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Electrical and Magnetic Properties of Holmium Single Crystals*

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ABSTRACT

Magnetic moment measurements have been made on holmium single crystals (hcp) over the range 1.3 to 300°K in magnetic fields from 250 to 18,000 oe with the field applied along the c-axis, the a-axis, and a $\langle 10\bar{1}0 \rangle$ direction. The $\langle 10\bar{1}0 \rangle$ direction is the direction of easy magnetization with an extrapolated effective moment per atom at saturation of 10.34 Bohr magnetons. Basal plane measurements showed antiferromagnetism below the Néel temperature of 132°K with basal plane anisotropy occurring below 80°K. Below the Néel point an anomalous type of transition to ferromagnetic behavior upon application of sufficient field was observed. Magnetization curves for the c-axis are linear down to 60°K, while measurements below 20°K show an initial magnetization of approximately 1.7 Bohr magnetons followed by nearly linear magnetization

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curves. Electrical resistivity measurements were made from 4.2 to 300°K. For the a-axis, the resistivity changes slope slightly at 20°K. A larger change in slope occurs at the Néel temperature of 132°K. For the c-axis, the resistivity changes slope slightly at 20°K, reaches a peak at 120°K, goes through a minimum at 132°K, and remains constant until approximately 150°K, after which it increases linearly with increasing temperature.

INTRODUCTION

The magnetic properties of metallic polycrystalline holmium have been investigated by Rhodes, et al.¹ from 4.2 to 300°K. Paramagnetic and antiferromagnetic behavior were observed, and the Néel temperature was estimated to be $133 \pm 2^\circ\text{K}$. A paramagnetic Curie temperature of 85°K and an effective paramagnetic moment per atom of 10.9 Bohr magnetons were determined. Remanance and magnetic hysteresis were observed at 4.2°K. The approach of the magnetic moment to saturation was observed to follow a $T^{3/2}$ law, and an absolute saturation moment of 310 cgs units/g was obtained.

Colvin, et al.² measured the electrical resistivity of polycrystalline holmium from 1.4 to 300°K. The resistivity vs temperature curve of their data which are plotted in Fig. 10 shows a change of slope at 19°K and a small peak at 127°K.

Specific heat measurements from 12 to 300°K made on polycrystalline holmium by Gerstein, et al.³ revealed two anomalous regions. A

small peak occurred at 19.4°K and a much larger one occurred at 131.6°K. The details of the curve just below the peak at 131.6°K have not been completely determined, and some irregularity exists in this region.

Hermann⁴ has determined the crystal structure and lattice constants for holmium at room temperature. He found that the metal has the hexagonal close-packed structure. Neutron diffraction measurements of Koehler⁵ have shown no change of crystal structure down to liquid helium temperatures.

Koehler⁶ has interpreted neutron diffraction measurements on a single crystal of holmium in the temperature region from 120 to 35°K as resulting from an antiferromagnetic helical spin arrangement where the magnetic moments are parallel within each hexagonal layer but rotate by an angle ω per layer in successive planes along the c-axis. The angle ω is temperature dependent and is 50° per layer at 120°K and decreases with decreasing temperature.

EXPERIMENTAL PROCEDURE

In order that the electrical and magnetic properties of holmium might be investigated with respect to the principal directions of the crystal, it was necessary to prepare single crystals oriented along the c-axis, along an a-axis, and along a direction halfway between two a-axes in the basal plane which is designated as the $\langle 10\bar{1}0 \rangle$ direction. The samples were cut in the form of rectangular parallelepipeds with dimensions of 1 mm x 1 mm x 10 mm.

The distilled holmium metal from which the single crystals were grown was prepared by methods previously reported.^{7, 8} Single crystals were grown from the distilled metal using a modified form of a strain-anneal method which has been described by Hall, et al.⁹ Spectrographic analysis of pieces of the single crystal from which the samples were cut showed the following impurities: Y < 0.01%; Dy < 0.04%; Er, 0.06%; Tm, 0.02%; Ca < 0.03%; Cr < 0.005%; Mg < 0.005%; Fe, 0.005%; Cu < 500 ppm; Al, B, Mg, Nd, Ni, Pb, Pr, Sc, Si, Sm, Ta, Tb, W, Yb, not detected.

Magnetic measurements were made using a standard version of the Faraday method in which the magnetic moment is determined from measurements of the force exerted on a sample which has been placed in a non-uniform magnetic field. Magnetic fields up to 18 koe were obtained with an electromagnet which has been described in a previous paper.¹⁰

A modified form of the heat leak chamber described by Anderson, et al.¹¹ and Colvin, et al.² was used to obtain temperatures from 1.3 to 300°K. Temperatures below 4.2°K were determined from the temperature of the liquid helium bath. A 51 ohm carbon resistor thermometer and a copper constantan thermocouple which were calibrated during each series of measurements were used for temperature measurement in the region from 4.2 to 20°K, and the copper constantan thermocouple was used for all temperatures above 20°K. Absolute temperature values were determined to $\pm 0.5^\circ\text{K}$ while the temperature variation during each series of measurements was controlled to $\pm 0.05^\circ\text{K}$.

Electrical resistivity measurements from 4.2 to 300°K were also made on the three holmium single crystals. The experimental procedure and the apparatus used for these measurements have been described by Colvin, et al.²

EXPERIMENTAL RESULTS

The data for the a-axis crystal are presented as isotherms in Fig. 1. Isofield curves obtained from these isotherms are given in Figs. 2 and 3. Figure 3 shows the details of magnetization curves near the Néel point. The position of the peak in the curves is seen to be field dependent, and the extrapolation to $\sigma_{H,T} = 0$ gives a Néel point of 132°K. Values of the reciprocal of the magnetic susceptibility, $\frac{1}{\chi}$, obtained from measurements in the paramagnetic region are plotted vs temperature in Fig. 4.

The anomalous behavior of the magnetic moment in the antiferromagnetic temperature region is shown in Fig. 1. The "knee" which appears at a magnetic moment of about 100 cgs units/g for all isotherms above 30°K was not observed in the measurements of Green, et al.¹² on single crystals of erbium and Behrendt, et al.¹³ on single crystals of dysprosium. They observed an almost discontinuous rise followed by rapid saturation of the magnetic moment.

The "knee" also appears in the isofield plot of Fig. 2 in which the circles indicate points taken from experimental isotherms. The details of the curves in the regions of the knees were established by drawing extra isotherms at one degree temperature intervals between those actually measured, using the experimental curves as guides.

Measurements of magnetic moment as a function of decreasing fields were made at several temperatures to check for the hysteresis reported by Rhodes, et al.¹ for polycrystalline holmium. Curves for decreasing fields are indicated by dashed lines in Fig. 1. The uncertainty of calibration of the magnet for decreasing fields results in an error estimation of about 2% in the value of magnetic moment and 0.2 koe in the value of the magnetic field. The hysteresis in the antiferromagnetic range, as shown at 45 and 61.8°K, occurs at the "knee" described previously. The decreasing curve runs parallel to the increasing curve below this knee and merges with the linear portion of the increasing curve at a lower value of applied field. The width of the hysteresis loop thus formed is approximately the same as the width of the "knee" on the increasing curve.

A small peak in the magnetic moment vs temperature isofield curve which occurs at 20°K for small magnetic fields is shown in the inset of Fig. 2. The peak is not present for magnetic fields greater than three koe.

The isotherm data for the $\langle 1010 \rangle$ crystal are displayed in Fig. 5, and isofield curves obtained from the isotherm data are given in Fig. 6. The data for the a-axis crystal and the $\langle 10\bar{1}0 \rangle$ crystal coincide above 80°K, so that the Neel point data of Fig. 3 and the $\frac{1}{X}$ vs T data of Fig. 4 for the a-axis crystal are also representative of the $\langle 10\bar{1}0 \rangle$ crystal behavior. At lower temperatures, anisotropy exists in the basal plane, and the $\langle 10\bar{1}0 \rangle$ direction is the direction of easy magnetization.

An anomalous behavior more complicated than that of the a-axis crystal is exhibited in Fig. 5 by the $\langle 10\bar{1}0 \rangle$ crystal in the antiferromagnetic temperature range. Two "knees" appear in the isotherm data above 45°K. The first "knee" appears at a magnetic moment of approximately 100 cgs units/g, and the second "knee" appears at approximately 200 cgs units/g. The widths of the "knees" increase with increasing temperature, but the values of magnetic moment at which they appear seem to be constant.

In Fig. 7 values of $\sigma_{\infty, T}$ and $\sigma_{0, T}$ are shown plotted vs $T^{3/2}$ and also T^2 to obtain values for the saturation magnetization, $\sigma_{\infty, 0}$, and the spontaneous magnetization, $\sigma_{0, 0}$, for the $\langle 10\bar{1}0 \rangle$ crystal.

Figures 8 and 9 show the isotherms and the isofields for the c-axis crystal. The isotherms below 20°K show an initial magnetization of about 60 cgs units/g. The small positive slopes of the curves up to 18 koe indicate that holmium is very hard magnetically in the direction of the c-axis. At temperatures below 50°K the sample tended to twist so as to align a more favorable crystal axis with the field direction. To overcome this difficulty a system of centering chains which held the c-axis parallel to the field while allowing vertical motion was used. The scatter of the data at fields below 1 koe may be attributed to a decrease in weighing sensitivity because of these chains and to the increased uncertainty of the field gradient calibration at these low fields.

In Fig. 4 the $\frac{1}{X}$ vs T plot for the c-axis crystal paramagnetic data is shown. Also shown are the experimental data points for polycrystal-

line holmium reported by Rhodes, et al.¹ Calculated values of magnetic susceptibility for a polycrystalline sample, X_{poly} , were obtained from single crystal results by use of the relationship

$$X_{\text{poly}} = \frac{2X_a + X_c}{3}$$

where X_a is the susceptibility of the a-axis crystal and X_c is the susceptibility of the c-axis crystal. The straight line between the a-axis and c-axis lines is a plot of $\frac{1}{X_{\text{poly}}}$ vs T. The data of Rhodes, et al. are seen to fall quite close to this line.

The electrical resistivities (minus residual resistivity) of the a-axis crystal and the c-axis crystal are displayed in Fig. 10 as functions of temperature. Since the data for the a-axis and the $\langle 10\bar{1}0 \rangle$ crystals coincided within experimental error limits, only the a-axis data are plotted.

At 132°K the curve for the a-axis crystal exhibits a change in slope. This is taken as the Néel point. Measurements made at increasing and decreasing temperatures revealed no thermal hysteresis at the Néel point. A very slight change of slope occurred at approximately 20°K.

Figure 10 shows the marked minimum in resistivity which occurred at the Néel point for the c-axis crystal. A temperature of 132°K is taken as the Néel point, although the essentially temperature-independent nature of the curve from 132 to 150°K indicates that the effects of magnetic ordering may extend well above the Néel temperature.

Also plotted in Fig. 10 is a curve of polycrystalline holmium data determined by Colvin, et al.² and a curve of calculated polycrystalline

data which were obtained from the single crystal data by the use of

$$\rho_{\text{poly}} = \frac{2\rho_a + \rho_c}{3}$$

where ρ_a is the a-axis resistivity, ρ_c is the c-axis resistivity, and ρ_{poly} is the calculated resistivity of a polycrystalline sample. This relationship has been verified for the hexagonal metal yttrium by Alstad, et al.¹⁴

DISCUSSION

The magnetic properties of holmium were found to be anisotropic over the entire temperature range covered in this investigation. The existence of magnetic anisotropy in the paramagnetic region has been shown experimentally in erbium by Green, et al.¹² and in dysprosium by Behrendt, et al.¹³ The anisotropy for the case of holmium is displayed in Fig. 4. No anisotropy was observed in the basal plane at temperatures above 80°K, and the c-axis is the direction of hard magnetization.

At very low temperatures, the $\langle 10\bar{1}0 \rangle$ direction is the direction of easy magnetization. The determination of the saturation moment, $\sigma_{\infty, 0}$, for the $\langle 10\bar{1}0 \rangle$ crystal is shown in Fig. 7, where the $T^{3/2}$ plot is seen to give a somewhat better fit. This is in agreement with the theoretical results of Kasuya¹⁵ and Bloch,¹⁶ but not with those of Niira,¹⁷ who obtained a T^2 dependence for single crystals of dysprosium. However, if only temperatures of 20°K and under are considered, the plots are about equally good. Measurements at higher magnetic fields are needed to resolve this point.

For the $\langle 10\bar{1}0 \rangle$ crystal, $\sigma_{\infty,0} = 350.2 \pm 3.5$ cgs units/g, and $N_{\text{eff}} = 10.34 \pm 0.10$ Bohr magnetons. For the a-axis crystal, $\sigma_{\infty,0} = 306.0 \pm 3.1$ cgs units/g, and $N_{\text{eff}} = 9.00 \pm 0.09$ Bohr magnetons. A theoretical determination of the saturation moment gives $N_{\text{eff}} = gJ = 10$ Bohr magnetons, so that slightly more than the total moment predicted by this treatment is obtained in the $\langle 10\bar{1}0 \rangle$ direction. The additional moment may arise from the contribution of polarized conduction electrons which has been discussed by Liu.¹⁸

If the saturation moment of the $\langle 10\bar{1}0 \rangle$ crystal is multiplied by the cosine of 30° , a value of 8.95 Bohr magnetons is obtained. This is equal, within the limits of experimental error, to the saturation moment of the a-axis crystal. Since the a-axis and the $\langle 10\bar{1}0 \rangle$ directions are 30° apart in the basal plane, a reasonable interpretation of this result is that although the external magnetic field is directed along an a-axis, the magnetic moments at the maximum fields available in this investigation lie along the easy $\langle 10\bar{1}0 \rangle$ directions and only their components in the direction of the field contribute to the magnetization.

The a-axis and the $\langle 10\bar{1}0 \rangle$ crystal magnetization curves at lowest temperatures have the characteristic shape of curves for ferromagnetic materials, and the decreasing field measurements show hysteresis. Neutron diffraction results of Koehler⁶ also showed that ferromagnetism could be induced in holmium at temperatures below 20°K by the application of a magnetic field in the basal plane.

For the c-axis crystal, the spontaneous magnetization of about 60 cgs units/g, or 1.7 Bohr magnetons/atom, followed by a very flat magnetization curve agrees quite well with the neutron diffraction results of Koehler.⁶ His results indicate that below 20°K in zero magnetic field a small component (about 2 Bohr magnetons) of the magnetic moment is directed along the c-axis in a ferromagnetic alignment, while the basal plane orientation remains a spiral. It is extremely difficult to turn the moments further away from the basal plane by the application of a magnetic field along the c-axis.

The effective moment, μ_{eff} , in the paramagnetic region which is obtained from the $\frac{1}{X}$ vs T plot of Fig. 4 is 11.2 Bohr magnetons for all three crystalline directions. The data reported by Rhodes, et al.¹ for polycrystalline holmium give an effective moment of 10.9 Bohr magnetons, while a theoretical value of 10.6 Bohr magnetons is obtained when a ground state of 5I_8 is assumed. It should be noted that the results of Green, et al.¹² for erbium gave a result which was approximately 3% higher than that predicted by $\mu_{\text{eff}} = g J(J + 1)^{1/2}$.

The a-axis and the $\langle 10\bar{1}0 \rangle$ crystal data show the existence of a Néel point at 132°K. It can be seen in Fig. 3 that the Néel temperature is field dependent and decreases with increasing magnetic field. Below 132°K, the a-axis and the $\langle 10\bar{1}0 \rangle$ crystal data indicate that the sample is in an antiferromagnetic state. However, there is no indication of antiferromagnetism in the c-axis data plotted in Fig. 8. These results agree with the neutron diffraction studies of Koehler⁶ who suggested that below 132°K the magnetic moments had in the absence

of an external field an antiferromagnetic helical spin arrangement with the magnetic moments lying in the basal plane.

The anisotropy in electrical resistivity at room temperature is indicated by the ratio $\frac{\rho_a}{\rho_c} = 1.70$. The slopes of the plots of resistivity vs temperature in the paramagnetic region are also indicative of the degree of anisotropy. The slope of the ρ_c curve is $0.099 \mu\text{ohm-cm/o}_K$, while the slope of the ρ_a curve is $0.176 \mu\text{ohm-cm/o}_K$.

The slope of the curve for the calculated polycrystalline holmium data is $0.147 \mu\text{ohm-cm/o}_K$, while the slope of the curve for the experimentally determined data of Colvin, et al.² for polycrystalline holmium is $0.144 \mu\text{ohm-cm/o}_K$. The two curves also show the same shape in the vicinity of the Néel point. Since "polycrystalline" samples of rare-earth metals often have some degree of preferred orientation, perfect agreement is not expected.

The magnetic measurements indicate that the specific heat anomaly near 132°K arises from the paramagnetic to antiferromagnetic transition at the Néel temperature. A "knee" occurs in the curve of ρ_a at this temperature.

The curve of ρ_c has a broad unsymmetrical peak with a maximum at 116°K followed by a minimum at 132°K , the Néel temperature. At and below this temperature, magnetic ordering is observed. The magnetic moments are aligned parallel to each other in atomic layers perpendicular to the c-axis. There is a turn angle for the moment from layer to layer and this gives rise to a different magnetic periodicity from the lattice periodicity. Mackintosh¹⁹ has proposed that extra

planes of energy discontinuity are introduced into the Brillouin zone structure as a result of the helical spin structure present in the antiferromagnetic phase of several of the rare earths. This causes a large change in the component of the Fermi surface vector in the c direction, while that in the basal plane is relatively unchanged. He has suggested that this is the cause of the peak in the c -axis resistivity curve.

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FIGURE CAPTIONS

- Fig. 1. Magnetic moment per gram vs field for the a-axis crystal.
Dashed lines are for H decreasing.
- Fig. 2. Magnetic moment per gram vs temperature for the a-axis crystal.
- Fig. 3. Magnetic moment per gram vs temperature for the a-axis crystal in the neighborhood of the Néel point.
- Fig. 4. The reciprocal of the susceptibility vs temperature for the a-axis and the c-axis crystals and for a polycrystalline sample of holmium.
- Fig. 5. Magnetic moment per gram vs field for the $\langle 10\bar{1}0 \rangle$ crystal.
Dashed lines are for H decreasing.
- Fig. 6. Magnetic moment per gram vs temperature for the $\langle 10\bar{1}0 \rangle$ crystal.
- Fig. 7. Saturation and spontaneous magnetization of the $\langle 10\bar{1}0 \rangle$ crystal as a function of $T^{3/2}$ and T^2 .
- Fig. 8. Magnetic moment per gram vs field for the c-axis crystal.
Dashed lines are for H decreasing.
- Fig. 9. Magnetic moment per gram vs temperature for the c-axis crystal.
- Fig. 10. Electrical resistivity, residual subtracted, as a function of temperature for the a-axis and the c-axis crystals and for a polycrystalline sample.

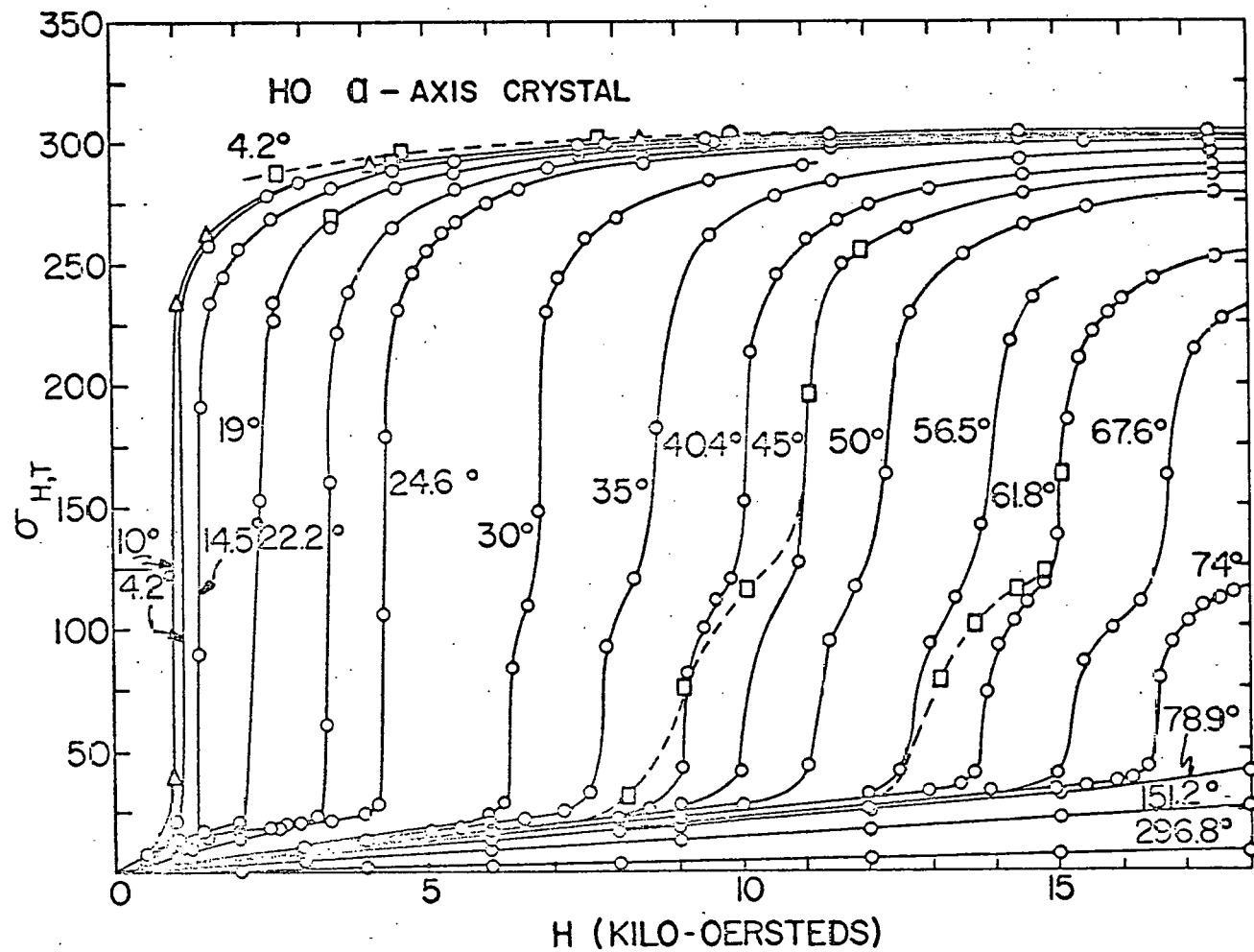


Fig. 1. Magnetic moment per gram vs field for the a-axis crystal.
Dashed lines are for H decreasing.

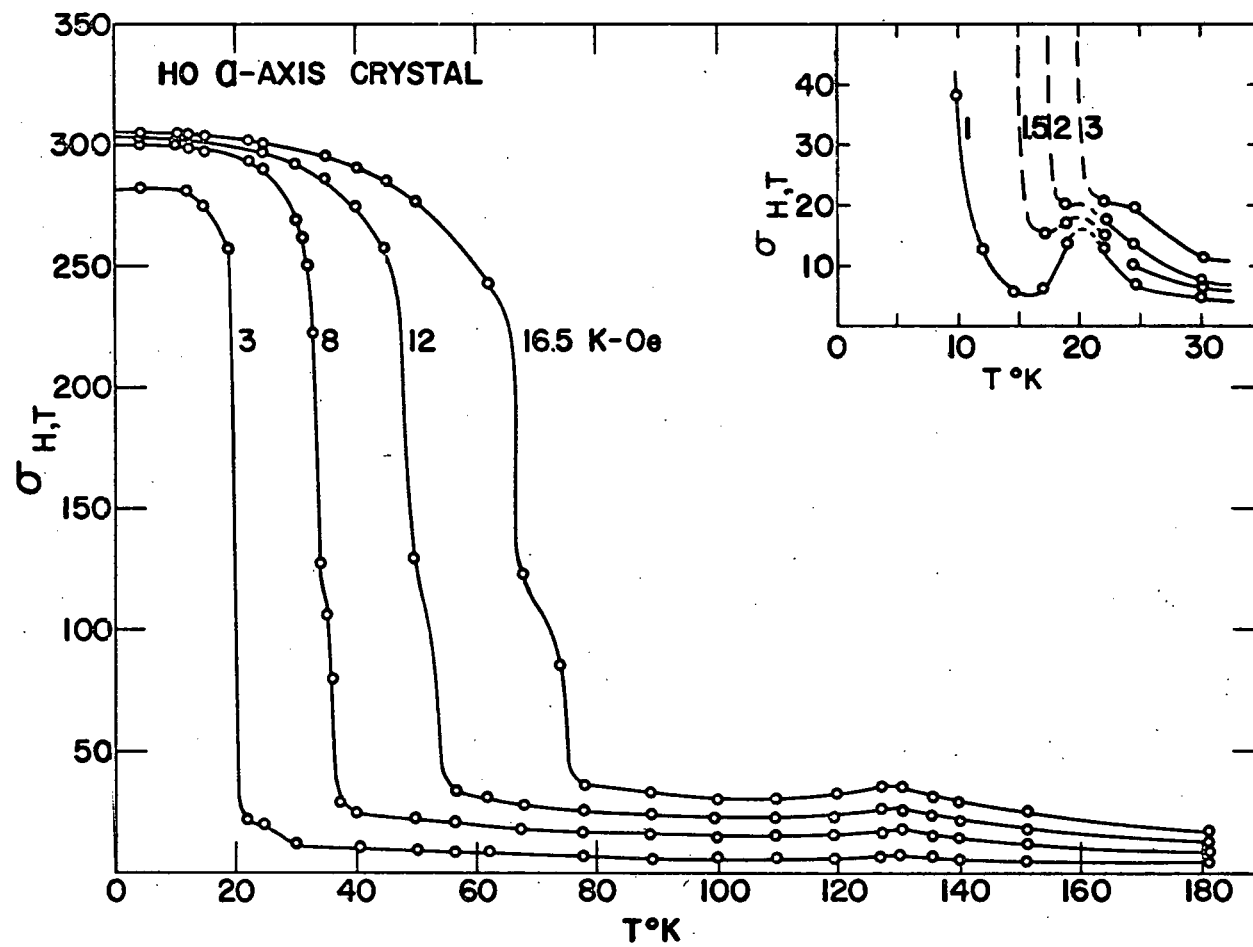


Fig. 2. Magnetic moment per gram vs temperature for the a-axis crystal.

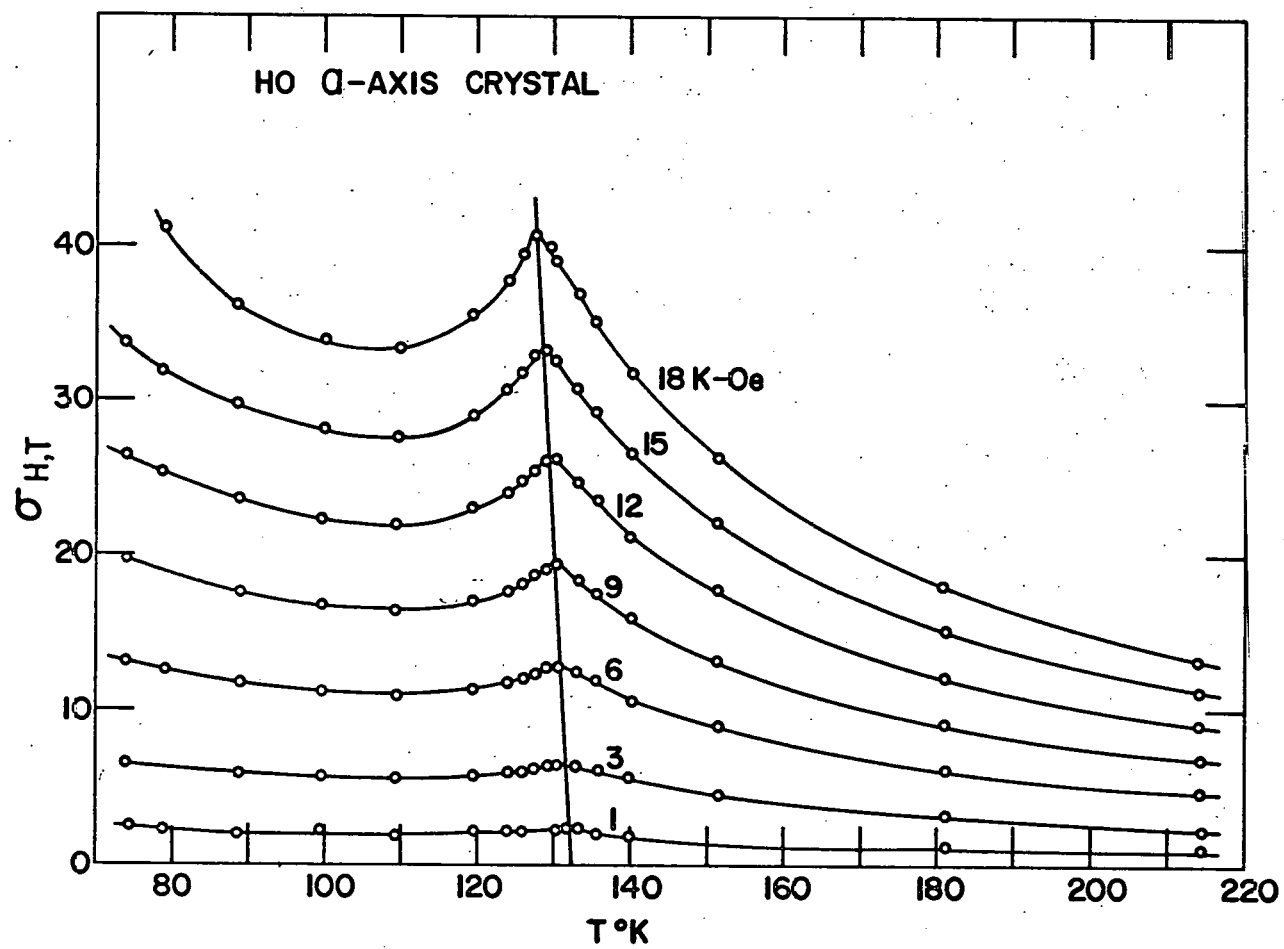


Fig. 3. Magnetic moment per gram vs temperature for the a-axis crystal in the neighborhood of the Néel point.

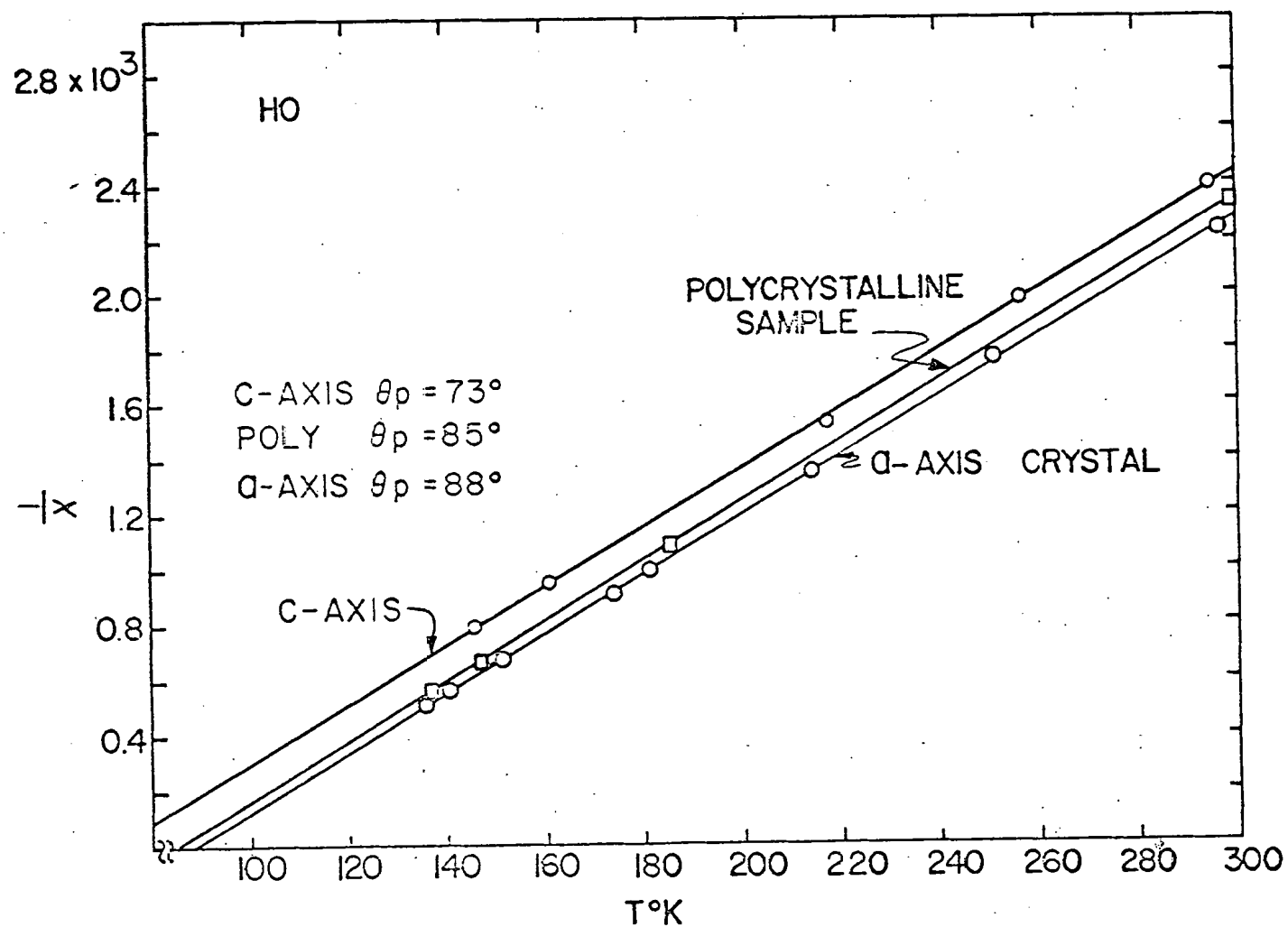


Fig. 4. The reciprocal of the susceptibility vs temperature for the a-axis and the c-axis crystals and for a polycrystalline sample of holmium.

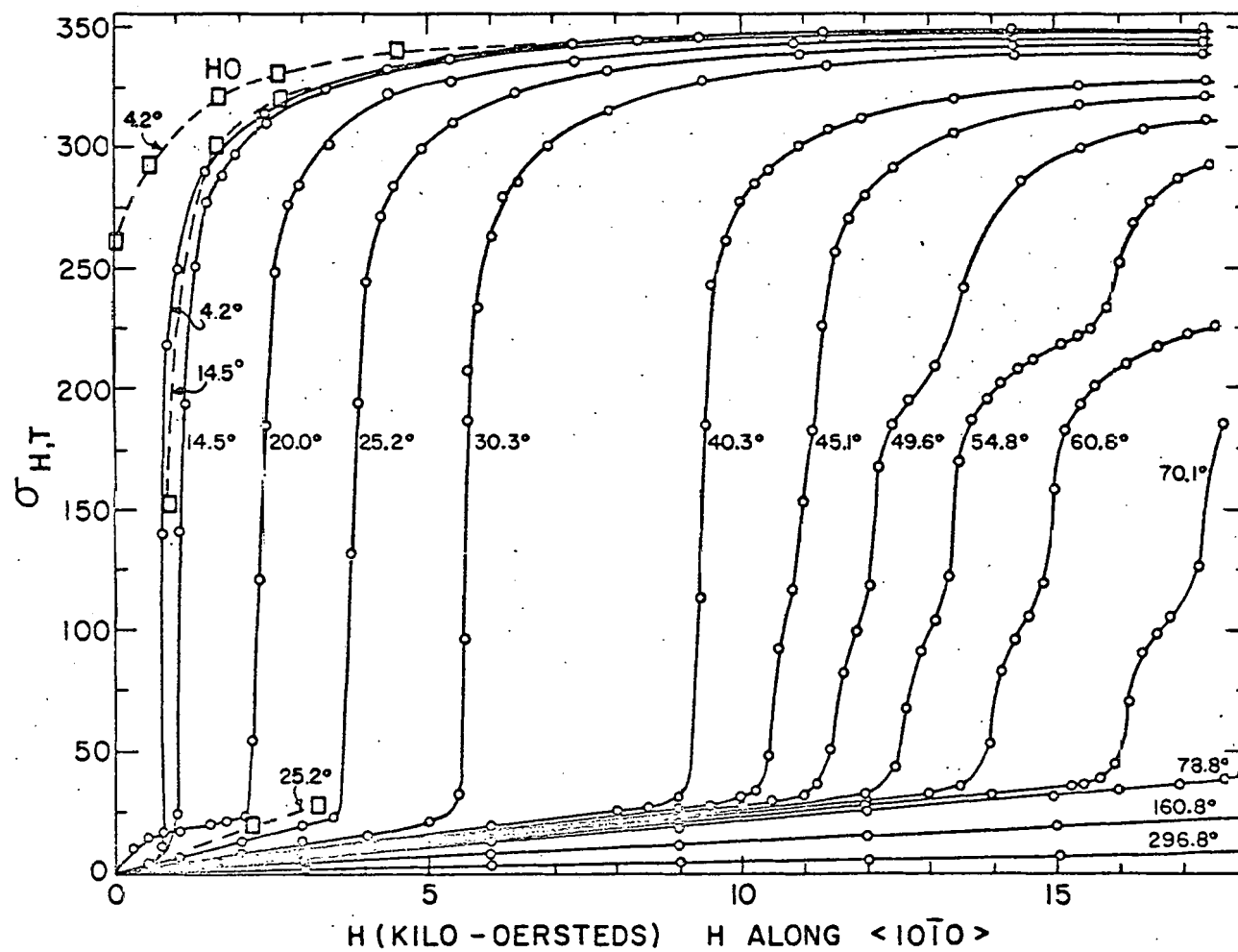


Fig. 5. Magnetic moment per gram vs field for the $\langle 10\bar{1}0 \rangle$ crystal. Dashed lines are for H decreasing.

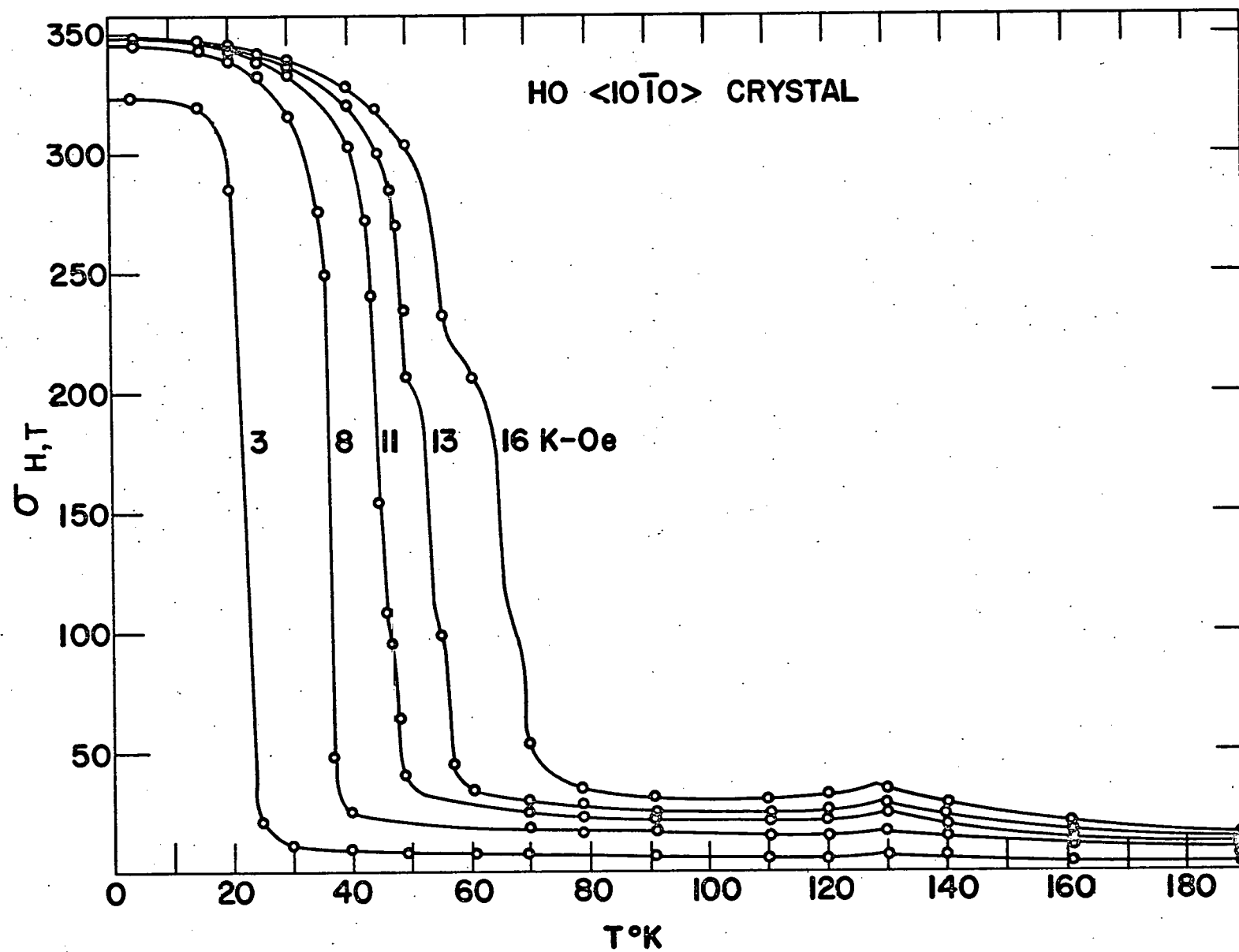


Fig. 6. Magnetic moment per gram vs temperature for the $\langle 10\bar{1}0 \rangle$ crystal.

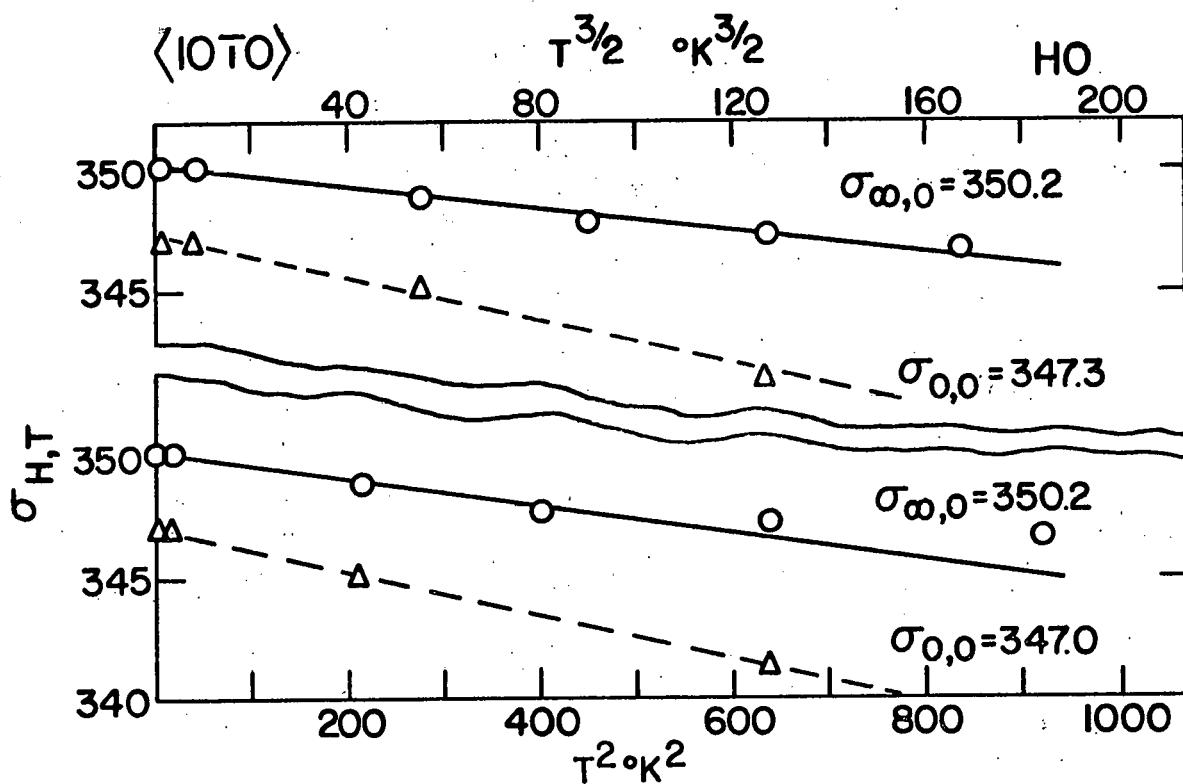


Fig. 7. Saturation and spontaneous magnetization of the $\langle 10\bar{1}0 \rangle$ crystal as a function of $T^{3/2}$ and T^2 .

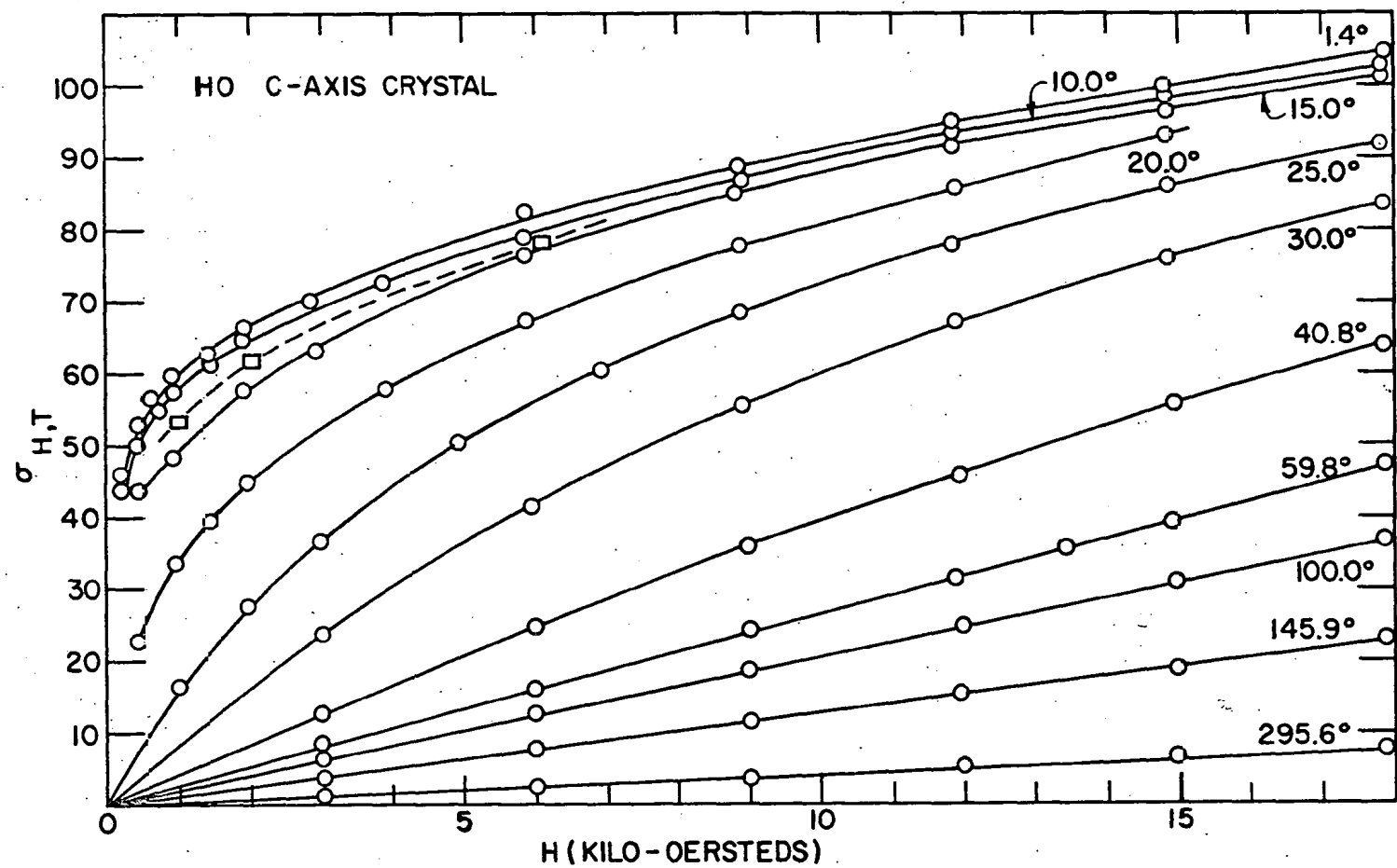


Fig. 8. Magnetic moment per gram vs field for the c-axis crystal. Dashed lines are for H decreasing.

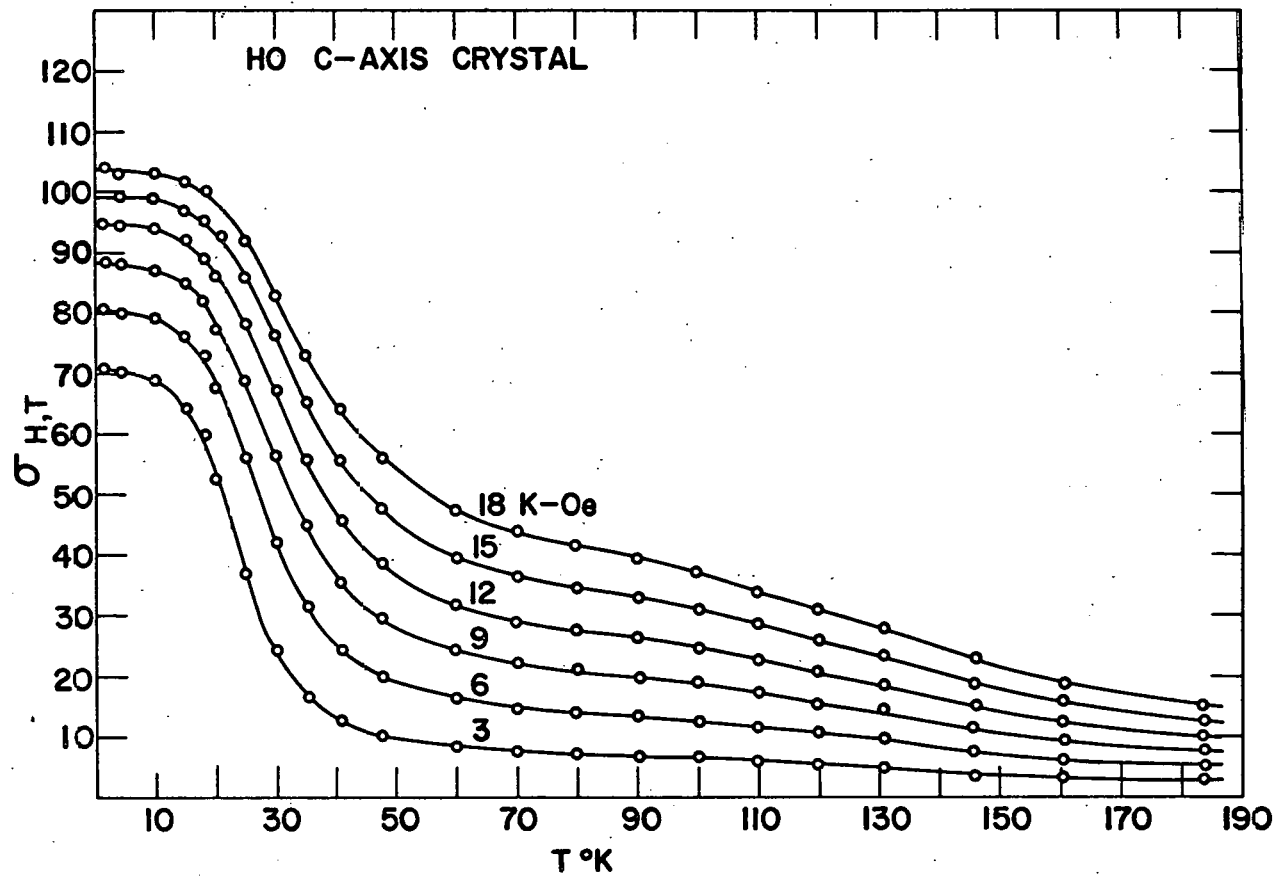


Fig. 9. Magnetic moment per gram vs temperature for the c-axis crystal.

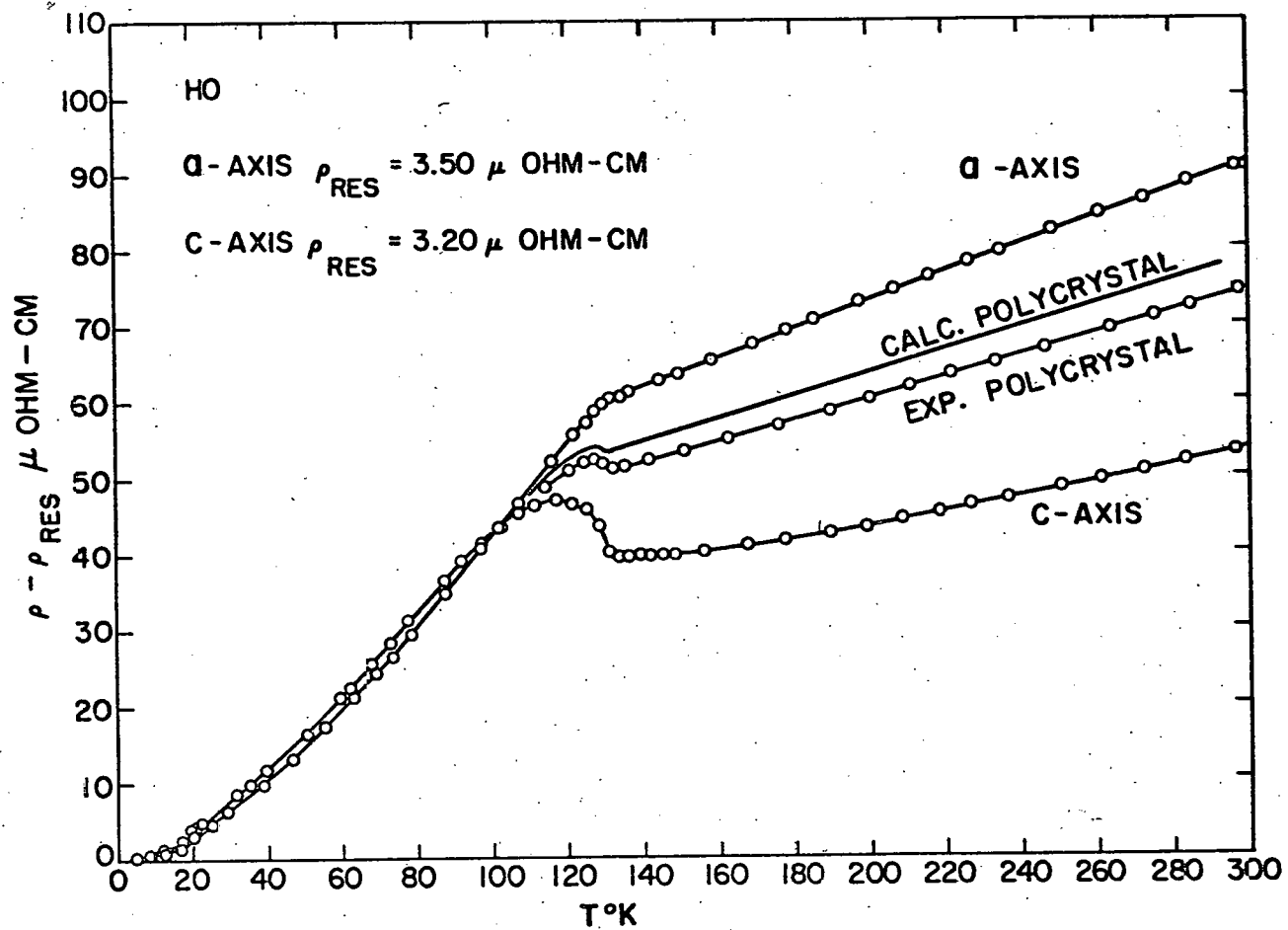


Fig. 10. Electrical resistivity, residual subtracted, as a function of temperature for the a-axis and the c-axis crystals and for a polycrystalline sample.