

FIG. 1. Temperature dependence of the vortex-core parameter. The points are the indicated experimental results. The solid line is the result of the quasithermodynamic theory. The dashed continuation of this line only indicates that the core parameter increases for higher temperatures.

thermodynamic quantities  $C$  and  $\gamma$  may be well represented by the free-phonon calculated quan-

ties. Inserting these we get

$$r^2 = 0.31\tau/(\tau - T) \quad (r \text{ in angstroms}).$$

The core radius is then defined by finding an  $r$  for which  $\tau = \beta T$ . This gives

$$r_c^2 = 0.31\beta/(\beta - 1).$$

In this region  $r_c$  is independent of temperature.

Figure 1 gives a comparison of the experimental results of Glaberson and Steingart with our result for  $r_c$ . It can be seen that the experiments agree well with the results of the thermodynamic picture in the temperature domain below  $0.5^\circ\text{K}$ .<sup>3</sup> To achieve this fit a value of  $\beta = 1.23$  was used.

As pointed out in Ref. 2 there is good qualitative agreement with the thermodynamic picture over a wide range of temperatures up to the  $\lambda$  point. The work of Glaberson and Steingart seems to give good quantitative agreement in the low-temperature domain.

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<sup>1</sup>W. I. Glaberson and M. Steingart, Phys. Rev. Lett. **26**, 1423 (1971).

<sup>2</sup>F. Pollock, J. Low Temp. Phys. **1**, 123 (1969).

<sup>3</sup>The authors of Ref. 1 apparently calculated the consequences of the quasithermodynamic theory on the assumption that  $\tau$ , the effective temperature, is constant. As a result they found gross disagreement.

## Anisotropy of the Upper Critical Field of Superconducting Technetium\*

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The anisotropy of the upper critical field  $H_{c2}$  of a noncubic superconductor was studied for the first time. A torque magnetometer was used to detect  $H_{c2}$  between 2 and  $7^\circ\text{K}$  as a function of orientation in a small single crystal of technetium. The relative anisotropy of  $H_{c2}$  consists of a large temperature-independent and possibly a small temperature-dependent part. The temperature-independent contribution can be attributed to the anisotropy of the effective mass.

A number of experimental investigations<sup>1-4</sup> have established that the upper critical field  $H_{c2}$  of several cubic type-II superconductors is anisotropic. Hohenberg and Werthamer<sup>5</sup> have shown

that this anisotropy can be attributed to the first nonlocal corrections to the Ginsburg-Landau-Abrikosov-Gor'kov (GLAG) theory. This type of anisotropy is expected to decrease with increas-

ing temperature and to vanish at the transition temperature  $T_c$ .<sup>5,6</sup>

Earlier generalizations of the GLAG theory incorporate an anisotropy of the normal metal Fermi surface<sup>7-9</sup> and predict a temperature-independent relative anisotropy of  $H_{c2}$  in *noncubic* materials.<sup>5,9</sup> Magnetization measurements<sup>10</sup> on two differently oriented hexagonal Tc<sup>99</sup> single crystals containing tungsten and carbon impurities indicated that  $H_{c2}$  might be appreciably anisotropic. In this Letter we will describe the anisotropy of  $H_{c2}$  in a small Tc<sup>99</sup> sample. A torque magnetometer was used to determine  $H_{c2}$  as a function of orientation.

We obtained Tc<sup>99</sup> powder from the Isotopes Division of the Oak Ridge National Laboratory. Compaction and melting have been described previously.<sup>11</sup> In the present case the hydrogen anneal was shorter; and, in the final step, ingots of 3.2 mm diam and 30 mm length were drop cast. These could be used directly to grow a single crystal in an electron-beam zone refiner.<sup>10</sup> Two small pieces of the crystal were used for chemical analysis. The results show that this material is much purer than that used in the previous studies.<sup>10</sup> Main impurities are 280 ppm Ta and 800 ppm C. A cylindrical sample of 3 mm diam and 3 mm length with the  $[10\bar{1}0]$  orientation along the axis was spark machined from the crystal, electropolished,<sup>12</sup> coated with GE 7031 varnish, and placed on a self-compensating torque magnetometer.<sup>13</sup> If a homogeneous magnetic field  $\vec{H}$  acts in the  $(10\bar{1}0)$  plane of the hexagonal crystal, the torque observed in the  $[10\bar{1}0]$  direction will be<sup>14</sup>  $D = 0.5mH^2(\chi_a - \chi_c)\sin 2\theta$ , where  $\chi_a$  ( $\chi_c$ ) is the susceptibility along the  $[1\bar{2}10]$  ( $[0001]$ ) direction,  $\theta$  is the angle between the field and  $[1\bar{2}10]$ , and  $m$  is the sample mass. Hence in the normal paramagnetic state the torque will be proportional to  $H^2$  at a fixed angle  $\theta$ . In an anisotropic type-II superconductor, a torque is expected for  $\theta \neq \frac{1}{2}n\pi$  ( $n = 0, 1, \dots$ ) as soon as magnetic flux penetrates. The detailed field dependence of the torque is complicated by demagnetizing effects and will not be discussed further in this context. Bulk superconductivity ceases to exist at  $H_{c2}$  for a particular orientation and the torque-versus- $H$  curve will start to follow the normal  $H^2$  relationship at higher fields.

Temperatures were kept constant to  $\pm 0.01^\circ\text{K}$  (except at  $2^\circ\text{K}$ , and there to  $\pm 0.06^\circ\text{K}$ ) and measured with an accuracy of  $0.01^\circ\text{K}$ . The external field was swept at a constant rate using a Varian field dial controller. The sweep rate was kept to

below 1 kOe/min in order to eliminate rate effects of flux penetration. The torque as a function of magnetic field was recorded directly on an  $x$ - $y$  recorder. A typical curve for ascending and descending field is shown in Fig. 1(a). The resolution in  $H$  was usually  $\pm 10$  Oe. The torque below  $H_{c2}$  is several orders of magnitude larger than in the normal state so that in the field range shown in Fig. 1(a) the normal state behavior is represented by a horizontal line. For angles  $\theta$  more than  $4^\circ$  off the symmetry orientations ( $\theta = 0^\circ$  and  $\theta = 90^\circ$ ),  $H_{c2}$  could reproducibly ( $\leq 1\%$ ) be defined as indicated in Fig. 1(a). The average be-

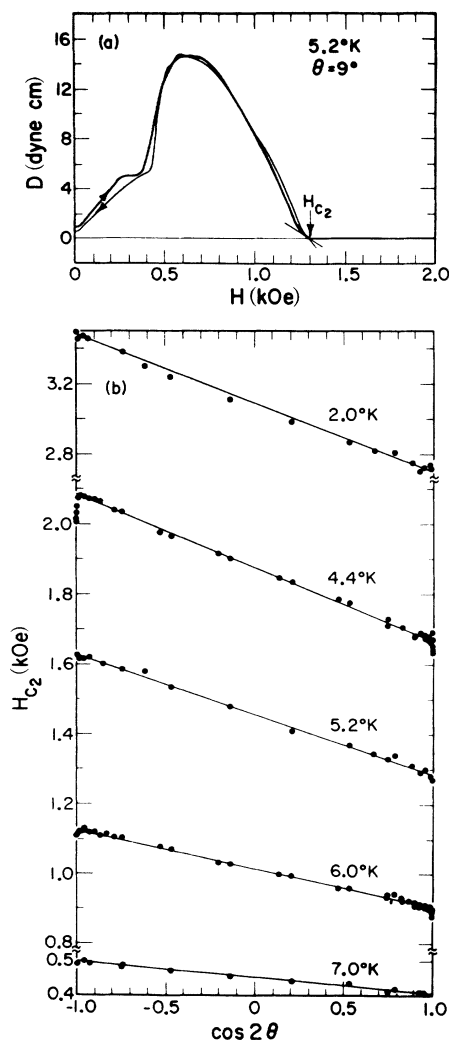


FIG. 1. (a) Torque  $D$  as a function of magnetic field  $H$  as recorded for a technetium single crystal in increasing and decreasing fields.  $\theta$  is the angle between basal plane and field direction. (b) The upper critical field  $H_{c2}$  for technetium as a function of  $\cos 2\theta$  where  $\theta$  is the angle between the basal plane and magnetic field at different temperatures.

tween the values found in ascending and descending fields was taken as  $H_{c2}$  at a particular angle. Data were obtained for a large number of angles  $\theta$  and  $\pi - \theta$  at 7, 6, 5.2, 4.4, and 2.0°K. No data were taken at higher temperatures since the signal becomes more spurious when  $T_c$  is approached. Figure 1(b) shows that at all five temperatures  $H_{c2}(\theta)$  as a function of  $\cos 2\theta$  follows a straight line within 1% if the values for  $0^\circ \leq \theta \leq 4^\circ$  and  $86^\circ \leq \theta \leq 90^\circ$  are excluded. There may be some deviations from the  $\cos 2\theta$  dependence at these angles, but no conclusive results can be obtained with the method employed here because of the uncertainties in the detection of  $H_{c2}$  in this narrow range of orientations. Assuming that the relationship suggested by Fig. 1(b) holds for all angles, we can extrapolate to  $\theta = 0^\circ$  and  $\theta = 90^\circ$  and obtain the extreme values  $H_{c2}(a) = H_{c2}([1\bar{2}10])$  and  $H_{c2}(c) = H_{c2}([0001])$ .

Experiments on another crystal with a  $[0001]$  axis showed no measurable (1%) anisotropy in the basal plane, so that  $H_{c2}$  depends only on  $\theta$  and can be written as

$$H_{c2}(\theta) = H_{c2}(a) + \Delta H_{c2} \sin^2 \theta, \quad (1)$$

with  $\Delta H_{c2} = H_{c2}(c) - H_{c2}(a)$ . The average value of  $H_{c2}$  over all orientations,  $\bar{H}_{c2}$ , is given by

$$3\bar{H}_{c2} = 2H_{c2}(c) + H_{c2}(a). \quad (2)$$

The values for  $H_{c2}(a)$ ,  $H_{c2}(c)$ ,  $\bar{H}_{c2}$ , and  $\Delta H_{c2}/\bar{H}_{c2}$  for the five temperatures are given in Table I.

Figure 2(a) shows  $H_{c2}(a)$ ,  $H_{c2}(c)$ , and  $\bar{H}_{c2}$  as functions of temperature. From this plot the critical temperature can be estimated to be  $T_c = 7.82 \pm 0.02^\circ\text{K}$ . The impurity content of the sample implies that effects from an energy-gap anisotropy are removed<sup>15</sup> and nonlocality effects<sup>5</sup> become small. The present results should therefore be primarily related to Tilley's expression for  $H_{c2}$  in dirty anisotropic superconductors.<sup>9</sup>

TABLE I. Upper critical fields at different temperatures for a technetium single crystal.  $H_{c2}(a)$  and  $H_{c2}(c)$  are the extrapolated values for the field perpendicular and parallel to the  $c$  axis,  $\Delta H_{c2}$  is their difference, and  $\bar{H}_{c2}$  is the average over all orientations.

$T$ (°K)	$H_{c2}(a)$ (kOe)	$H_{c2}(c)$ (kOe)	$\bar{H}_{c2}$ (kOe)	$\Delta H_{c2}/\bar{H}_{c2}$
2.0	$2.71 \pm 0.6\%$	$3.47 \pm 0.5\%$	3.22	$0.236 \pm 0.011$
4.4	$1.665 \pm 0.3\%$	$2.085 \pm 0.2\%$	1.95	$0.216 \pm 0.006$
5.2	$1.286 \pm 0.5\%$	$1.627 \pm 0.3\%$	1.51	$0.225 \pm 0.008$
6.0	$0.905 \pm 0.8\%$	$1.125 \pm 0.8\%$	1.05	$0.209 \pm 0.017$
7.0	$0.405 \pm 1.0\%$	$0.500 \pm 1.0\%$	0.47	$0.203 \pm 0.022$

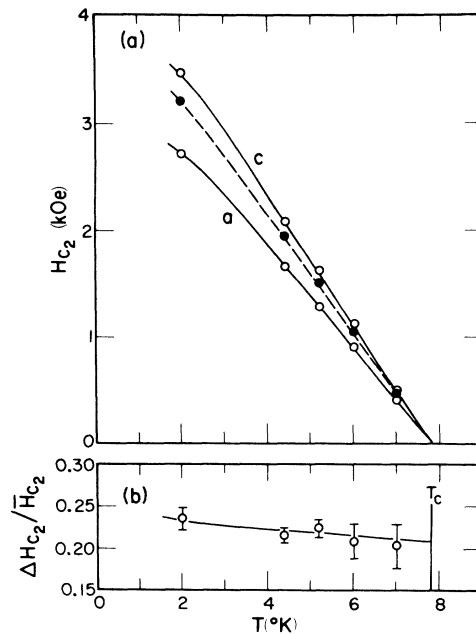


FIG. 2. (a) Upper critical field of a technetium single crystal versus temperature for the magnetic field parallel, curve  $c$ , and perpendicular, curve  $a$ , to the  $c$  axis. The dashed line shows the temperature dependence of the average upper critical field,  $\bar{H}_{c2}$ . (b) Relative anisotropy of the upper critical field,  $[H_{c2}(c) - H_{c2}(a)]/\bar{H}_{c2}$ , as a function of temperature.

$H_{c2}$  is given by

$$H_{c2} = (c|\alpha|/e\hbar)(m_1 m_2)^{1/2}, \quad (3)$$

where  $m_1$  and  $m_2$  are the principal values of the effective-mass tensor  $m_{ij}$  at right angles to the field direction, and  $|\alpha|$  is an implicit function of temperature, Fermi energy  $\epsilon_F$ , and (isotropic) relaxation time  $\tau$ <sup>9,16</sup>:

$$\ln(T_c/T) = \Psi(\frac{1}{2} + \epsilon_F \tau |\alpha| / \pi \hbar k T) - \Psi(\frac{1}{2}), \quad (4)$$

where  $\Psi$  is the digamma function  $\Gamma'/\Gamma$ .

The relative anisotropy can be expressed by

$$\frac{\Delta H_{c2}}{\bar{H}_{c2}} = \frac{3(m_{11}^{1/2} - m_{33}^{1/2})}{2m_{11}^{1/2} + m_{33}^{1/2}}, \quad (5)$$

where the 3 axis has been chosen parallel to [0001], so that the principal values of  $m_{ij}$  in a hexagonal crystal are  $m_{11} = m_{22}$  and  $m_{33}$ .

As evident from Fig. 2(b), a small increase of the measured  $\Delta H_{c2}/\bar{H}_{c2}$  with decreasing temperature cannot be completely ruled out although it is possible to draw a horizontal line through the error bars. This small temperature-dependent contribution would result from nonlocal effects, but the extrapolated value  $\Delta H_{c2}/\bar{H}_{c2} \approx 0.21$  at  $T_c$  is due to the anisotropy of the effective mass. From Eq. (5) we find  $m_{11} = 1.55m_{33}$ . This result will have to be compared with normal state conductivity measurements that are in preparation.

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<sup>1</sup>D. R. Tilley, G. J. van Gorp, and C. W. Berghout, *Phys. Lett.* **12**, 305 (1964).

<sup>2</sup>W. A. Reed, E. Fawcett, P. P. M. Meincke, P. C. Hohenberg, and N. R. Werthamer, in *Proceedings of the Tenth International Conference on Low Temperature Physics, Moscow, U.S.S.R., 1966*, edited by M. P. Malkov (VINITI Publishing House, Moscow, U.S.S.R.,

1967), p. 368.

<sup>3</sup>D. E. Farrell, L. S. Chandrasekhar, and S. Huang, *Phys. Rev.* **176**, 562 (1968).

<sup>4</sup>S. J. Williamson and L. E. Valby, *Phys. Rev. Lett.* **24**, 1061 (1970).

<sup>5</sup>P. C. Hohenberg and N. R. Werthamer, *Phys. Rev.* **153**, 493 (1967).

<sup>6</sup>K. Takana and T. Nagashima, *Progr. Theor. Phys.* **43**, 18 (1970).

<sup>7</sup>C. Caroli, P. G. de Gennes, and J. Matricon, *Phys. Kondens. Mater.* **1**, 176 (1963).

<sup>8</sup>L. P. Gor'kov and T. K. Melik-Barkhudarov, *Zh. Eksp. Teor. Fiz.* **45**, 1493 (1963) [*Sov. Phys. JETP* **18**, 1031 (1964)].

<sup>9</sup>D. R. Tilley, *Proc. Phys. Soc., London* **86**, 289, 678 (1965).

<sup>10</sup>G. Kostorz and S. Mihailovich, in *Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto, September, 1970*, edited by E. Kanda (to be published).

<sup>11</sup>C. C. Koch and G. R. Love, *J. Less-Common Metals* **12**, 29 (1967).

<sup>12</sup>C. C. Koch and G. R. Love, *J. Less-Common Metals* **15**, 43 (1968).

<sup>13</sup>J. W. Ross, ANL Report No. ANL-7155, 1965 (unpublished), p. 220.

<sup>14</sup>J. F. Nye, in *Physical Properties of Crystals* (Clarendon, Oxford, England, 1957), p. 61.

<sup>15</sup>G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. II, p. 665.

<sup>16</sup>P. G. de Gennes, *Phys. Kondens. Mater.* **3**, 79 (1964).

## Multiple Borrmann Diffraction\*

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High-resolution, divergent-beam x-ray diffraction photographs reveal previously unreported detail in multiple Borrmann (000), (111), (11 $\bar{1}$ ) reflections undergoing anomalous transmission through perfect germanium crystals. These have been accounted for satisfactorily using the plane-wave formulation of the dynamical theory of x-ray diffraction.

The anomalously high transmission of x rays through perfect crystals set at the exact angle for Laue diffraction was first reported by Borrmann in 1941.<sup>1</sup> In 1965 Borrmann and Hartwig<sup>2</sup> observed that a remarkable *additional* enhancement of the anomalously transmitted (111) reflection occurs when either the (11 $\bar{1}$ ) or (1 $\bar{1}$ 1) planes are brought to diffracting position simultaneously with the (111) planes. Several investigations of this multiple Borrmann diffraction phenomenon have since been reported.<sup>3-6</sup> These have been concerned primarily with Borrmann diffraction

at the exact  $n$ -beam setting, i.e., when the crystal is set at the exact angle for simultaneous Laue diffraction by  $n$  sets of planes.

The utilization of high-resolution, divergent x-ray beam techniques has enabled us to extend the study of multiple Borrmann diffraction to include crystal settings immediately adjacent to the geometrically exact  $n$ -beam settings. These have yielded useful information on details of the transition from one- or two-beam diffraction to the  $n$ -beam case, and have revealed several interesting and previously unreported features of