengths in which we are interested, the screening of the interaction between the "d" electrons cannot be as complete as that implied by the use of a Fermi-Thomas model which contains the "d" electron state density.[15] The effective screening action of the "d" electrons appears to be nearly constant throughout a given transition-metal series (extending, indeed, to those metals just beyond). Evidence for such behavior may be found in the plasmon spectrum of the metals,[11] where there is observed a nearly constant plasmon energy (of ~22 ev) from Ti through Zn, for instance.

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[13] J. Daunt in *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1955), Vol. 1, p. 202.

[14] The ideas in the remainder of this section were developed in collaboration with P. Nozières.

[15] J. Friedel, Nuovo Cimento (to be published). We should like to thank Professor Friedel for an illuminating discussion on this question.

Again, it is not unlikely that the phonon-induced "*d-d*" interaction is fairly constant for the transition metals with Z between 3 and 7. The matrix elements for the scattering of a "*d*" electron from one valley to another are the ones of importance (corresponding to a large $\mathbf{k}'-\mathbf{k}$) and these would not be expected to vary radically with changes in Z^* or r_s. Thus we are led to take V as approximately constant for the transition elements, confirming the speculations above. It should be emphasized that V is not strictly constant, as a comparison of $N(0)V$ with the known values of $N(0)$ quickly discloses.

The above considerations appear consistent with experiment for the variation in Z^* with r_s fixed. Compare, for instance Nb with Ta for $Z^*=5$, or the transition elements with $Z^*=4$ with those with $Z=3$, 5, or 7. It should be noted that once we consider appreciable changes in r_s, the quantity $N(0)V$ is no longer simply related to $N(0)$. Thus Zr and Ta have larger values of $N(0)V$ than Ti and V, respectively, despite the fact that the latter pair possess the larger values of $N(0)$. We note also that the values of $N(0)V$ for the transition metals with $Z^*=4$ lie substantially below their counterparts for Sn and Pb. It appears that $N(0)V$ is somewhat smaller for the transition metals than for the normal metals, where the state densities are roughly comparable, and that the large values of $N(0)V$ for the transition metals should be attributed to large values of $N(0)$.

V. CONCLUSION

The BCS theory, together with the simple model of electrons and ions interacting via screened Coulomb interactions, affords a good qualitative understanding of the appearance of superconductivity in the nontransition elements. We may also understand qualitatively the different behavior of the transition elements. Can we go beyond this, without carrying out detailed calculations of the electronic wave functions for each individual metal?

The variation of the portion of $N(0)V$ arising from H_{Coul} is comparatively smooth. In fact on our simple model this part depends only on r_s. It seems therefore likely that the inclusion of various effects of periodicity will not markedly alter the contribution H_{Coul} makes to $N(0)V$. The complications reside in the contribution made by H_{ph}, which does seem sensitive to the details of the calculation. One might hope that one could estimate the latter from the resistance of the metal in question, since at first sight the relaxation time and this part of $N(0)V$ depend only on slightly difference angular averages of $M_q(\mathbf{k}-\mathbf{k}')$. Such is indeed the case for any metal for which intraband scattering is the primary cause of resistance. (These are just the metals for which our simple model is most appropriate.) On the other hand, where interband scattering is important, as in the transition metals or the divalent metals, the matrix elements which are important for resistance are not those important for $N(0)V$, so that no simple estimate of $N(0)V$ along these lines is feasible.

One would also like to derive the shift in T_c with pressure from the BCS theory. The quantitative estimates of $N(0)V$ from (21) are certainly not sufficiently reliable for this purpose. However, it does seem feasible to attempt to estimate $N(0)V$ more accurately in a semiempirical way for the nontransition metals, in order to study its variation with pressure.[16] We may anticipate that the variation of $N(0)V$ with pressure will prove more decisive in its effect on T_c than the known variation in θ_d.

We have not discussed in this paper the empirical correlation between T_c and $N(0)$ noted by Daunt[13] and by Lewis.[17] The regularities they obtain are not consistent with the isotope effect. If they are made consistent, by considering T_c/θ_d for example, one then arrives at the regularities we have been discussing for $N(0)V$. As we have seen, the latter quantity does not depend on state density in any simple way. It should perhaps be noted that the apparent variation of T_c with isotopic mass ($T_c \propto 1/M$) proposed by Matthias[1] becomes somewhat ephemeral when one considers the difference in state densities for the metals discussed by Matthias. We do not expect $N(0)V$ to depend on the isotopic mass, even under the extreme assumption that $N(0)V$ in the transition metals is determined by the higher order corrections from the *s–d* interactions. Hence we expect the variation of T_c with isotopic mass to follow entirely from the variation in $\langle\hbar\omega\rangle_{\mathrm{Av}}$.

Finally we wish to reiterate our belief that the criterion for superconductivity expressed in Fig. 2 should afford a reliable positive test for superconductivity since the criterion is on the pessimistic side. If a metal is not divalent, ferromagnetic, or antiferromagnetic, if it is not ruled out by one of the crystalline structure arguments (for example, no center of symmetry, CdI crystal structure), and if it lies above the curve in Fig. 2, it should superconduct. Thus we expect Mo, W, Y, Sc, Pa, and metallic versions of Sb, As, Se, Te, and Po to superconduct.

We should like to thank Professor John Bardeen, Dr. Bernd Matthias, and Mr. Philippe Nozières for a number of stimulating conversations on these and related topics.

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[16] This possibility is currently being investigated by Mr. Pierre Morel.

[17] H. W. Lewis, Phys. Rev. **101**, 939 (1956).