

cision of about 1%. The  $H_0$  values are estimated from a parabolic extrapolation which, because of the limited range of  $T$ , is probably only accurate to about 10%. From the value of  $(dH_C/dT)_{T_C}$ , the specific heat discontinuity at  $T_C$  is computed to be 2.20 mJ/mole deg for Ru. Using the calorimetrically determined value<sup>8</sup> of  $\gamma = 3.35$  mJ/mole deg<sup>2</sup> (where  $\gamma$  is the normal electronic specific-heat coefficient), one obtains  $(\Delta C/\gamma T_C)_{T=T_C} = 1.37$ , in reasonable agreement with the Bardeen-Cooper-Schrieffer (BCS) value of 1.43.<sup>9</sup>

The  $T_C$  value obtained here is roughly intermediate between the values reported in previous measurements.<sup>1,10,11</sup> (The scatter of our points suggests that our absolute accuracy in  $T$  is no better than  $\pm 0.007^\circ\text{K}$ .) Our values of  $(dH_C/dT)_{T_C}$  are significantly larger than the results of Hulm and Goodman<sup>10</sup> but in reasonable agreement with the value of Carruthers and Connolly.<sup>11</sup> However, it seems noteworthy that, aside from the apparent absence of an isotope effect, these Ru specimens show no other discernable anomalies.

In conclusion we wish to express our appreciation to Dr. T. H. Geballe and Dr. B. T. Matthias for the loan of the Ru specimens and for valuable supplemental comments and discussions. The assistance of E. P. Harris, D. C. Montgomery, and W. R. Wilkes in carrying out the measurements is gratefully acknowledged.

\*This work received partial support from the U. S. Army Research Office, Durham, North Carolina and the Alfred P. Sloan Foundation.

<sup>1</sup>T. H. Geballe, B. T. Matthias, G. W. Hull, and E. Corenzwit, Phys. Rev. Letters **6**, 275 (1961).

<sup>2</sup>T. H. Geballe and B. T. Matthias, IBM J. Research Develop. **6**, 256 (1962).

<sup>3</sup>A. L. Schawlow and G. E. Devlin, Phys. Rev. **113**, 120 (1959). Measuring fields of the order of 0.01 gauss are used.

<sup>4</sup>J. F. Cochran, D. E. Mapother, and R. E. Mould, Phys. Rev. **103**, 1657 (1956).

<sup>5</sup>R. R. Hake, D. E. Mapother, and D. L. Decker, Phys. Rev. **112**, 1522 (1958).

<sup>6</sup>Unfortunately the relatively large transition width characteristic of a spherical specimen makes precise determination of  $H_C$  more difficult and contributes to the experimental scatter evident in Fig. 2.

<sup>7</sup>R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **121**, 86 (1961).

<sup>8</sup>N. M. Walcott, Conférence de Physique des Basses Températures, Paris, 1955 (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956), p. 286.

<sup>9</sup>J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

<sup>10</sup>J. K. Hulm and B. B. Goodman, Phys. Rev. **106**, 659 (1957).

<sup>11</sup>J. A. Carruthers and A. Connolly, Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 276.

## ULTRA-HIGH-FIELD SUPERCONDUCTIVITY

V. Jaccarino and M. Peter\*

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received September 13, 1962)

The polarization of the conduction electrons that is induced by a magnetic field lowers the free energy of the normal state relative to the superconducting state. Indeed, it has recently been shown<sup>1,2</sup> that, in the limit of complete field penetration,<sup>3</sup> this mechanism imposes an upper limit on the critical field obtainable in ordinary superconductors. In a rare earth ferromagnetic metal the effective exchange field  $H_{\text{eff}}$  impressed on the conduction electrons, via the exchange interaction with the rare earth spin  $S$ , is in general so large as to inhibit the occurrence of superconductivity in zero external field  $H$ . We would like to point out that in certain ferromagnetic metals  $H_{\text{eff}}$  opposes  $H$  and allows for the conduction electron polarization to be cancelled so that, if

in addition, these metals possess a predominantly attractive electron-electron interaction, the possibility arises that superconductivity will occur in the compensation region. Since the cancellation will presumably occur for  $H \sim -H_{\text{eff}}$ , critical fields may be obtained which exceed, by an order of magnitude, the limit derived for ordinary superconductors.<sup>1,2</sup>

The free energy of the normal state of a metal in zero field  $F_{n0}$  is lowered by an amount  $\frac{1}{2}\chi_p H^2$  in a magnetic field. Characterizing the free energy of the superconducting state requires that one specify the field configuration and spin magnetization. The assumptions underlying the Clogston limits were (1) complete field penetration (no Meissner effect) and (2) that the magnetic

field does not modify the superconducting ground state. The latter implies the persistence of spin as well as momentum pairing in the magnetic field. The free energies,  $F_{n1}(H)$  and  $F_{s1}(H)$ , of normal and superconducting states are then given by

$$F_{n1}(H) = F_{n1}(0) - \frac{1}{2}\chi_p H^2; \quad F_{s1}(H) = F_{s1}(0). \quad (1)$$

Conduction electrons can be polarized not only by external fields but also by interaction with any polarization that may exist in the lattice. For example, in a rare earth ferromagnetic metal an additional polarization is present as a result of the interaction of the conduction electrons with the spontaneously polarized rare earth ion moments. Whether this arises from an exchange interaction<sup>4</sup> or by configuration mixing,<sup>5</sup> it may be characterized by an effective interaction  $\mathcal{J} = (1/N)\mathcal{J}_{\text{eff}}\sum_n \vec{S}_n \cdot \vec{s}$  between the rare earth spin  $\vec{S}$  and the conduction electron spin  $\vec{s}$ . In terms of  $\mathcal{J}_{\text{eff}}$  we may write the spin polarization  $\bar{s}_z = (1/2N) \times \mathcal{J}_{\text{eff}}\eta(E)\sum_n S_{nz}$  and the polarization energy  $\Delta E = (s_z)^2/\eta(E)$ . Since  $\chi = (\frac{1}{2}g^2)\beta^2\eta(E)$ , we have

$$\Delta E = \frac{1}{2}\chi H_{\text{eff}}^2, \quad (2)$$

where

$$H_{\text{eff}} = \bar{s}_z/\beta\eta(E) = (\mathcal{J}_{\text{eff}}/Ng\beta)\sum_n S_{nz}. \quad (3)$$

In the presence of an external field we find for the total field acting on the conduction electrons  $H_T = H_0 + H_{\text{eff}}$  and  $\Delta E = \frac{1}{2}\chi H_T^2$  for the energy shift to second order. Now the screening of the 4f electrons by the 5s and 5p electrons prevents the quenching of the angular momentum  $\vec{L}$  by the "crystal fields" of the metal, and thus  $J$  ( $\vec{J} = \vec{L} + \vec{S}$ ) and  $J_z$  are the good quantum numbers. In the  $J, J_z$  representation,  $S_z = [J_z/J(J+1)]\langle \vec{S} \cdot \vec{J} \rangle$ , and we have

$$H_{\text{eff}} = (\mathcal{J}_{\text{eff}}/g\beta N)\sum_n [J_{nz}/J_n(J_n+1)]\langle \vec{S}_n \cdot \vec{J}_n \rangle. \quad (4)$$

Now the quantity  $\langle \vec{S} \cdot \vec{J} \rangle$  reverses sign when the 4f shell becomes half filled. Recent resonance experiments have demonstrated that  $\mathcal{J}_{\text{eff}}$  is negative for a number of rare earth metals.<sup>6</sup> However,  $H_{\text{eff}}$  can be made of either sign regardless of the sign of  $\mathcal{J}_{\text{eff}}$  as is shown in the following table:

$H_{\text{eff}} < 0$		$H_{\text{eff}} > 0$	
$\mathcal{J}_{\text{eff}} < 0, S_z > 0$	$\mathcal{J}_{\text{eff}} > 0, S_z > 0$	$\mathcal{J}_{\text{eff}} > 0, S_z > 0$	$\mathcal{J}_{\text{eff}} < 0, S_z < 0$
$\mathcal{J}_{\text{eff}} > 0, S_z < 0$	$\mathcal{J}_{\text{eff}} < 0, S_z < 0$	$\mathcal{J}_{\text{eff}} < 0, S_z < 0$	$\mathcal{J}_{\text{eff}} > 0, S_z > 0$

When  $H_{\text{eff}} < 0$  there will be a value of  $H$  for which  $H_T = 0$  and therefore  $\Delta E = 0$ . The cancellation at the compensation point has restored the degeneracy between electrons of opposite spin and momentum making possible the formation of Cooper pairs and a Bardeen-Cooper-Schrieffer (BCS) ground state.

However, in the superconducting state the conduction electrons will suffer an additional interaction via the virtual excitation of spin waves in the ferromagnetic rare earth spin system. Bal-tensperger and Strässler<sup>7</sup> have shown this interaction to be repulsive in an antiferromagnet and estimate for its strength  $\mathcal{J}^2 S/2NkT_{AE}$  where  $kT_{AE}$  is the energy gap in the antiferromagnetic spin-wave spectrum. In the ferromagnetic case a similar analysis applies with  $g_J\beta H$  replacing  $kT_{AE}$ ;  $E_{\text{spin wave}} = \mathcal{J}^2 S/2Ng_J\beta H$ .

We are now in a position to examine the behavior of the free energies. In Fig. 1 we have plotted the dependence of the free energies of the normal and superconducting states on the external field  $H$  for the two cases considered.

$F_{n1}(H)$  and  $F_{s1}(H)$  represent normal and superconducting free energies of ordinary nonmagnetic superconductors as described by (1).  $F_{n2}(H) = F_{n2}(0) - \frac{1}{2}\chi_p H_T^2$  is the free energy of the normal state of a ferromagnetic metal for which  $H_{\text{eff}} < 0$ . (The case of  $H_{\text{eff}} > 0$  is of no interest here.)  $F_{s2}(H)$  is the free energy in the superconducting state for the same case and is given by  $F_{s2}(H) = F_{s2}(0) + E_{\text{spin wave}}$ . The intersections of the

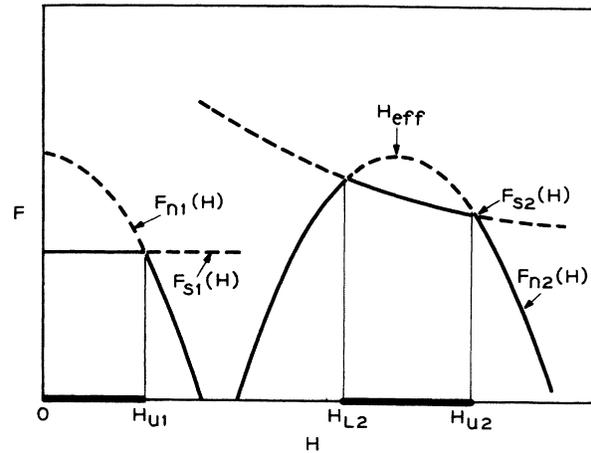


FIG. 1. The free energies versus external field for the normal and superconducting state of (1) a nonmagnetic metal and (2) a ferromagnetic metal for which the polarization of the conduction electrons opposes the external field. The notation is explained in the text.

normal and superconducting free energy curves define the region of superconductivity and are indicated by the heavy lines on the  $H$  axis for both cases.

Since the free energy considerations have as a prerequisite for the onset of superconductivity that  $H$  be of order  $H_{\text{eff}}$ , the strength of the repulsive interaction induced by the spin-wave excitations will have the magnitude  $\mathcal{J}S/2N$  in the compensation region. For the spin-wave repulsion to be less than the resultant of the phonon-induced attraction  $G^2$  and the Coulomb repulsion  $C^2$  requires that

$$G^2 - C^2 > \mathcal{J}S/2N. \quad (5)$$

Because of our previous relation between the  $H_{\text{eff}}$  and  $\mathcal{J}$  and since we require  $H \sim H_{\text{eff}}$ , we can parametrize this condition as a function of  $H$  as shown in Fig. 1. These relations together imply a new limit for the highest field  $H$  in which one can hope to obtain superconductivity; namely,  $H_{\text{max}} < (G^2 - C^2)/g_J\beta$ . From the preceding it is evident that a subsidiary condition for this limit to be reached is for the material to possess a negative  $H_{\text{eff}}$  of the same magnitude.

It is perhaps worthwhile to mention that we have discussed only the perturbing effects resulting from the lowest order of perturbation theory. In this approximation it appears that the optimum choice for the value of the external field is the one for which  $H + H_{\text{eff}} = 0$ . While effects resulting from higher order perturbations may not be cancelled exactly, they nevertheless may be minimized by a slightly different choice of  $H$ .

As to the realization of the high fields that we have discussed, we propose the following schematic configuration for operating a magnet with the desired properties. In consideration of the restricted range in which the free energy conditions allow for superconductivity, multistage concentric sole-

noids would of necessity be required to "boost" the field up to the highest values (of the order of megagauss). If  $H_{l,n}$  and  $H_{u,n}$  are the lower and upper limits, respectively, of the  $n$ th stage, then the condition for operation of the magnet would be that  $H_{l,n+1} < H_{u,n}$ . For a first stage one might use a conventional hard superconducting coil (e.g.,  $\text{Nb}_3\text{Sn}$ ) and have for successive stages ferromagnetic metals for which  $H_{\text{eff},n+1} > H_{\text{eff},n}$ .

There exists a large class of materials which satisfy the basic criteria given above for high-field superconductivity in ferromagnetic metals. As examples let us suggest superconducting inter-metallic compounds of La such as the Laves phase  $\text{LaX}_2$  where  $X = \text{Al, Os, Ir, Ru}$ , and their alloys. The isomorphic rare earth metals are known to be ferromagnetic and, as such, apart from the presence of the localized  $4f$  shell moments should have similar band-structure properties.

The authors are indebted to Professor W. Baltensperger for some illuminating discussions at the Orsay Conference on Metallic Solid Solutions and for private communications.

---

\*Present address: Physics Department, University of Geneva, Geneva, Switzerland.

<sup>1</sup>A. M. Clogston, Phys. Rev. Letters **9**, 266 (1962).

<sup>2</sup>B. S. Chandrasekhar, Appl. Phys. Letters **1**, 7 (1962).

<sup>3</sup>The case of the so-called "hard" superconductors which show no Meissner effect at high fields.

<sup>4</sup>T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956); K. Yosida, Phys. Rev. **106**, 893 (1957).

<sup>5</sup>P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. **2**, 124 (1961); M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. **126**, 1396 (1962); J. Kondo, Progr. Theoret. Phys. (Kyoto) (to be published).

<sup>6</sup>V. Jaccarino, B. T. Matthias, M. Peter, H. Suhl, and J. H. Wernick, Phys. Rev. Letters **5**, 221 (1960).

<sup>7</sup>W. Baltensperger and S. Strässler (to be published).