quoted in the introduction. The answer is that they clearly do not. Any "localization" of a photon in space-time implied by the photoelectric measurement automatically rules out the possibility of knowing its momentum, and with it the possibility of assigning the photon to one or other beam [cf. the symmetry of Eqs. (7) and (15)]. Just as in conventional interferometry, each photon is to be considered as being partly in both beams, and "interferes only with itself." In principle at least, the result of the experiment should be unchanged if on the average only one photon at a time were to traverse the interferometer.

PHYSICAL REVIEW VOLUME 134, NUMBER 1A 6 APRIL 1964

Simple Model for the Superconductivity of Lanthanum and Uranium*

C. G. KUPER,† M. ANTHONY JENSEN, AND D. C. HAMILTON
Department of Physics, University of California, San Diego, La Jolla, California
(Received 30 September 1963; revised manuscript received 18 December 1963)

It is postulated that La and U have a narrow f band above, but very close to, the Fermi surface. An exchange interaction, antiferromagnetic in sign, between electrons in the f band can lead to nonzero occupation of the f levels in a BCS-type wave function. This f-band condensation, through a weak coupling of the f band to the conduction band, enhances a BCS condensation of the conduction electrons. There are two energy gaps, for quasiparticle excitations in the two bands. The critical field at zero temperature is calculated, as is the transition temperature. The predicted isotope effect is extremely small. The ratio between the transition temperature and the energy gap at $T=0$ depends on the numerical values of the parameters; although this ratio is of order unity, it would not be expected to be too near the BCS value of 1/1.75.

1. INTRODUCTION

IT has recently been proposed by two of us[1] that Matthias' rule[2] for the superconductivity of the transition metals be modified as follows. The superconducting transition temperature T_c is a smooth function of the number of valence electrons, approximately symmetric about $n=6$, and with maxima at, roughly, $n=5$ and $n=7$. Matthias had suggested the existence of a third maximum at $n=3$, due mainly to the superconductivity of lanthanum [$T_c=4.9$°K (hex.) and 6.3°K (fcc)]. However, La is the only element in Group III B of the periodic table which is a superconductor. Uranium ($n=6$) has an anomalously large transition temperature (~1°K), and it has been suggested[1] that the superconductivity of these two elements arises from peculiarities of the band structure. La does not have any $4f$ electrons, but the next element Ce has one $4f$ electron; similarly U does not[3] have any $5f$ electrons, but Np probably does.[4] For this reason it was suggested that La and U have an f band above, but very close to, the Fermi surface, and that virtual excitation of electrons into the f band, together with exchange interactions within the band, can strongly enhance the formation of a superconducting state. The object of the present work is to investigate the suggestion quantitatively.

We will assume that there is an f band, of negligible width, at an energy not much (in fact $\lesssim\hbar\omega_D$, the Debye energy) above the Fermi surface. In the lanthanides and actinides the exchange interaction between f electrons is indirect (via s-f scattering); there is insufficient overlap of f-electron wave functions onto the neighboring atomic sites to make an important direct contribution. The scattering of f electrons by s electrons leads in second order to an f-f interaction[5] of the form

$$H_{ff}=-\tfrac{1}{2}\int d^3r_i d^3r_j J(\mathbf{r}_i-\mathbf{r}_j)\boldsymbol{\sigma}(\mathbf{r}_i)\cdot\boldsymbol{\sigma}(\mathbf{r}_j)\,, \qquad (1)$$

where we postulate[6] $J(a)>0$, a=interatomic distance, and where $\boldsymbol{\sigma}(\mathbf{r}_i)$ is the spin density of the ith electron. We will extract from H_{ff} the "pairing" part. Other interactions postulated are the usual s-band (phonon-mediated) pairing force, and a weak interband pairing force.

Using a BCS[7] ansatz, we will minimize the free energy. In the absence of any interband coupling, a condensation into the f band can occur (if J is large enough) but the conduction-band excitation spectrum

* Research supported in part by the U. S. Air Force and the National Science Foundation.
† On leave of absence from School of Natural Philosophy, University of St. Andrews, St. Andrews, Fife, Scotland.
[1] D. C. Hamilton and M. Anthony Jensen, Phys. Rev. Letters **11**, 205 (1963).
[2] B. T. Matthias, *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, Chap. V, p. 138.
[3] W. H. Zachariasen, Acta Cryst. **5**, 19 (1952).
[4] For a discussion of f electrons in Np and Pu, see W. H. Zachariasen, Acta Cryst. **5**, 660, 664 (1952); **16**, 369 (1963).
[5] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); A. Blandin, J. Phys. Radium **22**, 507 (1961).
[6] Blandin (Ref. 5) has shown that the f-f interaction is antiferromagnetic in character near the beginning of the lanthanide series; see also Y.-A. Rocher, Advan. Phys. **11**, 233 (1962).
[7] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

has no energy gap unless the temperature is below the BCS transition temperature of the conduction band (which, by comparison with the other Group III B metals, should be less than 0.1°K). When even a small interband pairing force is included, the f-band condensate can greatly enhance the conduction-band BCS condensation. In lowest approximation the temperature dependence of the conduction-band energy gap is governed entirely by the f-band condensation; in this approximation there is no isotope effect.

We will determine the transition temperature T_c, the low-temperature energy gaps Δ_s and Δ_f, and the condensation energy ($H_0^2/8\pi$ per unit volume); we do not find the BCS value 5.9 for the ratio $H_0^2/\gamma T_c^2$, and therefore expect that La and U should not follow the law of corresponding states.

The method we employ—the use of BCS variational ansatz—is entirely equivalent to the Bogoliubov transformation.[8] The Bogoliubov method has been applied to a two-band model by Suhl, Matthias, and Walker.[9] Although our physical assumptions are rather different from theirs, the only essentially new mathematical features are that the height of the f band above the Fermi surface and the width of the f band are both considerably less than $\hbar\omega_D$, and hence that summations over f states are not truncated. By neglecting the finite width of the f band, we make all sums over the f band trivial.

Kondo[10] has considered a two-band model with a repulsive pairing interaction in the narrow band. Even in this case, he finds an enhancement of superconductivity. However,[6] there is some reason to believe that the effective f-band pairing force is attractive. Kondo's solution remains valid for a small attractive interaction, but becomes singular at a critical value. Above this value we find a different superconducting solution, and in Sec. 5 we will present arguments which suggest that this may indeed be the situation in La.

A metal to which Kondo's solution might apply is Yb; the band structure is similar insofar as we have a full f band just below the Fermi surface. The f-f hole interaction is expected to be ferromagnetic[6] in sign. However, Yb is not a superconductor; there is evidence that it is weakly ferromagnetic at low temperatures instead, with about 1/200-f hole per atom.[11]

2. THE MODEL HAMILTONIAN

Let us consider a specimen, of unit volume, containing $N=a^{-3}$ atoms. We assume the existence of an f band, of negligible width, containing λ states per atom, lying at an energy $\zeta_0+\eta_0$, where ζ_0 is the "normal" Fermi energy (i.e., the Fermi energy in the absence of any electron-electron interactions).[12]

The conduction electrons (hereafter "s electrons," although this is not a completely accurate description) will be assumed to interact with each other according to the usual BCS model. Our estimate of the effective coupling constant $\Xi_0 V$ is $\lesssim 0.1$, by comparison with the other trivalent transition elements Sc, Y, and Lu which are nonsuperconducting down to 0.08, 0.07, and 0.35°K, respectively.[13] (Ξ_0, here, is the density of states at the Fermi surface.)

Electrons in the f band will repel one another strongly, at distances less than the interatomic separation, through Coulomb and exchange interactions.[14] This interaction, being repulsive, cannot lead to Cooper pair formation. At somewhat larger distances, there is an attraction, via the antiferromagnetic exchange energy (1),[15] for electrons with antiparallel spins. In the absence of the intra-atomic repulsion, the interaction (1) could certainly lead to pairing. The modification required by the intra-atomic forces is approximately to require the Cooper pair function to have a node at small electron separation. That is, the relative wave function will have ($2s$) rather than ($1s$) character, and the binding energy will be insensitive to the strength of the intra-atomic repulsion. Qualitatively (and in order of magnitude), the extra node in the Cooper wave function will make little difference.

To construct a tractible and simple model we will reject the intra-atomic interaction terms entirely, and restrict the range of the antiferromagnetic interaction to nearest neighbors only:

$$J(r)=J, \quad r<a, \tag{2}$$

$$J(r)=0, \quad r>a. \tag{3}$$

Since, in the trial wave functions to be introduced in Sec. 3, σ_z will be specified for every electron, we may replace $\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j$ by $(\sigma_i)_z(\sigma_j)_z$; the expectation values of $(\sigma_i)_x(\sigma_j)_x$ and $(\sigma_i)_y(\sigma_j)_y$ will be zero. Taking the Fourier

[8] N. N. Bogoliubov, Zh. Eksperim. i Teor. Fiz. **34**, 58, 73 (1958) [English transl.: Soviet Phys.—JETP **7**, 41, 51 (1958)]; J. G. Valatin, Nuovo Cimento **7**, 843 (1958).

[9] H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Letters **3**, 552 (1959).

[10] J. Kondo, Progr. Theoret. Phys. (Kyoto) **29**, 1 (1963). We wish to thank Dr. R. Traxler for bringing Kondo's work to our attention while the present paper was being prepared for publication.

[11] J. M. Lock, Proc. Phys. Soc. (London) **B70**, 476 (1957).

[12] In Ce the f level is thought to lie close to the Fermi surface, since the f electron will move to the conduction band at low temperatures or high pressures. If we assume a rigid band model, then in La the f level should lie just above the Fermi surface. Thus, for our model we assume a sharp f level at an energy η_0 above the Fermi surface, where η_0 is the width of the f level in Ce. This is of order 10^{-2} eV, or 100°K (see Rocher, Ref. 6).

[13] B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. **35**, 1 (1963).

[14] See, for example, P. W. Anderson, Phys. Rev. **124**, 41 (1961); J. Hubbard, Proc. Roy. Soc. (London) **A276**, 238 (1963); J. Kanamori, Rept. Progr. Phys. **30**, 275 (1963).

[15] As discussed in Sec. 1, the "direct" exchange interaction is unimportant compared with the "indirect" interaction via s-f scattering (Ref. 5). In principle we should eliminate the s-f scattering [whose Hamiltonian has the same form as (1), except that σ_i and σ_j refer to electrons in different bands] in favor of an f-f interaction, by a canonical transformation analogous to that of Fröhlich [Proc. Roy. Soc. (London) **A215**, 291 (1952)] and Bardeen and Pines [Phys. Rev. **99**, 1140 (1955)]. Since such a transformation will leave $n_s=\Sigma a_k^\dagger a_k$ and $n_f=\Sigma c_k^\dagger c_k$ invariant, it will not alter the interband pairing interaction.

transform, we write

$$H_{ff}=-\tfrac{1}{2}\sum_{\mathbf{k},s,s'}(J/N)\sigma_{\mathbf{k},s}\sigma_{\mathbf{k},s'}(1-2\delta_{s,s'}), \quad (4)$$

where $\sigma_{\mathbf{k}s}$ is the $\mathbf{k},s$th component of f-electron density,

$$\sigma_{\mathbf{k}s}=\sum_{\mathbf{p}} c_{\mathbf{p}+\mathbf{k},s}{}^{\dagger}c_{\mathbf{p}s}, \quad (5)$$

and $c_{\mathbf{p}s}{}^{\dagger}$, $c_{\mathbf{p}s}$ are canonical Fermi creation and annihilation operators for electron states in the f band. We are using a Bloch-wave description of the f band, with p as a quasimomentum. Since the band is assumed infinitely narrow this description is completely equivalent to one in terms of localized f electrons. Using $a_{\mathbf{p}s}{}^{\dagger}$, $a_{\mathbf{p}s}$ for creation and annihilation operators of s electrons, we take as our "reduced" model Hamiltonian ("reduced" in the sense of BCS[7])

$$\begin{aligned}H=&\sum_{\mathbf{k},s}\epsilon_k a_{\mathbf{k}s}{}^{\dagger}a_{\mathbf{k}s}+\sum_{\mathbf{k},s}(\zeta_0+\eta_0)c_{\mathbf{k}s}{}^{\dagger}c_{\mathbf{k}s}\\&+\sum_{\mathbf{k},\mathbf{l}}V_{\mathbf{k}\mathbf{l}}{}^{ss}a_{\mathbf{k}\uparrow}{}^{\dagger}a_{-\mathbf{k}\downarrow}{}^{\dagger}a_{-\mathbf{l}\downarrow}a_{\mathbf{l}\uparrow}\\&+\sum_{\mathbf{k},\mathbf{l}}V_{\mathbf{k}\mathbf{l}}{}^{sf}(a_{\mathbf{k}\uparrow}{}^{\dagger}a_{-\mathbf{k}\downarrow}{}^{\dagger}c_{-\mathbf{l}\downarrow}c_{\mathbf{l}\uparrow}+\text{c.c.})\\&-\sum_{\mathbf{k},\mathbf{l}}\frac{J}{2N}c_{\mathbf{k}\uparrow}{}^{\dagger}c_{-\mathbf{k}\downarrow}{}^{\dagger}c_{-\mathbf{l}\downarrow}c_{\mathbf{l}\uparrow}, \quad (6)\end{aligned}$$

where, following BCS, we take

$$V_{kl}{}^{ss}=-V \text{ if } |\epsilon_k-\zeta_0|<\hbar\omega_D \text{ and } |\epsilon_l-\zeta_0|<\hbar\omega_D, \quad (7a)$$
$$=0 \text{ otherwise.}$$

The simplest assumption for the interband coupling term is

$$V_{kl}{}^{sf}=V_1 \quad \text{if} \quad |\epsilon_k-\zeta_0|<\hbar\omega_1,$$
$$=0 \text{ otherwise.} \quad (7b)$$

The cutoff frequency ω_1 will be required to prevent a logarithmic divergence in Eq. (27); the exact value of ω_1 will not be important. The sign of V_1 is immaterial to the theory, though probably positive in fact. The f electrons are strongly localized and therefore are weakly coupled to the phonon field. In the absence of much phonon coupling, the most important contribution to the s-f pairing force arises from the exchange Coulomb integrals. The matrix element for a process in which two electrons scatter each other from the s band into the f band (or vice versa) will be $\sim e^2\int d^3r\{e^{i\mathbf{q}\cdot\mathbf{r}}/q^2\kappa(q)\}$, where the dielectric constant $\kappa(q)$ responsible for screening depends *inter alia* on the products of the "atomic" factors of the Bloch wave functions, $u_s(\mathbf{r}_i)$, $u_f(\mathbf{r}_i)$. On account of the strong localization of f electrons within a unit cell, the screening diameter cannot exceed the interatomic distance, so that $V_1\lesssim 0.1/\Xi_0$.[16] For definiteness we will accept Garland's estimate, $V_1\Xi_0\approx 0.05$.

[16] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962); J. W. Garland, Phys. Rev. Letters **11**, 111 (1963).

We have neglected Anderson's[14] "one-body" s-f coupling term, which will be of the form

$$\sum_{\mathbf{k}} V_2(\mathbf{k})(a_{\mathbf{k}s}{}^{\dagger}c_{\mathbf{k}s}+\text{c.c.}).$$

With the BCS ansatz (8), to be introduced in the next section, this interaction has zero expectation value. Of course we could try to include it, by perturbation theory, before resorting to the variational approach. In second order it will contribute to V_1, but as the theory is not excessively sensitive to V_1, we will merely assume its contribution already included, within the uncertainty of Garland's estimate. This one-body interaction cannot affect the f-f coupling below fourth order, and we therefore feel justified in neglecting it.

3. SUPERCONDUCTIVITY AT ZERO TEMPERATURE

To study the superconducting properties at $T=0$, we make the BCS-type ansatz

$$|\Psi_0\rangle=\prod_{\mathbf{k}}(u_{\mathbf{k}}+v_{\mathbf{k}}a_{\mathbf{k}\uparrow}{}^{\dagger}a_{-\mathbf{k}\downarrow}{}^{\dagger})\prod_{\mathbf{l}}(u_f\pm v_f c_{\mathbf{l}\uparrow}{}^{\dagger}c_{-\mathbf{l}\downarrow}{}^{\dagger})|0\rangle, \quad (8)$$

where $u_{\mathbf{k}}$, $v_{\mathbf{k}}$, u_f, and v_f are positive; $u_k{}^2+v_k{}^2=u_f{}^2+v_f{}^2=1$; the sign preceding v_f is chosen to be that of $-V_1$ (Kondo[10]) and where, because the f band is assumed infinitely narrow, we have taken u_f and v_f to be constant across the band.

The number operator of electrons is given by

$$N_e=\sum_{\mathbf{k},s}(a_{\mathbf{k}s}{}^{\dagger}a_{\mathbf{k}s}+c_{\mathbf{k}s}{}^{\dagger}c_{\mathbf{k}s}), \quad (9)$$

with expectation value

$$\langle\Psi_0|N_e|\Psi_0\rangle=2\textstyle\sum_{\mathbf{k}} v_{\mathbf{k}}{}^2+2N\lambda v_f{}^2, \quad (10)$$

where 2λ is the number of f states per atom. Under the assumption[17] that the crystalline field does not lift the degeneracy of the atomic f states, $2\lambda=14$.

Subject to the constraint that $\langle\Psi_0|N_e|\Psi_0\rangle$ is a constant; we minimize

$$\begin{aligned}\langle\Psi_0|H|\Psi_0\rangle=&2\sum_{\mathbf{k},s}\epsilon_{\mathbf{k}}v_{\mathbf{k}}{}^2+2\lambda N(\zeta_0+\eta_0)v_f{}^2\\&-\tfrac{1}{2}(J/N)(N\lambda)^2u_f{}^2v_f{}^2-V\sum_{\mathbf{k},\mathbf{l}}{}'u_{\mathbf{k}}v_{\mathbf{k}}u_{\mathbf{l}}v_{\mathbf{l}}\\&+2N\lambda V_1u_fv_f\sum_{\mathbf{k}}{}''u_{\mathbf{k}}v_{\mathbf{k}}, \quad (11)\end{aligned}$$

where the singly-primed summation is cut off by Eq. (7a), and the doubly-primed summation is restricted by Eq. (7b). The chemical potential ζ appears as a Lagrangian multiplier on expression (10). The

[17] Since Hund's rule applies well to the lanthanides, it is believed that for atoms with a partially filled f shell, the f level is split into two 7-fold levels, rather than three 4-fold and one 2-fold levels (Rocher, Ref. 6); i.e., the crystalline-field splitting is slight. For an empty f shell, of course, the two 7-fold levels remain degenerate.

minimization with respect to v_f gives

$$2(\zeta_0+\eta_0-\zeta)\lambda N-\tfrac{1}{2}JN\lambda^2(1-2v_f^2)$$
$$-(|V_1|/|u_fv_f|)(1-2v_f^2)\sum_{\mathbf{k}}{}''u_kv_k=0. \quad (12)$$

Provided that we may neglect the term in V_1 (see Appendix A), Eq. (12) has a solution

$$v_f^2=\tfrac{1}{2}(1-4\eta/\lambda J), \quad (13)$$

where

$$\eta=\eta_0+\zeta_0-\zeta. \quad (14)$$

The shift $\zeta_0-\zeta$ in the chemical potential (compared with the "normal" state) is neglected by Kondo,[10] but we find that it is quite important. It arises from the number of electrons transferred out of the s band into the f band. Thus

$$2N\lambda v_f^2=2\Xi_0(\zeta_0-\zeta), \quad (15)$$

where $2\Xi_0$ is the density of (s) states at the Fermi surface, including spin [Ξ_0 corresponds to $N(0)$ in BCS].

From (13) we have

$$\eta=(J\lambda/4)(1-2v_f^2). \quad (16)$$

Hence from (14) and (15), writing $\theta\equiv N/\Xi_0$

$$v_f^2=\frac{1}{2}\left(\frac{1-4\eta_0/\lambda J}{1+2\theta/J}\right). \quad (17)$$

If required, better solutions to (12) can be generated perturbatively, or even by solving the quartic equation for v_f^2 explicitly. We will not attempt this here, since the approximation (13) is probably quite good. However let us note that this solution becomes unphysical unless

$$J\lambda>4\eta_0. \quad (18)$$

Condition (18) is probably fulfilled (see Appendix B). If it does not hold, then, in the absence of interband coupling the only solution is the trivial one, $v_f=0$. With the interband coupling included, but with the approximation $v_f\ll 1$, (12) has the solution

$$|v_f|=|V_1|\sum_{\mathbf{k}}{}''u_kv_k/(4\eta-\lambda J), \quad (19)$$

which is equivalent to Kondo's[10] solution. We see at once the singularity of (19) as $\lambda J\to 4\eta-0$. Henceforth, in view of our estimates of J, η, and λ, we assume (18) is satisfied.

Minimizing $\langle\Psi_0|H-N_e\zeta|\Psi_0\rangle$ with respect to v_k, we have

$$2(\epsilon_k-\zeta)=\frac{1-2v_k^2}{u_kv_k}\left\{|V_1u_fv_f|N\lambda+V\sum_{\mathbf{k}}{}'u_kv_k\right\}, \quad (20)$$

whence

$$v_k^2=\tfrac{1}{2}\{1-\mathcal{E}_k/(\mathcal{E}_k^2+\Delta_s^2)^{1/2}\} \quad (21)$$

with

$$\mathcal{E}_k=\epsilon_k-\zeta \quad (22)$$

and

$$\Delta_s=N\lambda|V_1u_fv_f|+V\sum{}'u_kv_k$$
$$=N\lambda|V_1u_fv_f|+\Xi_0V\Delta_s\sinh^{-1}\hbar\omega_D/\Delta_s. \quad (23)$$

If $v_f=0$, we recover the BCS result as a limiting case. Provided V_1 is not too small compared to V, the second term in (23) is small, and

$$\Delta_s\simeq\Delta_0\equiv N\lambda|V_1u_fv_f| \quad (24)$$

[as may be verified by solving (23) by iteration, and remembering, from (17), that $v_f^2\sim 10^{-2}$ or 10^{-3}, while $\Xi_0V\lesssim 10^{-1}$].

To show that $2\Delta_s$ is the energy gap for creating two quasiparticles in the conduction band, we calculate the expectation value of $H-\zeta N_e$ for a state $\alpha_{\mathbf{k},\pm}{}^\dagger|\Psi_0\rangle$, where $\alpha_{\mathbf{k},\pm}{}^\dagger=u_ka_{\mathbf{k},\pm}{}^\dagger\mp v_ka_{-\mathbf{k},\mp}$ is a Bogoliubov quasiparticle creation operator. Thus

$$E_s\equiv\langle\Psi_0\alpha_{\mathbf{k}}|H-\zeta N_e|\alpha_{\mathbf{k}}{}^\dagger\Psi_0\rangle-\langle\Psi_0|H-\zeta N_e|\Psi_0\rangle$$
$$=(\epsilon_k-\zeta)(1-2v_k^2)+2u_kv_k\{N\lambda|V_1u_fv_f|+\sum{}'Vu_lv_l\}$$
$$=(\Delta_s^2+\mathcal{E}_k^2)^{1/2}, \quad (25)$$

from (21), (22), and (23). This is, as usual, the energy of a single quasiparticle; experimentally at least two excitations have to be produced together, so that the energy gap is $2\Delta_s$.

But this is not the only kind of excitation—we can also have quasiparticle excitations $\gamma_{\mathbf{k}\pm}{}^\dagger=u_fc_{\mathbf{k}\pm}{}^\dagger\mp v_fc_{-\mathbf{k},\mp}$ in the f band, with energy

$$E_f=\langle\Psi_0\gamma_{\mathbf{k}}|H-\zeta N_e|\gamma_{\mathbf{k}}{}^\dagger\Psi_0\rangle-\langle\Psi_0|H-\zeta N_e|\Psi_0\rangle$$
$$=(\eta_0+\zeta_0-\zeta)(1-2v_f^2)+J\lambda u_f^2v_f^2$$
$$+2|V_1u_fv_f|\sum_{\mathbf{k}}{}''u_kv_k. \quad (26)$$

Using (14) and (16), and evaluating the $\sum_{\mathbf{k}}{}''$ as in (23),

$$E_f=\tfrac{1}{4}J\lambda+2|V_1u_fv_f|\Xi_0\Delta_s\sinh^{-1}\hbar\omega_1/\Delta_s \quad (27)$$

where [see Eq. 7(b)] we have cut off the summation at an energy $\hbar\omega_1$ (not necessarily the Debye energy) to prevent a logarithmic divergence. By arguments similar to those used for (23), we can, to a good approximation, neglect the second term in (27), giving

$$E_f=\tfrac{1}{4}J\lambda. \quad (28a)$$

Alternatively, we could define an f-band "gap function" Δ_f, by analogy with BCS,

$$\Delta_f=\sum_f(J/N)(v_f(1-v_f))^{1/2}=J\lambda(v_f(1-v_f))^{1/2} \quad (28b)$$

to find

$$E_f=(\eta^2+\Delta_f^2)^{1/2}=\tfrac{1}{4}J\lambda. \quad (29)$$

The ratio of the gap functions Δ_s/Δ_f may be rather large. Assuming $\theta/J\sim\frac{1}{2}\times 10^2$ and $\Xi_0V_1\sim 0.05$, $\Delta_s/\Delta_f\lesssim 4$. However, Δ_f does not correspond to any experimentally observable quantity—the significant single-particle excitation energy is E_f, which is larger than Δ_f by a factor $2/v_f\sim 10$ say, i.e., $\Delta_s/E_f\sim 0.4$.

We thus expect the density of states to show some

structure. Let us assume (as is probably the case), that $\Delta_s<E_f$. Then tunneling should appear first at an energy $2\Delta_s$, but there should be an extra tunneling current (small, on account of the high effective mass of f electrons) at energy Δ_s+E_f.

There remains one other important quantity which we wish to find at $T=0$: the condensation energy $H_0^2/8\pi$. If $|\Psi_N\rangle$ is the "normal" ground state, we have

$$\begin{aligned}H_0^2/8\pi&=\langle\Psi_N|H-\zeta N_e|\Psi_N\rangle-\langle\Psi_0|H-\zeta N_e|\Psi_0\rangle\\&=2\sum_{k=0}^{k_0}\epsilon_k-2\sum_{k=0}^{\infty}\epsilon_k v_k^2-2\lambda N(\zeta_0+\eta_0)v_f^2\\&\quad+2|V_1|(\sum{}''u_kv_k)N\lambda|u_fv_f|\\&\quad+V\sum_{\mathbf{k},\mathbf{l}}{}'u_kv_ku_lv_l+\tfrac{1}{2}J\lambda^2Nu_f^2v_f^2,\end{aligned}\tag{30}$$

where k_0 is the normal Fermi surface, and where the singly-primed summation is to be cut off in accordance with (7a) and the doubly-primed one according to (7b). After straightforward but rather lengthy calculation, taking $\omega_1=\omega_D$ for definiteness, we find (see Appendix C)

$$\begin{aligned}H_0^2/8\pi&=\tfrac{1}{2}\Delta_s^2\Xi_0+\tfrac{1}{2}N\lambda|V_1u_fv_f|\Xi_0\Delta_s\sinh^{-1}(\hbar\omega_D/\Delta_s)\\&\quad-2\lambda N\eta_0v_f^2+\tfrac{1}{2}JN\lambda^2u_f^2v_f^2\\&=\tfrac{1}{2}\Delta_s^2\Xi_0\{1-2[1-\Xi_0V\sinh^{-1}(\hbar\omega_D/\Delta_s)]\\&\quad\times\sinh^{-1}(\hbar\omega_D/\Delta_s)\}\\&\quad+\tfrac{1}{8}(J^2/\theta)N\lambda^2(1-4\eta_0/\lambda J)^2,\end{aligned}\tag{31}$$

neglecting unity compared with θ/J.

If $v_f=0$, we recover the BCS relation $H_0^2/8\pi=\frac{1}{2}\Delta_s^2\Xi_0$; more generally, $H_0^2/8\pi>\frac{1}{2}\Delta_s^2\Xi_0$.

4. SUPERCONDUCTIVITY AT FINITE TEMPERATURES

The thermal properties of the system can be calculated by the BCS method—we have to consider real unpaired particles and excited pair states as well as ground pairs, both in the s band and the in f band. Defining f_k as the probability of occupancy of a state $\mathbf{k}$ in the s band, and f_f as the probability of occupancy of a state in the f band, we have for the expectation energy

$$\begin{aligned}\langle H-N_e\zeta\rangle_{\rm av}&=2\sum_{\mathbf{k}}(\epsilon_k-\zeta)\{v_k^2(1-2f_k)+f_k\}\\&\quad+2\lambda N\eta\{v_f^2(1-2f_f)+f_f\}-\tfrac{1}{2}JN\lambda^2u_f^2v_f^2(1-2f_f)^2\\&\quad-V\sum_{\mathbf{k},\mathbf{l}}{}'u_kv_ku_lv_l(1-2f_k)(1-2f_l)\\&\quad-2V_1|N\lambda|u_fv_f|(1-2f_f)\sum{}''u_kv_k(1-2f_k).\end{aligned}\tag{32}$$

The entropy is

$$S=k\Big\{\sum_{\mathbf{k}}f_k\ln f_k+(1-f_k)\ln(1-f_k)+N\lambda[f_f\ln f_f+(1-f_f)\ln(1-f_f)]\Big\}.\tag{33}$$

Minimizing the free energy $F=\langle H-N_e\zeta-TS\rangle_{\rm av}$ with respect to the f's and v's, we have

$$\begin{aligned}f_k&=\{\exp[\beta(\mathcal{E}_k^2+\Delta_s^2)^{1/2}]+1\}^{-1};\\f_f&=(e^{\beta E_f}+1)^{-1},\end{aligned}\tag{34}$$

$$\begin{aligned}v_k^2&=\tfrac{1}{2}\{1-\mathcal{E}_k/[\mathcal{E}_k^2+\Delta_s^2(T)]^{1/2}\};\\v_f^2&=\tfrac{1}{2}[1-4\eta(T)/J\lambda(1-2f_f)].\end{aligned}\tag{35}$$

The reason that $\eta(T)$ in (35) is temperature-dependent is, of course, that ζ varies with temperature. In particular, when $4\eta(T)=\lambda J[1-2f_f(T)]$, v_f will vanish—this, therefore, gives the transition temperature T_c, since the superconductivity of the whole system is dependent upon f-level occupancy

The finite-temperature version of (15) is

$$2N\lambda[v_f^2(1-2f_f)+f_f]=2\Xi_0(\zeta_0-\zeta),\tag{36}$$

whence

$$v_f^2=\frac{1}{2}\left\{1-\frac{4\eta_0}{J\lambda(1-2f_f)}-\frac{4\theta[v_f^2(1-2f_f)+f_f]}{J(1-2f_f)}\right\}.\tag{37}$$

At the critical temperature $v_f=0$, so that

$$\frac{1}{2}\left\{1-\frac{4\eta_0}{J\lambda(1-2f_f)}-\frac{4\theta f_f(T_c)}{J(1-2f_f)}\right\}=0,$$

or, assuming $2f_f\ll1$,

$$f_f(T_c)=\frac{J}{8\theta}\left(1-\frac{4\eta_0}{J\lambda}\right)\doteqdot\tfrac{1}{2}v_f^2|_{T=0}.\tag{38}$$

But, from (34) and (28a)

$$f_f(T_c)=(e^{E_f/kT_c}+1)^{-1}\simeq e^{-E_f/kT_c}.\tag{39}$$

Hence from (38) and (39)

$$E_f=\ln(2/v_f^2)kT_c.\tag{40}$$

Since from (17) we know that $v_f^2\lesssim10^{-2}$,

$$E_f\gtrsim5kT_c.\tag{41}$$

This prediction is insensitive to the parameters, and can therefore be made with some confidence. Thermodynamic considerations[18] will require $E_f/\Delta_s>2$, but unfortunately the exact value of Δ_s is much more sensitive to the estimated values of the parameters.

---

[18] Dr. B. B. Goodman (private communication) has drawn our attention to the fact that $H_0^2/\gamma T_c^2$ cannot exceed 4π unless the normal phase has a specific-heat anomaly below T_c. Equations (24), (31), and (41) will satisfy this condition if $\Delta_s\lesssim\frac{1}{2}E_f$, which is satisfied by our estimate in Sec. 3. Dr. D. Ginsberg (private communication) finds experimentally that $\Delta/kT_c\sim1.45$. This is significantly different from the BCS value 1.75 and is consistent with our considerations. It would imply $\Delta_s\sim0.3E_f$.

Note added in proof. J. D. Leslie, R. L. Cappelletti, D. M. Ginsberg, D. K. Finnemore, F. H. Spedding, and B. J. Beaudry (to be published) have found $\Delta_s=1.43\pm0.1kT_c$ and a possible second peak at $\sim4\Delta_s$. This implies $E_f\cong3.5\Delta_s$ and we should expect a second peak at $\Delta_s+E_f\cong4.5\Delta_s$. The agreement may be somewhat fortuitous.

5. DISCUSSION

The present model will yield "anomalous" values of several ratios, compared to BCS. Thus, from (41) and (24), we do not expect to find $kT_c/2\Delta_s=1/3.50$. (A precise statement would require better knowledge of the parameters J and η than are currently available.) Similarly $H_0^2/\gamma T_c^2$ would not be expected to take the BCS value 5.9; i.e., these elements should show an anomaly in the law of corresponding states. Reliable experimental data for La and U are not available, but extrapolation of the date of Anderson *et al.*[19] to $T=0$ gives $H_0\sim1600$ G for fcc La. This would give $H_0^2/\gamma T_c^2=14$. For all superconductors other than La (H_0 is not known for U), the BCS value is found, within 30%.

Let us note, from (38), that T_c will be extremely insensitive to V_1, the interband pairing force. [In contrast, Kondo's solution (19) will depend much more strongly on V_1.] This would help to explain the fact that, for La, T_c is not excessively sensitive to "dirt," which should effect V_1 rather drastically. Garland[16] has criticized not only the size of Kondo's interband pairing force, but even the use of an interband term as the mechanism of superconductivity in a "dirty" superconductor. He maintains that, in a dirty specimen, we should not think of s and d electrons, but rather of suitable mixed wave functions. However, f electrons, on account of their localization, are probably much less hybridized.

Finally, let us note that the model predicts at most a very small isotope effect—this prediction follows from the dependence of T_c only on the antiferromagnetic interaction and not (except to a very small extent) on the electron-phonon coupling.

ACKNOWLEDGMENTS

We wish to thank Professor B. T. Matthias and Professor H. Suhl, and Dr. T. H. Geballe for valuable and illuminating discussions.

APPENDIX A

The solution (13) to Eq. (12) follows if we can neglect

$$\mu\equiv\frac{2|V_1|\sum u_kv_k}{JN\lambda^2|u_fv_f|}$$

compared to unity.

The product u_kv_k is never greater than $\frac{1}{2}$ and is significantly different from zero only in a range of k such that $|\epsilon_k-\zeta|\lesssim\Delta_s$. Hence

$$\sum u_kv_k\sim2\Xi_0\Delta_s\tfrac{1}{2}\sim\Xi_0\Delta_s.$$

But, from (24),

$$\Delta_s\sim N\lambda|V_1|u_fv_f.$$

Hence

$$\mu\sim\frac{2V_1^2\Xi_0}{\lambda J}\ll1.$$

APPENDIX B

Two estimates of J can be made fairly easily. One estimate follows from the Ruderman-Kittel theory.[6] The s-f scattering matrix element is ~0.1 to 0.3 for all the lanthanides, so that the second-order f-f matrix element is $\sim(0.1\text{ to }0.3)^2/\zeta_0\sim1/20$ to $1/200$ eV. With $\lambda=7$, we then have $\frac{1}{3}$ eV $>\lambda J>1/30$ eV. Since the f-shell is least localized in La and Ce, the higher estimates are applicable, and (18) is easily satisfied.

The other estimate of J follows, if we assume that J alters fairly smoothly as we traverse the lanthanide series: For Ce, the susceptibility obeys a Curie-Weiss law, with $\theta_p=-45$°K, while for Pr, $\theta_p=4$°K, and Nd, $\theta_p=8$°K. From θ_p, we can estimate $-J\sim3k\theta_p/12$ (since in these metals there are 12 nearest neighbors[6]). Thus, $J_{\mathrm{Ce}}\sim12$°K, $J_{\mathrm{Pr}}\sim-1$°K, $J_{\mathrm{Nd}}\sim-2$°K. Extrapolating, we would guess $J_{\mathrm{La}}\sim50$°K, so that $\lambda J\sim350$°K, which is only a little too small for condition (18) with our assumed value of η_0.[12] On balance we incline to the view that (18) is probably fulfilled.

APPENDIX C: CALCULATION OF $H_0^2/8\pi$

$$\begin{aligned}H_0^2/8\pi&=\langle\Psi_N|H-\zeta N_e|\Psi_N\rangle-\langle\Psi_0|H-\zeta N_e|\Psi_0\rangle\\&=2\sum_{k=0}^{k_0}\epsilon_k-2\sum_{k=0}^{\infty}\epsilon_kv_k^2-2\lambda N(\zeta_0+\eta_0)v_f^2\\&\quad+2|V_1|(\textstyle\sum''u_kv_k)N\lambda|u_fv_f|\\&\quad+V\sum_{k,l}{}'u_kv_ku_lv_l+\tfrac{1}{2}J\lambda^2Nu_f^2v_f^2.\end{aligned}\tag{30}$$

Writing k_f for the superconducting Fermi surface (i.e., $\zeta=\epsilon_{k_f}$), we have, for the first three terms

$$A\equiv2\sum_0^{k_0}\epsilon_k-2\sum_0^{\infty}\epsilon_kv_k^2-2\lambda N(\zeta_0+\eta_0)v_f^2$$

$$=2\sum_0^{k_f}\epsilon_k-2\sum\epsilon_kv_k^2+2\sum_{k_f}^{k_0}\epsilon_k-2\lambda N(\zeta_0+\eta_0)v_f^2$$

$$=2\sum_0^{k_f}\epsilon_ku_k^2-2\sum_{k_f}^{\infty}\epsilon_kv_k^2+2\Xi_0\int_{\zeta}^{\zeta_0}\epsilon d\epsilon-2\lambda N(\zeta_0+\eta_0)v_f^2.$$

But, from (15),

$$\Xi_0(\zeta_0-\zeta)=N\lambda v_f^2,$$

and from (21), (22)

$$v_f^2=\tfrac{1}{2}[1-\mathcal{E}_k/(\mathcal{E}_k^2+\Delta_s^2)^{1/2}],$$

[19] G. S. Anderson, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 243 (1958).

so that

$$A=2\Xi_0\int\tfrac{1}{2}\epsilon d\epsilon\left\{1-\frac{\epsilon-\zeta}{[(\epsilon-\zeta)^2+\Delta_s^2]^{\frac{1}{2}}}\right\}$$
$$-2\Xi_0\int_{\zeta}^{\zeta+\hbar\omega_D}\tfrac{1}{2}\epsilon d\epsilon\left\{1-\frac{\epsilon-\zeta}{[(\epsilon-\zeta)^2+\Delta_s^2]^{1/2}}\right\}$$
$$+2\Xi_0\zeta_0(\zeta_0-\zeta)-2\lambda N(\zeta_0+\eta_0)v_f^2$$
$$=-2\lambda N\eta_0 v_f^2$$
$$+\Xi_0[-\hbar^2\omega_D^2+\hbar^2\omega_D^2(1+\Delta_s^2/\hbar^2\omega_D^2)^{1/2}$$
$$-\Delta_s^2\sinh^{-1}\hbar\omega_D/\Delta_s].$$

Using (23), we have approximately

$$H_0^2/8\pi=-2\lambda N\eta_0 v_f^2+\Xi_0(\tfrac{1}{2}\Delta_s^2-\Delta_s^2\sinh^{-1}\hbar\omega_D/\Delta_s)$$
$$+\tfrac{1}{2}JN\lambda^2u_f^2v_f^2+\textstyle\sum_k u_kv_k(1+N\lambda|V_1u_fv_f|)$$
$$=\tfrac{1}{2}\Xi_0\Delta_s^2+N\lambda|V_1u_fv_f|\Xi_0\Delta_s\sinh^{-1}\hbar\omega_D/\Delta_s$$
$$-2\lambda N\eta_0v_f^2+\tfrac{1}{2}JN\lambda^2u_f^2v_f^2. \quad \text{(C1)}$$

The last two terms can be rewritten as

$$\tfrac{1}{2}JN\lambda^2v_f^4(v_f^{-2}-1-4\eta_0\lambda N/JN\lambda^2v_f^2)$$
$$=\tfrac{1}{2}JN\lambda^2v_f^4[v_f^{-2}(1-4\eta_0/\lambda J)-1]$$
$$=\tfrac{1}{2}JN\lambda^2v_f^4(1+4\theta/J),$$

from (17). Combining the first two terms in (C1), using (23) to eliminate V_1, and using (17) to eliminate v_f, and neglecting unity compared with θ/J, we finally get Eq. (31).

PHYSICAL REVIEW VOLUME 134, NUMBER 1A 6 APRIL 1964

Superconductivity in Indium Antimonide*

T. F. Stromberg and C. A. Swenson
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa
(Received 8 October 1963)

Two samples of the metallic phase of indium antimonide were stabilized at atmospheric pressure by cooling semiconductor grade material from 100°C to 77°K at a pressure of 27 kbars, and then removing the pressure. Measurements of the magnetic moment of these samples down to 1.1°K were made using a sample-motion technique in a uniform magnetic field. Below 1.89°K, the samples exhibited bulk superconducting properties, in agreement with previous work. A high-field tail on the magnetization curves and the existence of considerable locked-in flux as the magnetic field was reduced were taken to be indications of a high state of residual strain in the sample. The slope of the critical field curve at 1.89°K was found to be $(\partial H_c/\partial T)_{Tc}=-103$G/°K. This is consistent with values found for soft superconductors with similar transition temperatures, and implies a normal state electronic specific heat per cm³, which is roughly half that of white tin. White tin has the same average ionic mass as metallic indium antimonide, and presumably the same electronic density.

INDIUM antimonide and several other III-V semiconducting compounds, as well as germanium and silicon, exhibit transitions into a high-pressure modification which has metallic properties.[1,2] This transition has been studied in some detail for indium antimonide by Jayaraman *et al.*,[3] who showed that the transition should occur near 23 kbars at room temperature, and that the transition pressure should depend only very slightly on temperature. It was suggested that the properties of metallic InSb should be reasonably close to those of white tin, since tin separated In and Sb in the periodic table, and these two metallic solids should have the same average ionic mass, and from elementary considerations, the same electronic density.[3] Jamieson subsequently showed that the crystal structure of this phase was very close to, if not identical with, that of white tin.[4] Since white tin is a superconductor with a transition temperature $T_c=3.7$°K, it was interesting to speculate on the possibility that this new phase of InSb and the metallic phases of the other semiconductors would become superconducting. InSb appeared to be ideally suited for an investigation of this point, since Jayaraman *et al.* commented on the slow transition rate of this transformation in InSb at room temperature,[3] and Jayaraman suggested the possibility that the metallic phase of this solid might be quenched in by cooling a transformed sample under pressure to liquid-nitrogen temperatures, and then removing the pressure.[5] This method would appear to be feasible only for InSb, partially because of the transition kinetics, and partially because of the relatively low transition pressure.

* Contribution No. 1389. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.
[1] H. A. Gebbie, P. L. Smith, I. G. Austin, and J. H. King, Nature **188**, 1095 (1960).
[2] S. Minomura and H. G. Drickamer, Phys. Chem. Solids **23**, 451 (1962).
[3] A. Jayaraman, R. C. Newton, and G. C. Kennedy, Nature **191**, 1288 (1961).
[4] J. C. Jamieson, Science **139**, 847 (1963).
[5] A. Jayaraman (private communication, November 1962).