were considered. The first term  $[\operatorname{Re}(w_{0,0,0}) = 10 \text{ V}]$  is the amount of energy the electron gains when it enters the crystal (i.e., the inner potential). This was determined experimentally by observing the energy shift of the Bragg reflection peaks. Because of the symmetry of the fcc lattice, all coefficients  $w_{p,q,s}$ with "mixed" indices are zero. The remaining coefficients were calculated by using the method outlined in Ref. 5. The imaginary part of the potential was assumed to be constant, i.e.,  $\operatorname{Im}[W(\mathbf{\hat{r}})] = 2.5 \text{ V}.$ 

Figure 1 is a plot of  $|\psi_{l,m,n}|^2$  as a function of *l* and *m*, on a plane (*n* = const) in reciprocal space. The distance between the plane and the center of the Ewald sphere is less than one reciprocal lattice spacing. It is seen that  $|\psi_{l,m,n}|^2$ drops off very rapidly with increasing indices *l* and *m*. Similar graphs are obtained for other sections through the Ewald sphere. Figure 2 shows the intensities of the (0, 0), (1, 1), and (0, 2) beams as a function of electron energy. V. <u>Conclusions</u>. – First, it has been demonstrated that LEED intensities can be calculated by using Bethe's theory.<sup>5</sup> Second, the calculated curves of intensity versus energy (Fig. 2) show the well-known (integer order) Bragg reflection peaks as well as additional noninteger order peaks, similar to the ones predicted by McRae.<sup>3</sup> Third, it is found that, both inside and outside the crystal, the expansion of the wave function includes many terms whose coefficients are of similar order of magnitude. All these "waves" should be considered, and the "two-beam" treatment appears to be unsatisfactory.

<sup>2</sup>E. G. McRae and C. W. Caldwell, Surface Sci. <u>2</u>, 509 (1964).

- <sup>4</sup>K. Kirabayashi and Y. Takeishi, Surface Sci.  $\underline{4}$ , 150 (1966).
- <sup>5</sup>H. Bethe, Ann. Physik <u>87</u>, 55 (1928).

## MAGNETIZATION OF THE SUPERCONDUCTING SHEATH

A. S. Joseph, A. C. Thorsen, E. R. Gertner, and J. W. Savage North American Aviation Science Center, Thousand Oaks, California (Received 22 May 1967; revised manuscript received 10 November 1967)

Torque measurements on Type-II superconducting foils in nearly parallel applied magnetic fields H indicate that the torque above  $H_{C2}$  can provide a direct measure of the <u>magnetization</u>. From the results above  $H_{C2}$  we deduce two magnetizations,  $M_b$  associated with the bulk sample, and  $M_s$  associated only with the superconducting sheath. The measurements indicate that  $M_s$  is irreversible with H, contrary to prediction, and that the sheath itself behaves as if it is multiply connected.

Since the theoretical prediction<sup>1</sup> and the experimental verification<sup>2</sup> of a sheath state in Type-II superconductors above the critical field  $H_{c2}$ , there has been considerable experimental effort<sup>3</sup> to characterize the properties of the sheath state. In addition, recent theoretical work<sup>4-6</sup> has led to a model of the current distribution in the sheath which has met with some success in explaining magnetization measurements above  $H_{c2}$ . This model is shown schematically in Figs. 1(a) and 1(b) for a superconductor of rectangular cross section and of unit length. (In the following discussion we treat the currents in the superconducting sheath as average line currents although of course they have a finite spatial distribution.) Clockwise and counterclockwise currents  $J_1$  and  $J_2$ 

are predicted to flow perpendicular to the magnetic field H in a region extending a few coherence lengths below the surface. According to the theory, the direction of each current remains fixed for a given applied field direction, while the magnitudes of  $J_1$  and  $J_2$  may change continuously such that the difference  $\Delta J = J_1 - J_2$  can be positive or negative depending on whether the field is increasing [Fig. 1(a)] or decreasing [Fig. 1(b)].

In order to facilitate the following discussion we designate the current  $J_2$  which flows around the inner path as J and denote the current  $J_1$ flowing around the outer surface as  $J + \Delta J$ . The current  $J + \Delta J$  encloses the total crosssectional area of the bulk, A, and the current J encloses the inner area  $A - \Delta A$ , where  $\Delta A$ 

<sup>&</sup>lt;sup>1</sup>G. Gafner, Surface Sci. <u>2</u>, 534 (1964).

<sup>&</sup>lt;sup>3</sup>E. G. McRae, J. Chem. Phys. <u>45</u>, 3258 (1966).



FIG. 1. Schematic cross sections of the superconducting foil (not to scale) perpendicular to the magnetic field showing various current distributions above  $H_{c2}$ . The shaded regions denote the superconducting sheath. In (a) and (b) the theoretical current distribution is shown and the magnitudes of  $J_1$  and  $J_2$  are indicated by the sizes of the arrows for increasing and decreasing field sweeps, respectively. The remaining configurations are discussed in the text.

is the cross-sectional area of the sheath. The total magnetic moment (per unit length),  $m_{\text{tot}}$ , of this current distribution may be written as

$$m_{\text{tot}} = A \Delta J + J \Delta A \equiv m_b + m_s, \tag{1}$$

where the magnetic moment  $m_b = A \Delta J$  is associated with the current  $\Delta J$  that flows around the bulk, and the moment  $m_b = J \Delta A$  is related to the current J that flows around the sheath as shown schematically in Fig. 1(c). The corresponding bulk magnetization  $M_b$  and sheath magnetization  $M_S$  may be defined as

$$M_{b} = m_{b}^{\prime} / V_{b} = \Delta J,$$
  
$$M_{s} = m_{s}^{\prime} / V_{s} = J,$$
 (2)

where  $V_b = A$  and  $V_s = \Delta A$  are the volumes (per unit length) of the bulk and sheath, respectively.

Theoretical calculations<sup>4,5</sup> of the quantities  $M_b$  and  $M_s$  have indicated that  $M_b < M_s$  above  $H_{c2}$ , but for the large specimens used in the present experiment, where  $V_b \gg V_s$ , one calculates that  $m_b \gg m_s$ . Magnetic-moment measurements of the type reported by Sandiford and Schweitzer<sup>7</sup> and Barnes and Fink<sup>8</sup> which determine the total magnetic moment  $m_{tot}$  effectively measure  $m_b$ . No measurements of  $m_s$  or  $M_s$  have as yet been reported.

In this paper we interpret the torque  $\tau$  exerted by an applied magnetic field H on a Type-II superconducting foil above  $H_{c2}$  as providing direct measures of the two magnetizations  $M_S$ and  $M_b$ .

We briefly derive a relation for the torque as a function of  $H < H_{C1}$  which makes a small angle  $\theta \ll 1^{\circ}$  with the plane of a long flat superconducting ellipsoid. If the axes of the ellipsoid are  $a \gg b \gg c$ , the components of the *B* field perpendicular and parallel to the plane of the ellipsoid are

$$B_{\perp} - H_{\perp} = 4\pi M_{\perp} - N_{\perp} M_{\perp} = 4\pi (1 - N_{\perp} / 4\pi) M_{\perp}$$
$$= 4\pi (c/a) M_{\perp}, \qquad (3a)$$

$$B_{\parallel} - H_{\parallel} = 4\pi (1 - N_{\parallel} / 4\pi) M = 4\pi (1 - c / a) M_{\parallel}, \quad (3b)$$

where the demagnetization coefficients  $N_{\perp}$  and  $N_{\parallel}$  are calculated by Osborne.<sup>9</sup> The torque in this case is

$$\tau = VM \times H = V[M_{\perp}H_{\parallel} - M_{\parallel}H_{\perp}] = V\left[\left(\frac{B_{\perp} - H_{\perp}}{4\pi c/a}\right)H_{\parallel} - \left\{\frac{B_{\parallel} - H_{\parallel}}{4\pi (1 - c/a)}\right\}H_{\perp}\right] \approx V\left[\frac{B\varphi - H\theta}{4\pi c/a}H\right] \approx \alpha \left(\frac{\varphi}{\theta} - H\right)H, \quad (4)$$

where  $B_{\perp} \approx B \varphi$ ;  $H_{\perp} = H \theta$ ;  $H_{\parallel} \cong H$ ;  $B_{\parallel} \approx B$ . The angles  $\varphi$  and  $\theta$  are between the plane of the ellipsoid and the directions of *B* and *H*, respectively; *V* is the volume; and  $\alpha = a^2 b \theta / 24$  is independent of the thickness *c*. In Eq. (4) the term due to  $M_{\parallel}H_{\perp}$  can be neglected when  $c/a \ll 1$ . In the Meissner state, B = 0 and Eq. (4) becomes

$$\tau = 4\pi \alpha H M. \tag{5}$$

For the rectangular parallelepiped foil used

in this experiment, having a length a, width b, and thickness c (where  $a \gg b \gg c$ ),  $\alpha \approx a^2 b\theta/4\pi$ . Using this value for  $\alpha$  in Eq. (5), we have found that by measuring the absolute values of  $\tau$  and H,  $M = H/4\pi$  can be measured absolute-ly to within 25%. We have also verified that Eq. (5) is independent (within 3%) of the thickness in the range 0.3  $\mu < c < 150 \mu$ .

If below  $H_{c1}$  some flux density  $B_0$  is trapped

(6a)

in the specimen, an absolute value for M cannot be deduced from torque measurements unless the angle  $\varphi$  is known. Intuitively one would think that  $\varphi \approx \theta$ . We found that this is indeed the case by comparing torque results with those of the standard magnetic-moment measurements<sup>8</sup> on the same foils. In the case that  $\varphi \approx \theta$ , we then have

 $\tau = \alpha (B_0 - H)H$ 

 $=4\pi\alpha HM$ 

and

$$\tau/H = \alpha(B_0 - H)$$

$$=4\pi\alpha M.$$
 (6b)

So far we have limited the above discussion to fields below  $H_{c1}$ . Assuming that Eq. (6) holds also above  $H_{c2}$ , we expect the following to occur: (1) Since  $\tau$  is independent of the thickness c, the fact that superconductivity occurs only at the surface should not appreciably affect the amplitude of  $\tau$ . Therefore, if the current J is as large as theoretically predicted,<sup>5</sup> we can expect the torque above  $H_{c2}$  to be comparable with that near  $H_{c1}$ . (2) We should also expect that above  $H_{c2}$ , along the sections of minor hysteresis paths where  $B_0$  is constant,  $\tau/H$  vs H would be a straight line having a slope predicted by Eq. (6b) which is also the same as that predicted by Eq. (5) in the Meissner state. (3) This straight line should intersect the *H* axis at  $H = B_0$ . Knowing  $B_0$ , one can deduce a value for *M* which is equivalent to that calculated from the absolute values of  $\tau$ ,  $\alpha$ , and H.

In Fig. 2, we show torque data for a Type-II superconducting foil  $(2.0 \times 0.5 \times 0.01 \text{ cm}^3)$ of Pb+5% Tl at 4.2°K situated in a nearly parallel ( $\theta \approx 0.2^{\circ}$ ) field. Curves I and II are for increasing and decreasing field sweeps, respectively. Below  $H_{c1}$ , curve I is quadratic in Hand obeys Eq. (5). In all of our specimens the values for  $H_{c1}$  (defined experimentally as the point at which  $\tau$  has the steepest decrease) agreed with those of Bon Mardion, Goodman, and Lacaze.<sup>10</sup> Between  $H_{c1}$  and  $H_{c2}$  both curves are complicated. Discussion of this region does not pertain to the main theme of this manuscript, and will be deferred to a later paper. We mention only that the negative torques obtained in this region can be attributed to the manner in which vortices align themselves relative to H and the plane of the sample.

Above  $H_{c2}$  the results are indeed striking.  $\tau$  along the diamagnetic curve I and the paramagnetic curve II is comparable with  $\tau$  near  $H_{c1}$ . By contrast, in the standard magneticmoment measurement, the moment near  $H_{c2}$ is in fact negligible when compared with that near  $H_{c1}$ . The observation of large torques above  $H_{c2}$  is consistent with Eq. (6), assuming that M is of the order of magnitude of that given by theory.<sup>5</sup>

Now consider a minor hysteresis path as shown by the dashed curve PQRS. Along the initial portion PQ,  $\tau$  exhibits a rapid change  $(\Delta \tau)_{PQ}$  over a field increment  $(\Delta H)_{PQ} \approx 9$  G, followed by a slower change between Q and Ras H is further increased by  $(\Delta H)_{QR}$ . Over the increment QR,  $\tau/H$  vs H is nearly a straight line having the Meissner slope predicted by Eq. (6b). This linear behavior indicates that B is nearly constant and that  $B_0 - H = (A H)_{QR}$ =400 G is a measure of the magnetization at the point Q. Since this value is two orders of magnitude larger than the experimentally determined value for  $4\pi M_b$  (see below), we tentatively associate it with  $4\pi M_s$  and hence the current J.

An additional contribution to  $\tau$  must be due to  $\Delta J$  and hence  $4\pi M_b$ . Since  $4\pi M_b$  is expected<sup>8</sup> to be only about 4 G,  $\tau/H$  vs *H* associated with  $4\pi M_b$  should be linear over field measurement of about 8 G as *H* is increased along the path *PR*. The only structure that occurs over



FIG. 2. Torque versus H for a Type-II superconducting foil of Pb+5% Tl at 4.2°K, with the magnetic field nearly parallel to the plane of the foil.

this increment is the rapid change  $(\Delta \tau)_{PQ}$ . From its corresponding field increment, a value  $4\pi M_b = \frac{1}{2}(\Delta H)_{PQ} = 4.5$  G is obtained which is in good agreement with that obtained by Barnes and Fink.<sup>8</sup> Since one cannot reliably test for the linearity of  $\tau/H$  vs *H* over the path *PQ*, we calculate the change  $(\Delta \tau)_{PQ}$  for the dashed curve by taking the differentials of Eq. (6a) and then substitute the respective values  $B_0$  associated with the currents *J* and  $\Delta J$ . We then have

$$(\Delta \tau)_{PQ} = \alpha [(B_0 - 2H) \Delta H]_J + \alpha [(B_0 - 2H) \Delta H]_{\Delta J}$$
$$= \alpha (1400 - 2H) \Delta H + \alpha (4.5 - 2H) \Delta H.$$
(7)

The calculated ratio  $[(\Delta \tau)_{PQ}]_{calc}/[(\Delta \tau)_{PQ}]_{exp}$  = 0.9 which indicates that Eq. (6) is approximately valid over the curve PQ.

To test further the assignment of  $(\Delta H)_{PQ}$ to  $4\pi M_b$  and  $(\Delta H)_{QR}$  to  $4\pi M_s$  we plated a small portion of the surface of the foil with chromium metal to quench the surface superconductivity in this region. The current  $\Delta J$  is now prevented from circulating around the sample whereas the current J may still flow around the sheath in the manner illustrated in Fig. 1(d). If the above assignment is correct we would expect  $M_b$  and hence  $(\Delta \tau)_{PQ}$  to vanish since  $\Delta J$  would be zero, while  $(\bar{\Delta}\check{H})_{QR}$  and  $\tau$ should not change appreciably. Experimentally, we find that  $(\Delta H)_{QR}$  changes only slightly while  $(\Delta \tau)_{PQ}$  vanishes, and the amplitude of  $\tau$  decreases by an added amount proportional to the fraction of the surface that was coated. We therefore conclude that the above assignments are correct. From the family of curves PQRS obtained from different starting points on curve II, Fig. 2, we deduce values of  $4\pi M_S$ as a function of field above  $H_{c2}$ . Values for  $4\pi M_S/H \text{ vs } H/H_{C2}$  are plotted in Fig. 3 for a number of samples and are compared with the predictions of Fink and Kessinger. The agreement is considered good in view of the fact that there exists some variation from sample to sample depending on the surface condition. It is interesting to note that near  $H_{c2}$  the magnetization  $M_{\rm S}$  is nearly equal to the bulk magnetization at  $H_{c1}$  and the corresponding critical current  $J = 10(\Delta H)_{QR}/4\pi \approx 320$  A/cm is about the same as the Meissner currents at  $H_{c1}$ .

Torque measurements have also been used to illustrate that flux pinning takes place in the sheath. We have found experimentally that Eqs. (5) and (6) apply equally well below  $H_{c1}$ whether *H* is varied at constant  $\theta$ , or  $\theta$  is varied (by rotating the magnet) at constant field value. Above  $H_{c2}$ , on the other hand, these equations are valid for a changing field at constant  $\theta$ , but if  $\theta \approx 0.2^{\circ}$  is increased by as much as 1° at constant *H* unusually large torques are observed. This behavior suggests that the internal field is pinned at  $\varphi \approx 0.2^{\circ}$  while  $\theta$  has changed by 1°.

Although the theoretical and experimental values for  $M_S$  are in fair agreement, the theoretical model<sup>4,5</sup> of the current distribution in the sheath is inconsistent with two major features of our data. First of all, the theoretical current distribution above  $H_{c2}$  would lead to a reversible  $\tau$  vs *H* for the partially plated foil and secondly, it does not account for the flux pinning discussed in the preceding paragraph. The observations that curve I is always diamagnetic while curve II is always paramagnetic (Fig. 2) and that negligible flux trapping occurs below  $H_{c1}$  suggest that the sheath itself is multiply connected, and that the current J can change its direction from clockwise to counterclockwise flow depending on the direction of the field sweep. In other words, the sheath behaves as if it had a normal core as shown schematically in Fig. 1(e). It is not clear whether such a situation by itself would lead to flux pinning or whether a "vortexlike" structure as schematized in Fig. 1(f) would be re-



FIG. 3. Plots of  $4\pi M_S/H$  vs *H* for a number of superconducting foils. The solid lines are predicted by theory and the points are the experimental values deduced from the torque measurements above  $H_{c2}$ .

quired. If a vortexlike structure exists in the sheath, the "vortices" should necessarily be aligned nearly parallel to the plane of the foil and not perpendicular as was suggested by Hart and Swartz.<sup>11</sup> If they are pinned nearly normal to the plane of the foil and hence nearly normal to the field, then upon changing the angle by  $1^{\circ}$  as described in the previous paragraph, large torques are not expected to occur since the effective angle of the vortices is changed to  $90^{\circ} \pm 1^{\circ}$ . On the other hand, if these vortices are parallel to *H*, a change of  $1^{\circ}$  is indeed considerable and large torques would occur.

We summarize the results as follows: (1) Equation (6) is consistent with the observed large torques above  $H_{C2}$ , the straight-line relation of  $\tau/H$  vs H along the minor hysteresis paths, and the correct calculation of  $(\Delta \tau)_{PQ}$  and  $M_b$ . (2) The partially plated sample did exhibit a vanishing  $(\Delta \tau)_{PQ}$ . Using Eq. (6) we deduce for the first time values for  $M_s$  and J and a new model for the current distribution above  $H_{C2}$ . In this model the sheath contains either a normal core or a "vortexlike" structure parallel to the plane of the foil.

The authors acknowledge many profitable discussions with H. J. Fink, T. G. Berlincourt, R. R. Hake, L. J. Barnes, and J. A. Cape.

<sup>3</sup>References to much of the experimental and theoretical work carried out on the sheath state can be found in R. W. Rollins and J. Silcox, Phys. Rev. <u>155</u>, 404 (1967).

<sup>4</sup>H. J. Fink and L. J. Barnes, Phys. Rev. Letters <u>15</u>, 793 (1965).

<sup>5</sup>H. J. Fink and R. D. Kessinger, Phys. Rev. <u>140</u>, A1937 (1965).

<sup>6</sup>J. G. Park, Phys. Rev. Letters 16, 1196 (1966).

<sup>7</sup>D. J. Sandiford and D. G. Schweitzer, Phys. Letters 13, 98 (1964).

<sup>-6</sup>L. J. Barnes and H. J. Fink, Phys. Rev. <u>149</u>, 186 (1966).

<sup>9</sup>J. Osborn, Phys. Rev. 67, 351 (1945).

<sup>10</sup>G. Bon Mardion, B. B. Goodman, and A. Lacaze, Phys. Letters 2, 321 (1962).

<sup>11</sup>H. R. Hart and P. S. Swartz, Phys. Rev. <u>156</u>, 402 (1967).

## SYMMETRY OF GROUND STATE IN A DILUTE MAGNETIC METAL ALLOY

D. C. Mattis\*

Physics Department, Yale University, New Haven, Connecticut (Received 19 October 1967)

It is proved that the spin of the ground state of a magnetic atom having exchange interaction with a nonmagnetic host metal is  $s \pm \frac{1}{2}$ , where s = spin of noninteracting magnetic atom, the upper sign is appropriate to antiferromagnetic coupling, and the lower, to ferromagnetic coupling. This result is generalized to any number of conduction bands and to nonpointlike impurities, provided that the exchange interactions with the number of conduction bands, or with the various partial waves, are all of the same sign. For p such bands or partial waves, the result is that the ground-state spin= $|s \pm \frac{1}{2}p|$ .

The present paper concerns the ground state of a magnetic atom in a nonmagnetic host metal. We use the s-d exchange Hamiltonian to describe this situation, the exchange perturbation having been first shown by Kondo<sup>1</sup> to result in a logarithmic singularity in third and higher orders of perturbation theory. It is not known, in fact, whether the perturbation series converges when carried out to all orders, despite reasonable results of various methods of partial series summations which have been carried out to infinite order<sup>2</sup> in the coupling constant J. Indeed, Silverstein and Duke<sup>3</sup> have demonstrated that even methods which agree to within logarithmic accuracy above the Kondo temperature will disagree below it, and potentially can result in a plethora of predicted ground-state properties. However, recent variational solutions, some of which are based on the assumption that the ground state is a nonmagnetic singlet state,<sup>4</sup> have circumvented the difficulties of perturbation theory, although the problem is far from an exact solution at the present time. For this reason it might be useful to have some exact theorems, and in the present work we shall prove that

<sup>&</sup>lt;sup>1</sup>D. St. James and P. G. de Gennes, Phys. Letters  $\underline{7}$ , 306 (1963).

<sup>&</sup>lt;sup>2</sup>C. F. Hempstead and Y. B. Kim, Phys. Rev. Letters <u>12</u>, 145 (1964); W. J. Tomasch and A. S. Joseph, <u>ibid</u>. <u>12</u>, 148 (1964).