Magnetization and Electrical Resistivity of Terbium Single Crystals*

D. E. HEGLAND, S. LEGVOLD, AND F. H. SPEDDING
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa
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Magnetic-moment measurements have been made on single crystals of terbium (hcp) with fields of 50 to 18 000 Oe applied along the $\langle 11\bar{2}0\rangle$ (*a* axis), $\langle 10\bar{1}0\rangle$ (b axis), and $\langle 0001\rangle$ (*c* axis) directions. The temperature range covered was 1.4 to 500°K. The *b* axis was found to be the easy direction of magnetization with an extrapolated saturation moment of 9.34 Bohr magnetons/atom. Anisotropy was observed in the basal plane below the ferromagnetic Curie temperature but not above. A weak antiferromagnetic state was observed between 229°K and the ferromagnetic Curie point at 221°K. Electrical resistivity measurements were made from 4.2 to 360°K (*a*-axis crystal) and from 4.2 to 300°K (*b*- and *c*-axis crystals). The basal plane curve changed slope at 221 and 229°K. The *c*-axis curve changed slope at 221°K, exhibited a nearly symmetrical maximum about 226°K, and returned to linear behavior near room temperature. The application of a magnetic field of 11 kOe along a *b* axis caused the pronounced maximum at 226°K to disappear.

INTRODUCTION

A FEW years ago Thoburn *et al.*[1] examined polycrystalline terbium magnetically and observed Curie-Weiss behavior above 250°K with a paramagnetic Curie temperature of 232±2°K. Weak antiferromagnetic ordering was observed between approximately 218°K and the Néel point at 230°K. An applied field of 800 Oe was found to be sufficient to quench the antiferromagnetic state. Below 80°K the magnetic moment was found to be nearly temperature-independent, in agreement with the earlier work of Leipfinger.[2]

Arajs and Colvin[3] found that polycrystalline terbium follows a Curie-Weiss law up to 1500°K, and they report an experimental paramagnetic Curie temperature of 236°K and an effective magnetic moment of 9.62 Bohr magnetons.

The heat capacity of terbium has been measured by Jennings *et al.*[4] over the range 15 to 350°K. They observed two anomalies, a "bump" at about 221°K and a sharp peak at 227.7°K.

Neutron diffraction studies of a terbium single crystal by Koehler *et al.*[5] have revealed that terbium has a helical magnetic structure in the antiferromagnetic region with the magnetic moments parallel to the basal plane and the *c* axis as the screw axis. They found a Néel temperature of 230±1°K and observed the onset of ferromagnetism at 223±1°K.

The electrical resistivity of polycrystalline terbium has been measured by Colvin *et al.*,[6] who observed a sharp change in slope at 229°K and a slight increase in slope with increasing temperature at 219°K.

EXPERIMENTAL PROCEDURE

The single crystals of terbium used in this investigation were grown from a piece of polycrystalline terbium metal which was prepared by methods previously reported.[7,8] A strain-anneal technique described by Hall *et al.*[9] and modified by Nigh of this Laboratory was used to grow the crystals.

Spectrographic and vacuum fusion analyses of pieces of the crystals from which the samples were cut show the following impurities:

c-axis sample (0001):

Dy≤0.02%; Y<0.025%; Gd≤0.01%; Sm≤0.075%; Fe, Ni, Ca, Cu, Pr, Si, and Ta present as trace impurities; O_2≃0.09%; N_2≃0.02%; H_2≃0.01%.

a- and *b*-axis samples $(11\bar{2}0)$ and $(10\bar{1}0)$:

Dy≤0.01%; Y<0.02%; Gd≤0.01%; Sm≤0.03%; Al, Ca, Cu, Fe, Mg, Ni, Si, Ta, and W present as trace impurities; O_2≃0.19%; N_2≃0.02%; H_2≃0.01%.

The experimental procedure and the cryogenic apparatus used for the magnetic measurements in the range

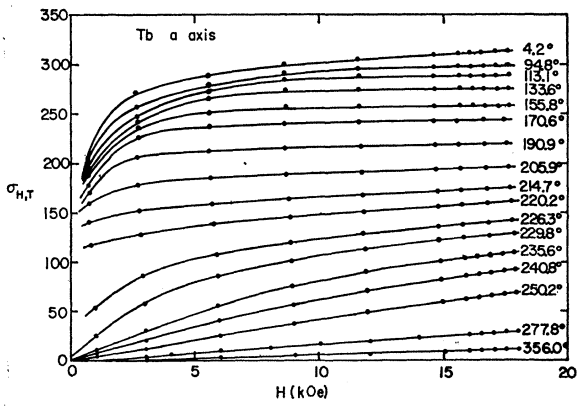

FIG. 1. Magnetic moment/*g* vs field for the *a*-axis crystal.

* Contribution No. 1220. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[1] W. C. Thoburn, S. Legvold, and F. H. Spedding, Phys. Rev. **112**, 56 (1958).

[2] H. Leipfinger, Z. Anorg. Allgem. Chem. **231**, 138 (1937).

[3] S. Arajs and R. V. Colvin, J. Appl. Phys. **32**, 336S (1961).

[4] L. D. Jennings, R. M. Stanton, and F. H. Spedding, J. Chem. Phys. **27**, 909 (1957).

[5] W. C. Koehler, H. R. Child, E. O. Wollan, and J. W. Cable, J. Appl. Phys. **34**, 1335 (1963).

[6] R. V. Colvin, S. Legvold, and F. H. Spedding, Phys. Rev. **120**, 741 (1960).

[7] F. H. Spedding and J. E. Powell, J. Metals **6**, 1131 (1954).

[8] F. H. Spedding and A. H. Daane, J. Metals **6**, 504 (1954).

[9] P. M. Hall, S. Legvold, and F. H. Spedding, Phys. Rev. **117**, 971 (1960).

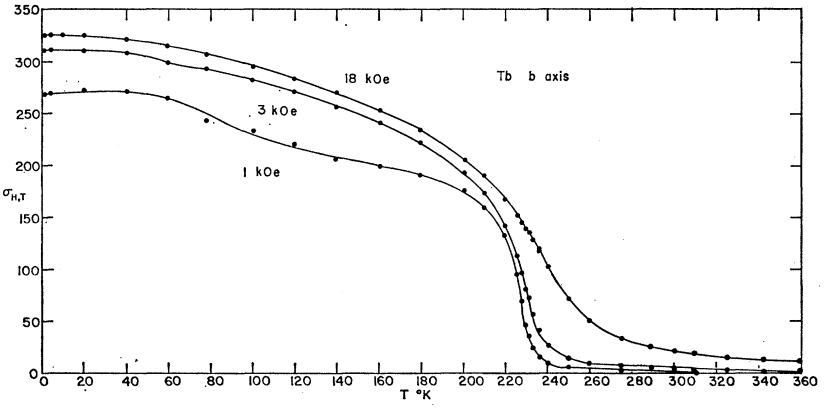

FIG. 2. Magnetic moment/g vs temperature for the a-axis crystal.

1.4 to 360°K have been described by Strandburg *et al.*[10] An identical procedure was used in the 300 to 500°K range with the Dewar replaced by a standpipe furnace.

The experimental procedure and apparatus used for the electrical resistivity measurements have been described by Colvin *et al.*[6]

EXPERIMENTAL RESULTS

The data for the a-axis crystal are plotted as isotherms in Fig. 1 and as isofield curves in Figs. 2 and 3. Figure 3 shows the field-dependent nature of the Néel point and also the extrapolation to zero field which gives 229±1°K as the Néel temperature. The paramagnetic data are plotted as the reciprocal of the susceptibility $(1/X)$ vs T in Fig. 4.

The data for the b-axis crystal are plotted as isotherms in Fig. 5, as isofield curves in Figs. 6 and 7, and as $(1/X)$ vs T in Fig. 4. The Néel point in Fig. 7 extrapolated to 229±1°K.

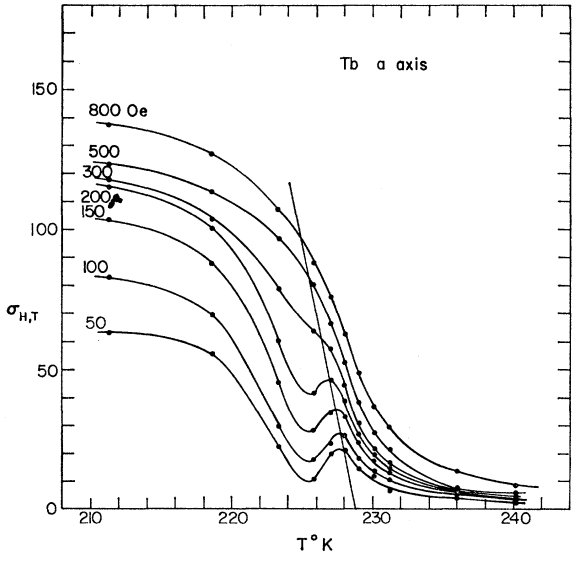

FIG. 3. Magnetic moment/g vs temperature for the a-axis crystal in the neighborhood of the Néel point. External fields are indicated.

The isofield curves are obtained from the isotherms. Since the points of the 1 and 3 kOe isofield curves are taken from the steep portions of the isotherms, these curves are only qualitatively correct.

The magnetic moment per gram, σ, is plotted vs $(1/H)$ in Fig. 8 for the b-axis crystal and the resulting straight lines extrapolated to $(1/H)=0$ to obtain $\sigma_{\infty T}$. The $\sigma_{\infty T}$ values are plotted vs $T^{5/2}$ in Fig. 9, and extrapolated to $T=0$ to obtain the saturation moment $\sigma_{\infty 0}$. The saturation moment was 328±3 emu/g.

It was difficult to determine whether a $T^{5/2}$ fit was better than a T^2 fit. It would appear that Niira's energy-gap approach[11] is more appropriate. This has been done by Mackintosh[12] with excellent results.

Two techniques for determining the ferromagnetic transition temperature were applied to the basal plane data. In one case, plots of σ^2 vs T at constant field were extrapolated to $\sigma^2=0$ and the resulting T values plotted vs field. This curve was then extrapolated to $H=0$ to yield the ferromagnetic Curie temperature. The result was 221±2°K for both the a- and b-axis crystals. In the other method employed, H was plotted vs T for several constant values of σ and these curves were extrapolated to $H=0$. The resulting temperatures were plotted vs σ and this curve was extrapolated to $\sigma=0$, again yielding the ferromagnetic Curie temperature. The result was 224±2°K for both the a- and b-axis crystals.

The c axis in terbium is very hard magnetically and for temperatures below 220°K constraining chains were needed to prevent sample rotation. The chains permitted vertical motion but decreased the weighing sensitivity. The data at 219.3°K and above are plotted as isotherms in Fig. 10. The 219.3°K curves are indicative of the general behavior and the lack of reproducibility of the data for temperatures below 220°K. The c-axis data above 220°K are also plotted as $(1/X)$ vs T

[10] D. L. Strandburg, S. Legvold, and F. H. Spedding, Phys. Rev. **127**, 2046 (1962).

[11] K. Niira, Phys. Rev. **117**, 129 (1960).

[12] A. R. Mackintosh, Phys. Letters (to be published).

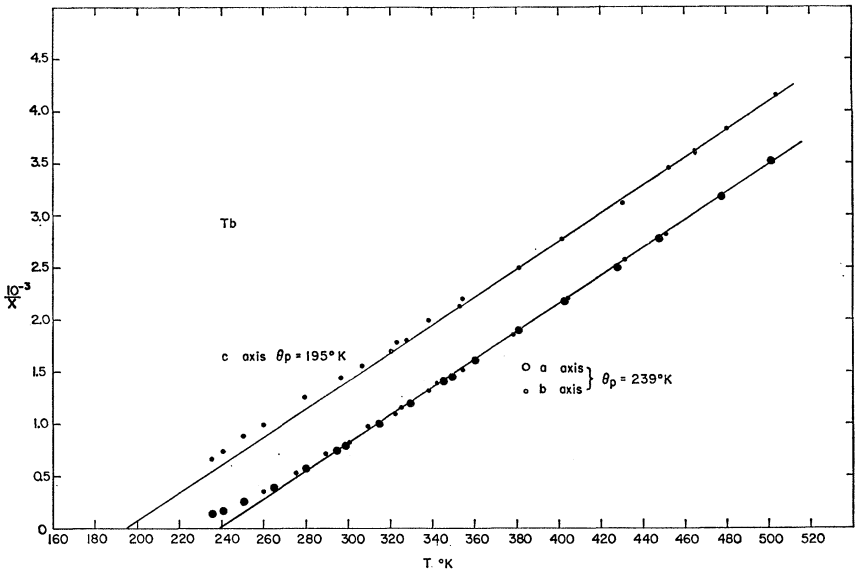

FIG. 4. The reciprocal of the susceptibility ($1/X$) vs temperature for the a-, b-, and c-axis crystals.

in Fig. 4 and the anisotropy between the c axis and the basal plane susceptibilities is clearly evident.

The electrical resistivities (residual subtracted) of the a- and c-axis crystals are plotted vs T in Fig. 11. The residual resistivities were 4.51, 5.22, and 4.13 $\mu\Omega$ cm for the a-, b-, and c-axis crystals, respectively. Since the a- and b-axis data agreed within the experimental error, only the a-axis data are plotted. Also plotted in Fig. 11 are the experimental data of Colvin *et al.*[6] for polycrystalline terbium and a theoretical curve calculated using the relation $\rho_{\text{poly}}=\frac{1}{3}(\rho_c+2\rho_{\text{basal plane}})$, which has been verified for yttrium by Alstad *et al.*[13]

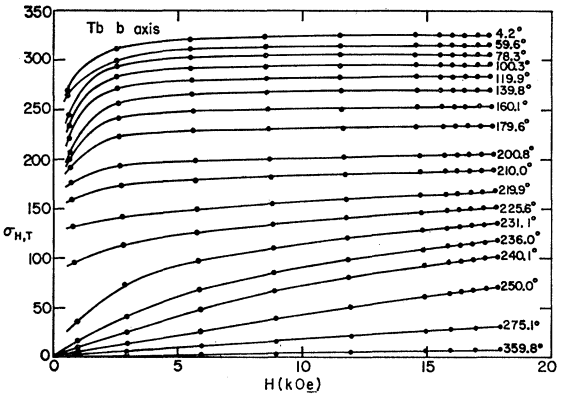

FIG. 5. Magnetic moment/g vs field for the b-axis crystal.

A sharp change in slope at 220±1°K is evident in the c-axis curve displayed in Fig. 12. The basal-plane curve also shows a well-defined change in slope at 229±1°K which does not appear in the c-axis curve. The c-axis curve goes through a nearly symmetrical maximum about 226°K and returns to a linear behavior near room temperature.

The electrical resistivity of the c-axis crystal was also measured in the temperature range 200 to 250°K with magnetic fields applied along a b axis. These data are plotted (residual subtracted) vs T in Fig. 12. Below 220°K the resistivity could be decreased slightly by the

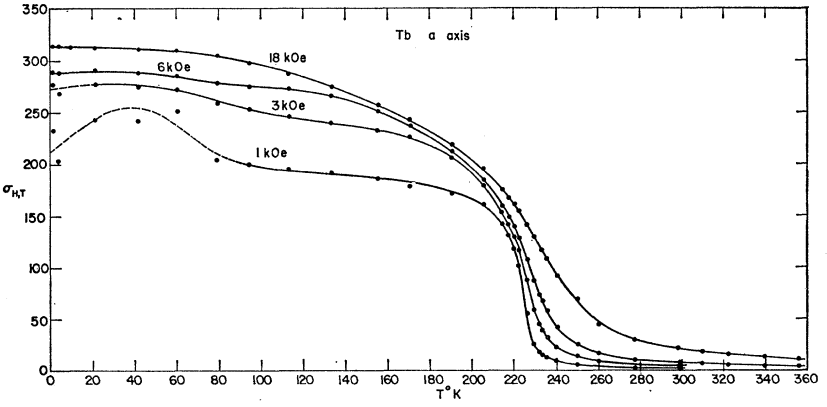

FIG. 6. Magnetic moment/g vs temperature for the b-axis crystal.

[13] J. K. Alstad, R. V. Colvin, and S. Legvold, Phys. Rev. **123**, 418 (1961).

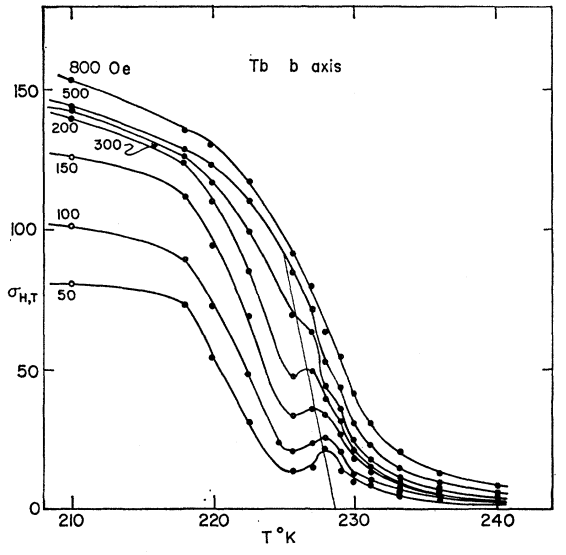

FIG. 7. Magnetic moment/g vs temperature for the b-axis crystal in the neighborhood of the Néel point. External fields are indicated.

application of the magnetic field, but above 240°K the change in resistivity resulting from the application of the field was of the order of magnitude of the experimental error. The peak around 226°K could be nearly eliminated by a sufficiently strong magnetic field, leaving a curve very similar to that for gadolinium as reported by Colvin *et al.*[6]

DISCUSSION

The isotherms for the a-axis crystal below 80°K showed a small positive slope at high fields. This behavior was also observed by Thoburn *et al.*[1] for polycrystalline terbium. This positive slope indicates that the moments spontaneously align along a b axis. If this is so, then the spontaneous moment, σ_{0T}, for the a axis should be equal to σ_{0T} for the b axis multiplied by cos 30°, since the a and b axes lie 30° apart in the basal plane. When the linear high field parts of the isotherms at low temperature were extrapolated to $H=0$ to obtain σ_{0T}, it was found that the difference between σ_{0T} (a axis) and σ_{0T} (b axis) (cos 30°) was less than 3%. Since the experimental error is of the order of 1%, the agreement is regarded as sufficient to substantiate the conclusion that the moments align spontaneously along a b axis. Hence, the saturation moment $\sigma_{\infty 0}=328\pm3$ emu/g, obtained from the b-axis data, is the true saturation moment. This value corresponds to 9.34 ±0.09 Bohr magnetons/atom and is to be compared with the theoretical prediction $gJ=9.0$ Bohr magnetons/atom, calculated assuming a $^7F_6$ state for the tripositive free ion. Thoburn *et al.*[1] report a saturation moment of 9.25 Bohr magnetons/atom for polycrystalline terbium. Liu[14] has suggested that the excess over the theoretical prediction may be due to the polarization of conduction electrons.

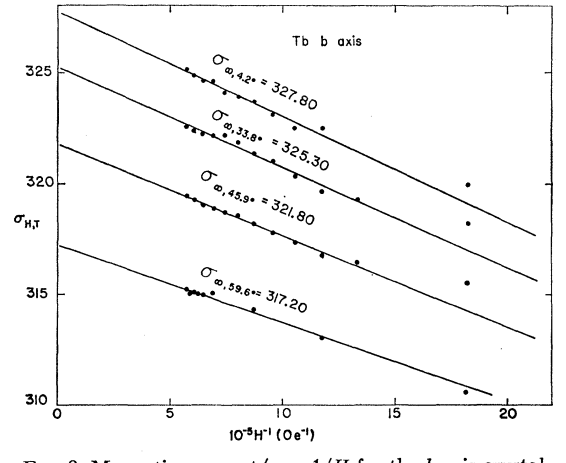

FIG. 8. Magnetic moment/g vs $1/H$ for the b-axis crystal.

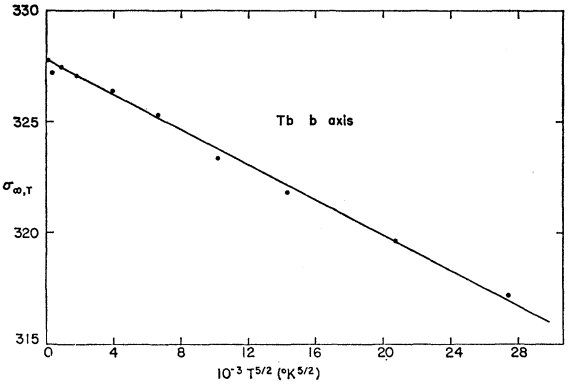

FIG. 9. Saturation magnetization of the b-axis crystal vs $T^{5/2}$.

The effective moment in the paramagnetic region, obtained from the slope of the $(1/X)$ vs T plot, was $\mu_{\text{eff}}=9.77$ Bohr magnetons for all three crystalline directions. The theoretical prediction is $\mu_{\text{eff}}=g[J(J+1)]^{1/2}=9.72$ Bohr magnetons, while Thoburn *et al.*[1] report $\mu_{\text{eff}}=9.7$ and Arajs and Colvin[3] report $\mu_{\text{eff}}=9.62$.

The basal-plane resistivity of terbium was found to be isotropic, within experimental error, over the temperature range covered in this investigation. The basal plane to c-axis anisotropy, given by ρ_a/ρ_c, was 1.29 at room temperature.

The room-temperature resistivities of the terbium crystals were from 30 to 120% greater than the corresponding values for erbium and holmium reported by Green *et al.*[15] and Strandburg *et al.*,[10] respectively. The room-temperature anisotropy, however, is smaller than the value 1.7 reported for erbium and holmium by the same authors.

[14] S. H. Liu, Phys. Rev. **123**, 470 (1961).
[15] R. W. Green, S. Legvold, and F. H. Spedding, Phys. Rev. **122**, 827 (1961).

The sharp change in slope in the resistivity observed at 220±1°K for the c-axis crystalline direction, which presumably occurs at the ferromagnetic Curie temperature, agrees very well with one of the determinations from the magnetic data, but not with the other. The weakly bound antiferromagnetic state results in considerable difficulty in determining the ferromagnetic Curie temperature accurately from the magnetic data; hence the change in slope of the resistivity is probably just as reliable an indication of the transition temperature.

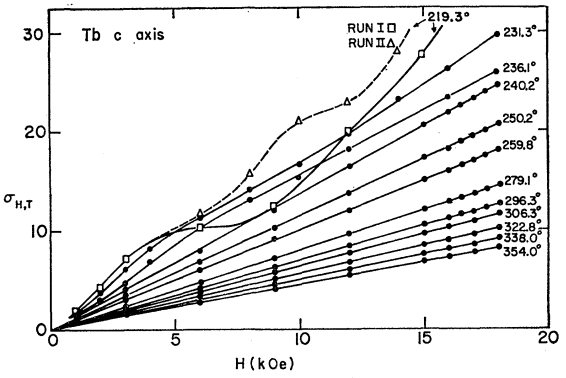

FIG. 10. Magnetic moment/g vs field for the c-axis crystal.

Proposals about the resistivity have been made by Mackintosh,[16] Miwa,[17] and Elliott.[18] They state that extra planes of energy discontinuity are introduced into the Brillouin zone structure when the magnetic lattice periodicity differs from the ionic lattice periodicity in the c direction. This causes a large change in the component of the Fermi surface vector along the c axis while leaving the component in the basal plane relatively unchanged. It is suggested that this is the cause of the peak in the c-axis resistivity curve and postulated that, if the antiferromagnetism could be quenched by the application of a magnetic field, the peak would disappear.

The antiferromagnetic ordering is very easily overpowered in terbium, and the c-axis resistivity in a magnetic field behaved as predicted, as can be seen in Fig. 12. The slight decrease in resistivity below 220°K with the field on is attributed to a slight increase in the magnetic order which causes a decrease in the magnon scattering term.

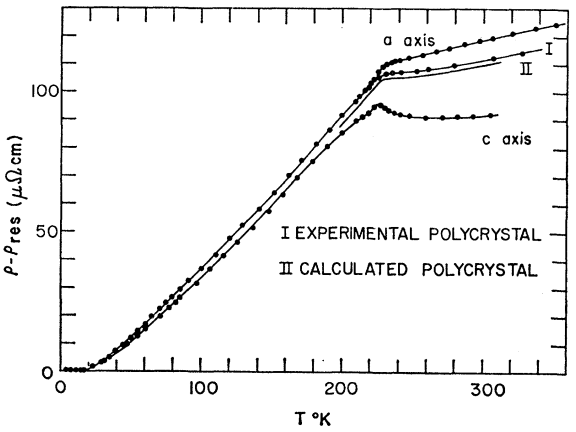

FIG. 11. Electrical resistivity (residual subtracted) vs temperature for the a- and c-axis crystals and for a polycrystalline sample.

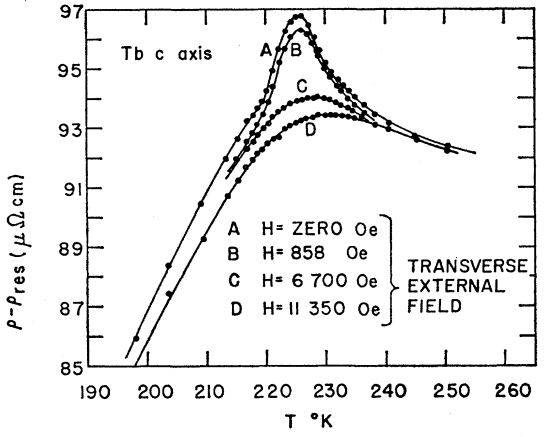

FIG. 12. Electrical resistivity (residual subtracted) for the c-axis crystal with a magnetic field applied along a b-axis.

ACKNOWLEDGMENTS

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[16] A. R. Mackintosh, Phys. Rev. Letters **9**, 90 (1962).
[17] H. Miwa, Progr. Theoret. Phys. (Kyoto) **28**, 208 (1962).
[18] R. J. Elliott and F. A. Wedgwood, Proc. Phys. Soc. London (to be published).