consists of an unsplit component and an unresolved broad absorption whose width indicates that it is of magnetic origin. The width is too great to be of quadrupolar origin resulting from slow relaxation.[13] Experiments with crystals of widely differing impurity contents prove that this effect is not due to transition-metal impurities. The effect extends over much too great a temperature range to be related to critical-point fluctuations. The most probable explanation lies in lattice strain sufficient to perturb the threefold degenerate ground states by an amount sufficiently large to cause a spatial variation of the Néel temperature.

[13] F. S. Ham (to be published).

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Magnetic Structures of Holmium. II. The Magnetization Process*

W. C. Koehler, J. W. Cable, H. R. Child, M. K. Wilkinson, and E. O. Wollan
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received 9 January 1967)

Neutron-diffraction measurements have been made on single-crystal holmium at temperatures ranging from 4.2 to 120°K in applied magnetic fields up to 22.3 kOe in order to study the magnetization process of this material. At low temperatures, the *b* direction in the basal plane is an easy axis. For a field applied parallel to an *a* direction, the moments are aligned parallel to the closest *b* directions. At higher temperatures the effect of a field applied parallel to a *b* direction is to transform the system to a *b*-axis ferromagnet after causing it to pass through one or two (depending upon the temperature) intermediate fanlike oscillatory structures. Similar oscillatory configurations are produced by the application of a field parallel to an *a* direction. The *a*-axis ferromagnet is not produced in fields up to 22.3 kOe. A characterization of the four intermediate structures observed at 50°K was made and schematic phase diagrams in the H-T plane were extracted from the diffraction and magnetization data. Studies of the remanent state at 4.2°K were made, and are reported.

INTRODUCTION

In an earlier paper[1] we have described the virgin-state magnetic structures of holmium as deduced from single-crystal neutron-diffraction experiments. From the Néel temperature to about 20°K, the moments order in a helical structure in which the *c* axis is the screw axis. Below 20°K the structure is a ferromagnetic spiral in which a net moment of $1.7\mu_B$ is found along the *c* axis. At low temperatures the configuration in the basal plane is a distorted helical one in which moments of magnitude $9.5\mu_B$ are bunched around the *b* directions. The work was based on studies of two crystals: Ho(A), with a final turn angle of 36.7° per layer, and Ho(B), with a final turn angle at 4.2°K of precisely 30.0° per layer. As described earlier, the latter crystal appears to be more nearly representative of pure, strain-free, holmium.

In this paper we report results of neutron-diffraction studies which have been made on these crystals in applied magnetic fields. Most of the work reported deals with the crystal (B) for which accurate demagnetization corrections could be made. A few results, particularly those obtained at low temperature, are given for Ho(A).

These experiments were undertaken to understand the apparent discrepancy between the early magnetization data,[2] which indicated a transition to a completely ferromagnetic state, and the virgin-state diffraction results, and to investigate the origin of the many anomalies in the single-crystal magnetization curves reported by Strandburg, Legvold, and Spedding.[3] It seems particularly appropriate now to characterize as well as possible the magnetic structures induced by the application of a steady magnetic field because the knowledge of such structures will be important to the interpretation of experiments, such as magnetic resonance and inelastic neutron scattering, designed to investigate spin-wave excitations in the rare earths.

Theoretical studies of the magnetization process of a helical spin structure were made first by Herpin and Mériel,[4] and by Enz.[5] The most complete investigations have been made by Nagamiya and his associates[6] who studied the changes in helical and other oscillatory spin structures due to the application of a magnetic field at finite temperatures, as well as at absolute zero, and for a number of cases of different anisotropy energy.

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[1] W. C. Koehler, J. W. Cable, M. K. Wilkinson, and E. O. Wollan, Phys. Rev. **151**, 414 (1966).

[2] B. L. Rhodes, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1544 (1958).

[3] D. L. Strandburg, S. Legvold, and F. H. Spedding, Phys. Rev. **27**, 2046 (1962).

[4] A. Herpin and P. Mériel, Compt. Rend. **250**, 1450 (1960); J. Phys. Radium **22**, 337 (1961).

[5] U. Enz, Physica **26**, 69 (1960); J. Appl. Phys. **32**, 22S (1961).

[6] T. Nagamiya, K. Nagata, and Y. Kitano, Progr. Theoret. Phys. (Kyoto) **27**, 1253 (1962); Y. Kitano and T. Nagamiya, *ibid.* **31**, 1 (1964).

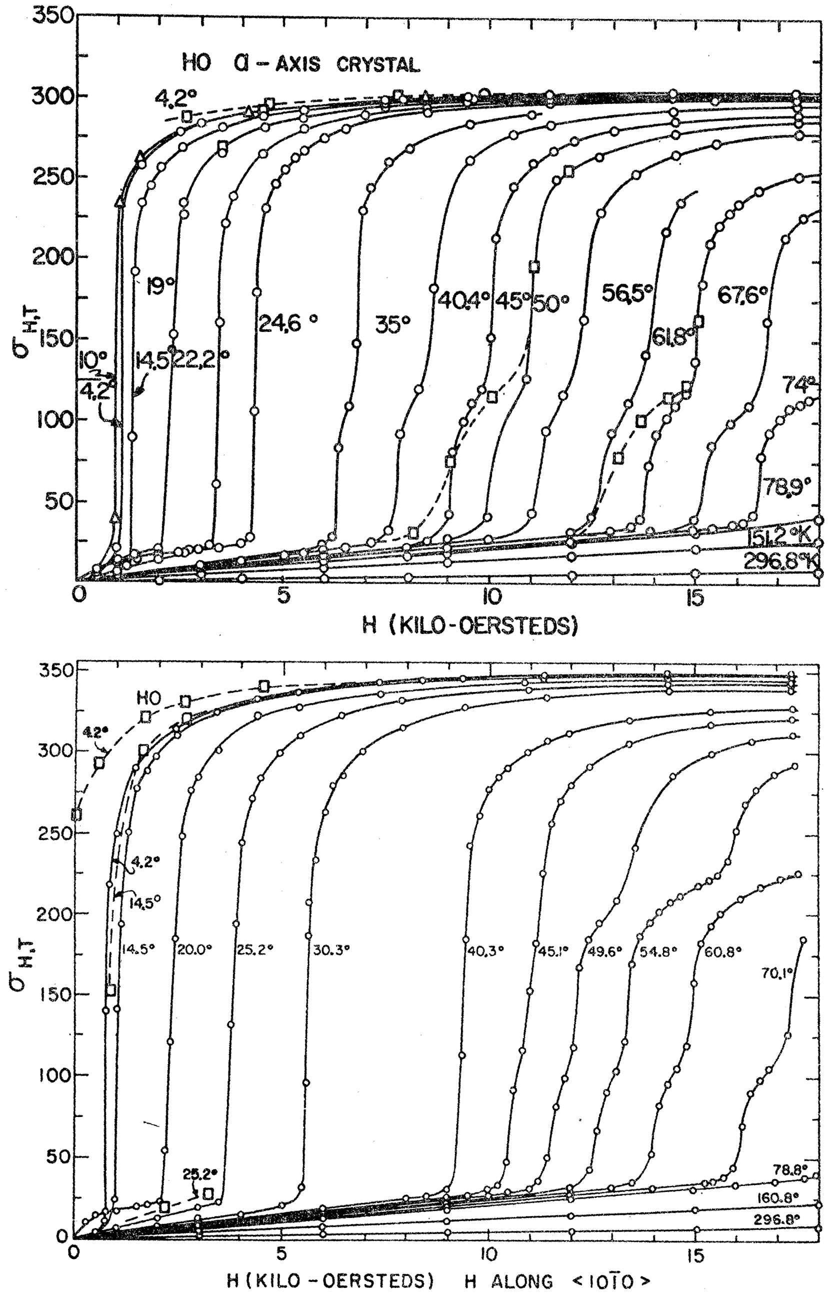

FIG. 1. Magnetization data for Holmium single crystals. The upper set of curves refers to magnetization parallel to an *a* direction, the lower for magnetization parallel to a *b* direction. The data are those of Strandburg, Legvold, and Spedding.

It will be of interest to compare the predictions of the theory with our observations, and we shall have occasion to refer frequently to their results in the appropriate sections of the text.

The magnetization data[3] which provided part of the motivation for this study are summarized in part in Fig. 1, in which magnetization isotherms measured with the field directed parallel to a hexagonal *a* axis are shown in the upper half of the figure; in the lower part are represented data obtained with the field parallel to a *b* direction. In the latter case, and at low temperatures, the magnetization increases abruptly for fields greater than about 1.0 kOe and approaches a saturation value of $10.3\mu_B$ in high fields, indicating that a transformation from the conical configuration to a ferromagnetic one with the moments parallel to the field direction has taken place. With increasing temperature the effect of the field is to produce a large net magnetic moment parallel to the *b* direction, but the character of the isotherms changes. One by one, two additional humps or plateaus develop.

When the field is parallel to the *a* direction, the magnetization at low temperature saturates at a value which is very nearly $0.866\times10.3\mu_B$. At higher temperatures, the magnetization isotherms develop one additional knee. The apparent saturation magnetizations

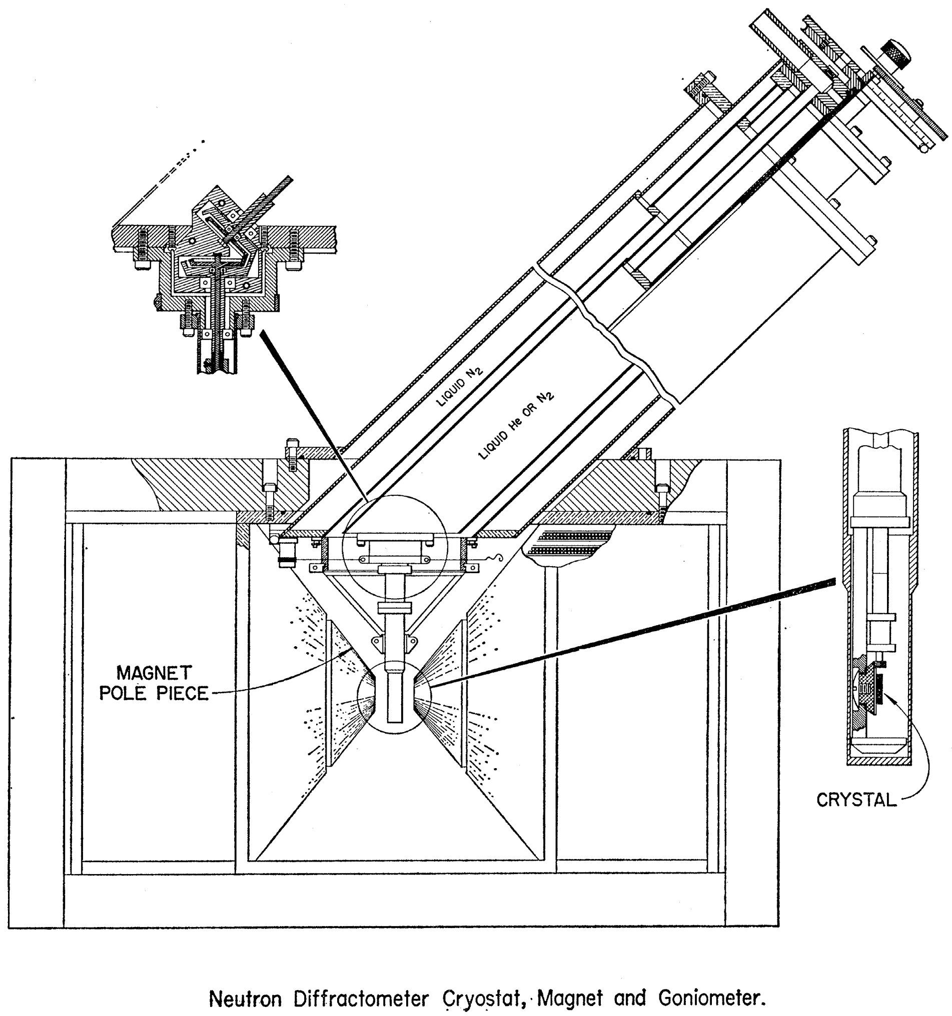

FIG. 2. The neutron diffractometer, cryostat, magnet, and goniometer.

for a given temperature in this case are always lower than for the field parallel to b, but the cos30° relationship is not carried over to the higher temperatures.

From results obtained at 4.2°K with a c-axis crystal (which results are not shown here) a spontaneous moment of $1.7\mu_B$ parallel to the c axis was deduced in agreement with the virgin-state neutron measurements.

EXPERIMENTAL

The neutron-diffraction studies were carried out in part by means of the instrument illustrated in Fig. 2.[7] The liquid coolant bathes the crystal so that the temperature ranges which are easily accessible are from 1.3 to 4.2°K and from 64 to 77°K with liquid helium and liquid nitrogen, respectively. With liquid nitrogen in the beam there is a high background due to the scattering from it, but this background can be made tolerable by stopping the beam so as to just illuminate the crystal.

The entire assembly is rotatable about a horizontal axis, thus permitting the application of the field in any direction between the horizontal and the vertical. In order to maintain coolant on the sample in all magnet orientations the cryostat is inclined at a 45° angle with the vertical.

In the right-hand insert of Fig. 2 is shown the single-crystal orienter which is similar, except for the nest of bevel gears shown on the left, to that which has been described earlier.[8]

The entire assembly, magnet, cryostat, and crystal can be rotated about the vertical axis of the diffractometer so that with the two independent rotations furnished by the goniometer, and the rotation of the magnet about a horizontal axis, it is possible to achieve a large number of relative orientations of field and scattering vector. Not all orientations are possible for a single mounting of the crystal because either the in-

[7] A description of the instrument was presented to the Gatlinburg Conference on Neutron Diffraction: E. O. Wollan, M. K. Wilkinson, W. C. Koehler, J. W. Cable, and H. R. Child, Bull. Am. Phys. Soc. 5, 464 (1960). A brief discussion of it appears in M. K. Wilkinson, E. O. Wollan, and W. C. Koehler, Ann. Rev. Nucl. Sci. 11, 303 (1961).

[8] E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, Phys. Rev. 110, 638 (1958).

cident or scattered beam may be stopped by a structural component of the instrument.

With Hyperco pole pieces and a gap of 0.75 in., fields up to 22.3 kOe could be applied to the specimens. However, the most convenient sample shape for intensity measurements, the flat disk, was not the most favorable for magnetization studies and the demagnetization corrections were often large.

The type of experiment most often done in the 45° system was carried out as indicated in Fig. 3. With the crystal oriented so that the c axis was parallel to the horizontal rotation axis of the goniometer, the plane normal to the c axis was made accurately parallel to the field direction. Then an a axis, say, in that plane, was made parallel to H, and as large a region as possible of reciprocal space along a line parallel to b_3 and passing through (110) [Fig. 3(b)] was scanned. Then, the entire assembly, magnet, cryostat and crystal was rotated through 30° so that with the field in the same aspect relative to the crystal the neighborhood of a different reciprocal lattice point, for example the (010), was studied. The magnet was then again rotated through 30° and the region around ($\bar{1}20$) scanned, and so on.

This procedure was used at 4.2°K, and at 64°K, with the field parallel to an a and to a b direction, and it was adopted in order to avoid possible changes in the demagnetization correction for different directions of application of the field.

In a few experiments, particularly at low temperatures where saturation could be approached, the direction of the field was varied, and the crystal was kept fixed.

In another type of experiment, the 45° cryostat was replaced by a more conventional vertical one in which means for continuous and controlled temperature variation were incorporated.[9] The relative orientation of the scattering vector and field direction was changed

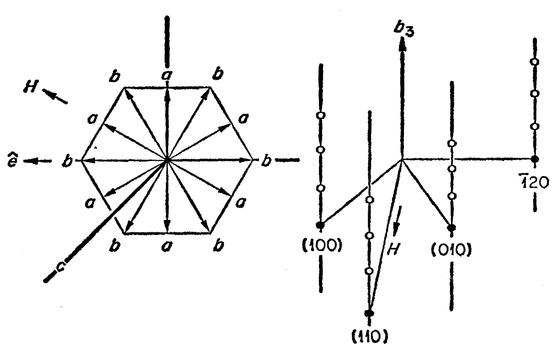

FIG. 3. Schematic representation of experimental methods used in the magnetization studies. The crystal, as in (a) was mounted with its c axis parallel to the horizontal goniometer axis. The field was applied, as shown, parallel to an a or b direction. By suitable rotation of the entire assembly the region of reciprocal space illustrated in (b) was explored.

[9] See, for example, J. W. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, Phys. Rev. **140**, A1896 (1965).

by first rotating the crystal about the vertical axis, and then rotating the entire assembly so that the crystal was in reflecting position.

With this technique, a component of the field was applied parallel to the c axis, as well as perpendicular to it, but this parallel component appeared not to be a disturbing factor in the majority of the measurements. Indeed, the c component of the field provided a sensitive indication for the transformation to a configuration with a net moment. When this occurred a torque resulted, and the crystal was turned off the Bragg angle. This latter condition was easily detected.

RESULTS AND DISCUSSION

1. Magnetization at 4.2°K

It is convenient to consider first the results of experiments done at 4.2°K, and a summary is given in Fig. 4. The manner in which the observations were made is indicated by the sketches in the inserts of Figs. 4(a) and 4(c). In Fig. 4(a) are shown the intensities, expressed as $|F|^2$, of a (100) reflection and one of its satellites, of the crystal Ho(A) in various fields applied parallel to the scattering vector for the particular (100) reflection under study.[10] The intensity of the satellite was reduced to zero when the magnitude of the applied field reached about 15 kOe. In high fields the intensity of the (100) reflection approached the contribution from nuclear scattering alone, as shown by the point measured at 50°K, which observation implies that the c component of the moment present in the virgin state, was being turned into the direction of the field. [That the magnetic intensity in the (100) reflection was not completely extinguished is probably due to lack of magnetic saturation.] Shown also in this part of the figure are the results of turn angle measurements, and it may be seen that the turn angle remained constant, within the error of observation, at 36.7° per layer.

In the experiments summarized in Fig. 4(c), a particular (110) reflection and one of its satellites $(110)^-$ were studied. The results shown by the dashed curves were obtained with the field parallel to the scattering vector for (110), and those given by the solid curves were measured with the field perpendicular to the scattering vector. In both cases the satellite intensity dropped to zero at about 15 kOe of applied field, and in both cases the turn angle remained constant.

The intensity of the (110) reflection was found to increase, even in that experiment in which the field was along the scattering vector for (110).

When the field was applied along the b direction normal to the (110) scattering vector, the magnetic intensity in the reflection in high fields was found to be

[10] The magnetic scattering from the helical arrangement of moments manifests itself in the form of satellites, reflections symmetrically disposed around the allowed nuclear positions on lattice rows parallel to the reciprocal c axis, $\mathbf{b}_3$. At 4.2°K, the magnetic intensity due to the ferromagnetic c-axis component is superimposed upon the nuclear peaks. For details see Ref. 1,

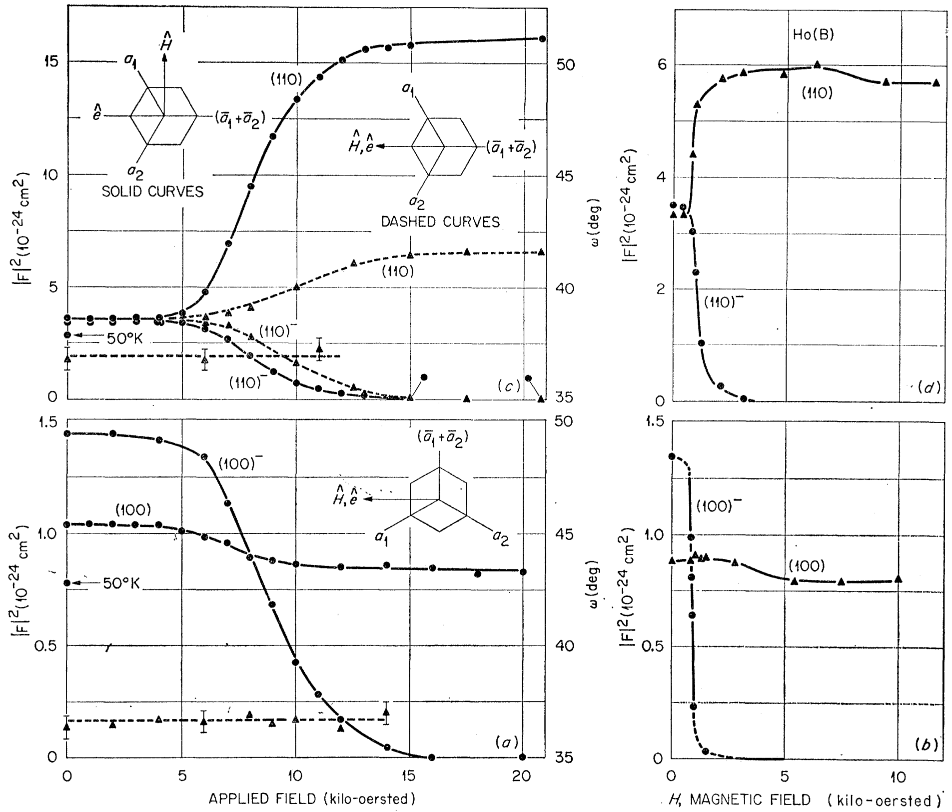

FIG. 4. Magnetic field dependence of magnetic reflections of Holmium at 4.2°K. Data for Ho(A) are illustrated on the left-hand side [(a) and (c)] and for Ho(B) on the right (b), (d). The inserts show the relative orientation of applied field and scattering vector. The intensities of the several reflections are expressed as $|F|^2$. For Ho(A) the field values given are applied fields: for Ho(B), correction has been made for demagnetization effects.

very nearly that expected if the full moment of $10.0\mu_B$ lay along the field direction.

With the highest field parallel to the scattering vector, hence to an a axis, the magnetic intensity was just $\frac{1}{4}$ that found in the case just cited. Since the intensity in a given reflection is determined by the component of the moment normal to the scattering vector, the observation of intensity in the (110) reflection implies that the magnetization cannot be parallel to the direction of the field. The factor $\frac{1}{4}$ means that the angle between the magnetization and the field direction is 30°, a result in accord with the macroscopic magnetization data.

Similar results were obtained for Ho(B) and a few illustrative curves are shown in Figs. 4(b) and 4(d). The interlayer angle ω remained constant at 30.0° per layer.

A somewhat higher field value was available for these experiments than in the ones just described and a dimnuition of intensity in the (110) reflection at high fields could be observed. Furthermore, it was possible to make good estimates of the demagnetizing fields and corrections have been made to the applied field values. The aspect of the satellite intensity–magnetic field curves appears to be complementary to the corresponding magnetization isotherms shown in Fig. 1.

From the above mentioned observations the following conclusions may be drawn: (1) The application of a magnetic field to holmium at 4.2°K induces a transformation from the conical configuration to a ferromagnetic structure in which the moments are tipped out of the basal plane in low fields, and become parallel to the basal plane in higher fields; (2) the easy direction is the b direction and the moments align themselves parallel to the easy axes nearest the direction of the applied field; (3) the transformation, helix to ferromagnet takes place evidently without going through an intermediate oscillatory configuration, except possibly, through a slightly distorted helix.

The theoretical treatment of Nagamiya *et al.* is not directly applicable to the experimental results obtained for Ho(B) at 4.2°K, but it is probably not a bad approximation for Ho(A). In both cases the hexagonal anisotropy energy in the plane is large, but in the former the fundamental wave vector of the magnetic configuration in the absence of the field corresponds to precisely 30° per layer. As discussed in our earlier paper,[1] a considerable distortion of the simple helix, a bunching of the moments around the easy b directions, results. In Ho(A) the distortion is less pronounced.

A theoretical discussion exists for the case that the moments are rigorously restricted by second-order axial anisotropy to lie in the plane normal to c with a hexagonal anisotropy energy the magnitude of which is treated as a parameter but which is not so large as to violently distort the simple helix. A discussion has been given also for the case that the zero-field configuration is a conical one, namely the higher-order axial anisotropy terms have been considered but the hexagonal anisotropy neglected. In either case, for low

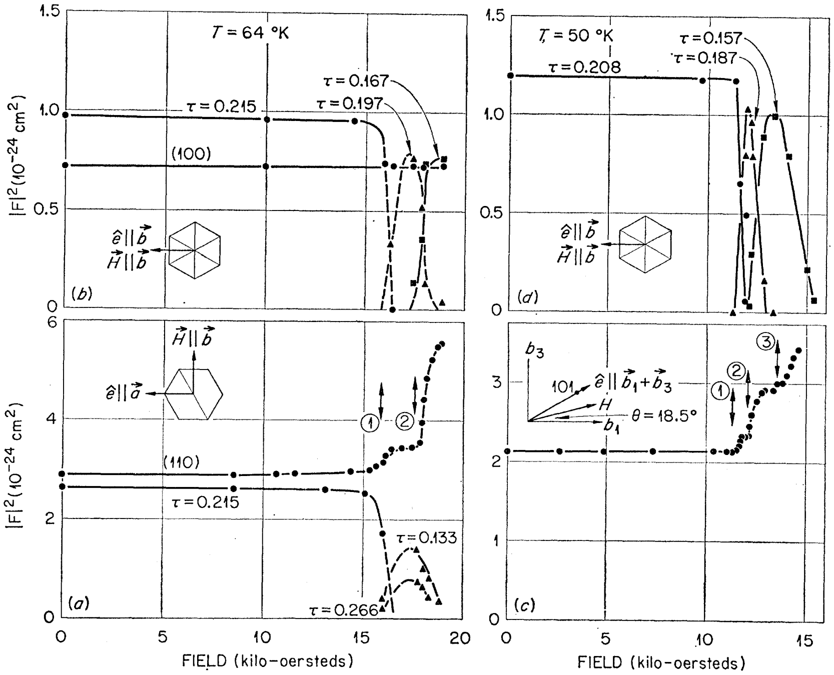

FIG. 5. Magnetic field dependence of magnetic reflections of holmium at 50 and at 64°K. Data for $H \parallel b$ at 64°K illustrate the development of the fan-type intermediate structures. At 50°K, the fully collapsed fan is approached. Numerals (1), (2), and (3) designated the "humps" in the magnetization curves which are correlated with changes in the wave number of the strong satellites. Demagnetization corrections have been applied to the field values cited. The intensities are given in absolute units as $|F|^2$. The inserts show in each case the experimental arrangement.

fields, a slightly distorted configuration of the basal plane components is to be expected in which the moments tip slightly in the direction of the field.

Such a slightly distorted configuration may be described by[11]

$$\mu_n^x = \mu \cos\phi_n,$$
$$\mu_n^y = \mu \sin\phi_n,$$
$$\mu_n^z = 0, \qquad (1)$$

where $\phi_n = \phi_n^0 - \delta \sin\phi_n^0$ is the angle made by the moments in the nth layer with a reference direction, ϕ_n^0 is the corresponding angle in the absence of the field, and δ is equal to twice the induced relative magnetization.

The distorted helix should give rise, in the diffraction pattern, to a second harmonic, and to a zeroth harmonic (the net magnetization) the intensities of which would be proportional to $J_1^2(\delta)$, where $J_1(\delta)$ is the first-order Bessel function of the argument δ. However for the relative magnetization typical of Ho at low fields, the intensities of the zeroth and second harmonics would have been of the order of 1×10^{-3} as intense as the fundamental and would not have been detected.[12]

At higher fields a sine oscillation may develop. One such structure may be described by Eqs. (1) above where now $\phi_n = \Phi \sin\phi_n^0$ with Φ the angular amplitude for the oscillation of the moments about the field direction, taken here to be the x axis, and ϕ_n^0 is as above. This is a special case of what we shall call a "fan configuration." It produces in the diffraction pattern a whole series of satellites, harmonics of the fundamental wave vector corresponding to ϕ_n^0, whose intensities are proportional to

$$|F|^2_{p=2n}$$
$$=0.0725\mu^2 f^2 |G|^2 J_{2n}^2(\Phi) \sin^2(\hat{e}, \hat{x}), \qquad n=0, 1, \cdots,$$
$$|F|^2_{p=2n+1}$$
$$=0.0725\mu^2 f^2 |G|^2 J_{2n+1}(\Phi) \sin^2(\hat{e}, \hat{y}), \qquad n=0, 1, \cdots, \qquad (2)$$

where f is the form factor, μ the moment, $|G|$ the geometrical structure factor for the reflection whose unit scattering vector is $\hat{e}$ and $J_n(\Phi)$ is the nth order Bessel function of argument Φ. For the even harmonics, the intensities are proportional to $\sin^2(\hat{e}, \hat{x})$, and for the odd harmonics, to $\sin^2(\hat{e}, \hat{y})$. This striking angular dependence is to be found in more general configurations as well and we shall refer to such configurations as "fan-type structures" reserving the name sine oscillation for the particular one described above. The intensity of the zeroth harmonic, the ferromagnetic component, is proportional to $J_0^2(\Phi)$. With increasing field, Φ goes continuously to zero, $J_0(\Phi)$ goes to unity, and the ferromagnetic configuration obtains. With sufficiently great hexagonal anisotropy, the transition from slightly distorted helix to ferromagnet may occur directly. This appears to be the case in holmium at low temperatures, but it must be emphasized that the satellite intensities get small very rapidly as Φ goes to zero. For example with $\Phi=5.7°$, $J_0=0.998$ and $J_1=0.05$ and the relative intensity of the 1st to 0th harmonic would be 2.5×10^{-3}.

[11] For simplicity we neglect the small c-axis component.

[12] The structure factors for this configuration and for others to be discussed can be derived easily from a generalization of a method suggested in W. C. Koehler, Acta Cryst. **14**, 535 (1961).

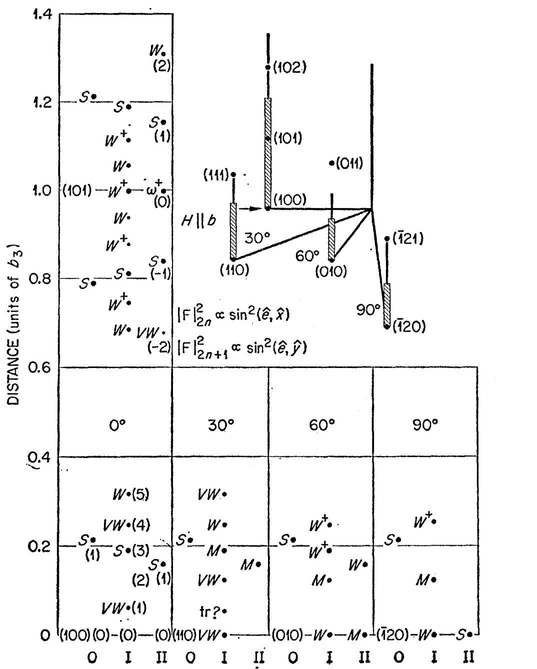

FIG. 6. Summary of intermediate temperature magnetization data. Results for the two sets of measurements (64 and 50°K), with H ∥ b are shown qualitatively for the two intermediate regions. In both cases the intensities of the magnetic reflections vary with angle as shown in the figure. The region of reciprocal space which was investigated is shown by the insert. Note that for intermediate region I, the strong satellite with wave number close to that of the virgin state is a third harmonic. The abbreviations are: S (strong), M (medium), W (weak), VW (very weak), and Tr (trace).

2. Magnetization at Temperatures in the Range 40–70°K

In the temperature region from about 40 to 70°K, the magnetization isotherms present the most complex aspect. In this section we describe neutron measurements at 64°K in the 45° unit, and at several temperatures in the range of interest in the vertical cryostat.

A partial summary of results obtained when the field was applied along a b direction (or with a component along b) is shown in Fig. 5. Intensities are given as $|F|^2$ values and the fields have been corrected for demagnetizing fields. The inserts show the manner in which the data were taken.

At 64°K, with H perpendicular to $\hat{e}$ [Fig. 5(a)] the intensity of the (110) nuclear peak increases with increasing field but the intensity-field curve exhibits two kinks analogous to those observed in the macroscopic magnetization data. The presence of magnetic intensity in the (110) peak implies that there is a component of the induced moment perpendicular to the a axis. When, as in Fig. 5(b), both H and $\hat{e}$ are parallel to b, no magnetic intensity is found in the (100) reflection and, one is led to the conclusion that the induced magnetization is parallel to the inducing field.

Associated with the abrupt changes in magnetization are changes in the distribution of magnetic satellite reflections. At the field at which the first knee occurs, indicated by the numeral (1) at about 15.8 kOe, the intensity of the satellite characteristic of the simple helix, $\tau=0.215$ falls precipitously to zero, and satellites of different wave number grow in instead. Thus in Fig. 5(a) two satellites of wave vector 0.133 and 0.266 are shown. These reflections achieved maximum intensity at a field of approximately 17.5 kOe, marked by the numeral (2) at which value the magnetization began to rise abruptly. With still higher fields, the satellites at $\tau=0.133$ and $\tau=0.266$ fell off almost to zero, and the magnetization appeared to be leveling off.

Similarly, Fig. 5(b), the satellite at $\tau=0.215$ was replaced by one at $\tau=0.197$ corresponding to the region between the field points (1) and (2). In higher fields, this satellite, too, disappeared but was itself replaced by another with still smaller wave number, $\tau=0.167$.[13]

At the lower temperature of 50°K, the available field of 22.3 kOe became more effective in bringing the system toward saturation. As seen in Fig. 5(d), the changes in satellite structure found at 64°K were reproduced (except for the actual magnitudes of the wave vectors) but in the highest fields, the satellite structure could be nearly completely eliminated. Furthermore, the three discontinuities in the magnetization were brought into evidence by the study of the intensity at the position of the (101) nuclear reflection [Fig. 5(c)]. In this experiment the field was directed at an angle of 18.5° to the b direction. The field component parallel to the basal plane was found to be the only component effective in producing the magnetic structure transformation, and it it is that component corrected for demagnetization which is given in the figure.

A summary of results obtained in experiments of the type described for the field parallel to a b direction is given in Fig. 6.[14] Data obtained in both types of experiments are represented on the same plot, and, because two different temperatures were involved, only qualitative designations of intensity are given. Moreover, the positions of the reflections as plotted in the figure represent an average between those observed at 64°K and at 50°K. In the upper right-hand corner is a sketch of the reciprocal lattice showing, by the broad stripes, that part of the reciprocal lattice which was studied.

In the virgin-state condition, indicated by the symbol 0 at the bottom of the figure, there is a single pair of strong satellites associated with each nuclear reflection. These are shown at positions corresponding to $\tau=0.213$,

[13] The wave vectors cited here are not necessarily the fundamentals but refer to the most intense reflections. The wave vectors are discussed more fully below.

[14] In this temperature range a weak second harmonic of the fundamental characteristic of the zero-field helix was observed in fields weaker than those required to bring about the transformation to Fan-I. Analysis according to the model of the slightly distorted helix gives a value for the relative magnetization not inconsistent with that observed. We shall not be concerned further with this part of the magnetization process.

intermediate between the values actually observed at 64 and 50°K. In what we call the intermediate configuration I, [the region near the point (2) in Fig. 5] six harmonics, including the zeroth harmonic were detected. With the field parallel to the scattering vector for (100), a scan parallel to b_3 revealed a strong (at maximum intensity) reflection with a smaller spacing than the virgin-state satellite which indexes, as shown, as a third harmonic. As the crystal and magnet were rotated in 30° steps about the c axis, the odd harmonics 1, 3, and 5, became weaker, and disappeared altogether at 90° while the even harmonics 0, 2, 4, either weak or zero to begin with, became more intense. The satellites $\tau=0.133$ and $\tau=0.255$ in Fig. 5(a) are the reflections indicated in the right-hand box of Fig. 6.

With a component of the field parallel to the scattering vector for (100) as in Fig. 5(d), a scan of the neighborhood of the (101) reciprocal lattic point showed the same six harmonics. A careful scan of the region between (100) and (101) showed no other magnetic reflections.

In the second, high field, phase, which we call intermediate phase II, only zeroth, first and second harmonics were detected. Again, the intensity of the first harmonic decreased and that of the zeroth, increased, as the angle between scattering vector and field direction changed from zero to 90° in the basal plane.

As the field was increased still further, the satellite structure tended to disappear completely (at 50°K, or lower) and the configuration became ferromagnetic.

It was noticed that the intensities in both intermediate structures obeyed the relation shown at the bottom of the diagram in Fig. 6. This can be seen, qualitatively, by inspection of the reflections measured from (100) past (101) along b_3. The even harmonics, in phase I, are very weak for reflections near (100); zero for (100) itself and for the second harmonic, very weak for the fourth. Near (101) however, $\sin^2(\hat{e}, \hat{x})$ is no longer negligibly small, and the even harmonics are visible. The odd harmonics here ought to be independent of the angle the scattering vector makes with the field direction, except for changes due to increasing $(\sin\theta)/\lambda$ and indeed, such appears to be the case. For data which are directly comparable, this relationship is followed quantitatively quite well. Similar remarks apply to the results obtained for intermediate phase II.

Measurements similar to those indicated in Figs. 5 and 6 were made, and corresponding diagrams were constructed, for the case that the fields was applied parallel to an a direction. In this case, as in the previous one, two oscillatory phases were found in each of which the same striking variation of intensity with angle was observed.

In the intermediate phase I, six harmonics were again observed. The intermediate phase II persisted to the highest field values, and at the highest field value only the zeroth and first harmonics were found.

Measurements were made over rather smaller regions of reciprocal space at a number of temperatures ranging from 4.2 to 120°K. With these results, some of which are to be presented in the next section, and with the more extensive measurements made at 50°K, and 64°K, which have just been discussed, we may cite some of the features of the magnetization process in the range 40–70°K. (1). With a sufficiently strong field parallel to b, a field-induced transformation from the helical configuration to a classical ferromagnetic configuration with the moments parallel to the field direction can be brought about. (2) The transformation takes place via two intermediate configurations, each of which has a net moment parallel to the field direction. In the neutron measurements, as in the macroscopic magnetization measurements, the development of each of the three phases is accompanied by a plateau or shelf in the magnetization isotherm. (3) With a comparably strong field parallel to a, a transformation from the helix to two successive intermediate phases is brought about in each of which again there is a net moment parallel to the field direction, that is to say, the a direction. The neutron and classical magnetization isotherms show one less shelf in this case as compared with the preceding one because the final ferromagnetic configuration is not brought about. (4) The intermediate structure in each case is a fan-type structure in the sense introduced above, but in no case are the observed intensities consistent with those predicted on the basis of the sine-oscillation structure. (5) A large change in wave vector is found on passing from the helix to intermediate phase I, and again to intermediate phase II; moreover, the change is different depending upon the direction of application of the field. (6) Some characteristics of the fan-type structures have been found from analysis, to be outlined below, of the partial sets of data obtained at 50°K.

It is assumed that the moments of atoms in the hexagonal layers remain parallel to each other, and that the thermal average moment is little changed by the field. The magnetic moment distribution may be represented by a Fourier series

$$\mathfrak{y}_k{}^L=\sqrt{N^{-1}}\sum_{p=0}^{N-1}\psi_p{}^k\exp i2\pi\mathbf{t}_p\cdot\mathbf{A}_L,\qquad \mathbf{t}_p=\frac{p}{N}\mathbf{b}_3,\quad (3)$$

where p is an integer ranging from 0 to $N-1$, N is the number of $\mathbf{a}_3$ lattice periods in a representative volume of the crystal, and $\mathbf{A}_L=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3$ is a lattice vector. The index k distinguishes the two nonequivalent atoms in a unit cell. The coefficients $\psi_p{}^k$ can be found by inversion of Eq. (3):

$$\psi_p{}^k=\sqrt{N^{-1}}\sum_{l_3=0}^{N-1}\mathfrak{y}_k{}^L\exp(-i2\pi\mathbf{t}_p\cdot\mathbf{A}_L).\qquad (4)$$

With the Fourier coefficients expressed in terms of their x and y components, and with the appropriate phase factor $\exp i\pi\mathbf{t}_p\cdot\mathbf{a}_3$ for the two sets of atoms, the intensity relative to one unit chemical cell is propor-

TABLE I. Analysis of magnetic structures of holmium at 50°K.

Coefficients (μ_B)	Helix	H ‖ b Fan I	H ‖ b Fan II	H ‖ b Ferro	H ‖ a Fan I	H ‖ a Fan II
A_0		2.0	4.4	8.87	2.7	6.2
B_1	$8.84=A_1$	1.3	8.0		1.2	6.0
A_2		5.4	1.8		8.4	
B_3		8.1			7.6	
A_4		4.4			4.4	
B_5		1.6			1.8	
Wave vector units of b_3	0.208	0.0623	0.157		0.0647	0.182

tional to

$$|F|^2_{\mathbf{B}_H+\mathbf{t}_p}=0.0725f^2|G|^2[|a_p|^2\sin^2(\hat{e},\hat{x})+|b_p|^2\sin^2(\hat{e},\hat{y})], \quad (5)$$

where $a_p\hat{x}+b_p\hat{y}$ is the pth Fourier coefficient for the set of atoms generated by lattice translations from (0,0,0).

From this equation it follows that the intensity scattered into the pth satellite of a reflection described by $\mathbf{B}_H$ is determined by the magnitude of the pth Fourier coefficient. Imposing the experimentally observed conditions one finds

$$|F|^2_{\mathbf{B}_H+\mathbf{t}_p}=0.0725f^2|G|^2 \begin{cases} \times|a_p|^2\sin^2(\hat{e},\hat{x}), & p=2n \\ \times|b_p|^2\sin^2(\hat{e},\hat{y}), & p=2n+1 \end{cases} \quad (6)$$

and the coefficients $|a_p|$ and $|b_p|$ can readily be evaluated from the observed integrated intensities. As given above, they are expressed in Bohr magnetons.

One of the important consequences of the angular dependence of the even and odd harmonics just mentioned is that the x component of the moment can be represented by a series in even multiples of the fundamental wave vector, and the y component by a series in odd multiples of it. Referring now to the moment in the nth *layer*, and with a convenient change in notation, one has

$$\mu_n^x=A_0+A_2\cos(2n\omega+\alpha_2)+A_4\cos(4n\omega+\alpha_4)+\cdots,$$
$$\mu_n^y=B_1\sin(n\omega+\beta_1)+B_3\sin(3n\omega+\beta_3)+B_5\sin(5n\omega+\beta_5)+\cdots, \quad (7)$$

where $\omega=\pi\boldsymbol{\tau}\cdot\mathbf{a}_3$, α_i and β_i are phase constants and $A_0=a_0$, $A_p=2|a_p|$, and $B_p=2|b_p|$.

The data obtained at 50°K were interpreted on the basis of the discussion just given, and sets of Fourier coefficients for the four structures were obtained. These are listed in Table I together with the values of the appropriate wave vectors. For completeness some characteristics of the helical configuration are included as well. The helix is not correctly described by Eq. (7), of course, but rather by Eq. (1) with $\phi_n=\phi_n^0=n\omega+\beta$. The amplitude $B_1=A_1=8.84\mu_B$ is the thermal average moment in zero field.

In the Fan-I structures both the x and y components are oscillatory in a complex way, and the list of coefficients given in the table is probably the simplest description one can give. The phases of the several terms must be adjusted so that the magnitude of the moments in a layer never exceeds the maximum allowed value of $10\mu_B$. The major contribution to the y component is due to the third harmonic, the amplitude of which is only a little less than that in the helix. The major difference between the two Fan-I structures is the magnitude of the coefficient A_2 in the two cases.

In the Fan-II configurations there is a single wave number for the y oscillation, and a constant or nearly constant component parallel to the field (for the field parallel to b there is a small second harmonic). When the field is parallel to b the oscillation is along an a direction, the hard direction at lower temperatures. This component can be turned relatively easily into the easy direction. When the field is along the a direction, the oscillation is along an easy direction, and the 22.3 kOe field was not sufficiently strong to turn that component out of the easy direction.

The wave vectors are smaller, in the corresponding configurations, for the field parallel to b, than for the field parallel to a. In this temperature range the theory predicts a possible transformation from helix to fan to ferromagnet as well as a configuration similar to the observed Fan-II structure for H parallel to a. However, the existence of two fan configurations is not explicable at present. Moreover, the large changes in wave vector are not predicted either. Indeed, a near constant wave vector is inherent in the theory since it is assumed that the Fourier transformed exchange energy is unchanged by changes in magnetic configuration.

3. Phase Diagrams in the *H-T* Plane

A series of measurements was made over a wide range of temperature and field values of magnetic reflections in the vicinity of (100) and (110) in order to establish a set of *H-T* diagrams. One set of results is summarized in Fig. 7, where the intensities of a (110) reflection and a satellite $(110)^+$ are displayed as a function of temperature in the virgin state, and in a field of 22.3 kOe applied parallel to that *a*-direction which is parallel to the scattering vector for the (110) reflection under study. The virgin-state curve for (110) shows the small increase in intensity below 20°K due to the development of the conical configuration.

In the strong field, the satellite is completely extinguished and there is a large magnetic contribution to the (110) reflection as has been described above. The ferromagnetic configuration persists, in the applied field, to a temperature of 33°K at which temperature a satellite reappears. In the temperature range between 33 and 42°K, the (110) reflection has a small

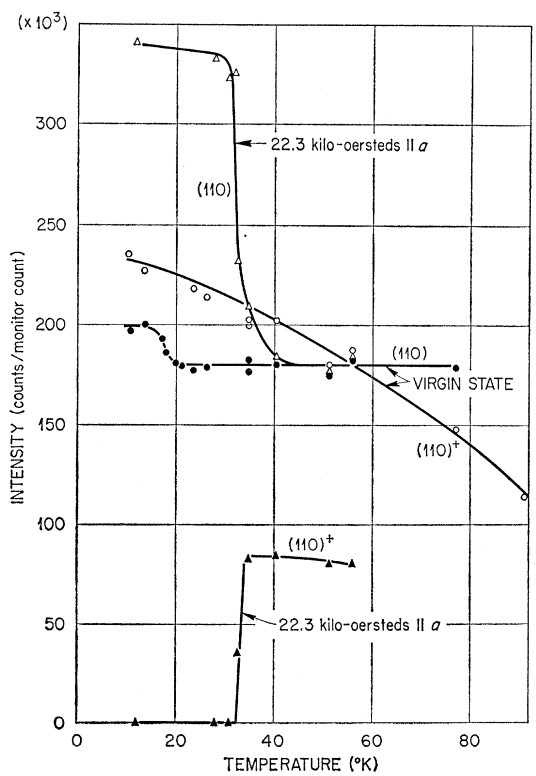

FIG. 7. Intensity of (110) and $(110)^+$ reflections of holmium. Measurements at different temperatures of the intensity of the (110) and $(110)^+$ reflections in the virgin state and with 22.3 kOe applied parallel to the scattering vector of the (110) reflection under observation.

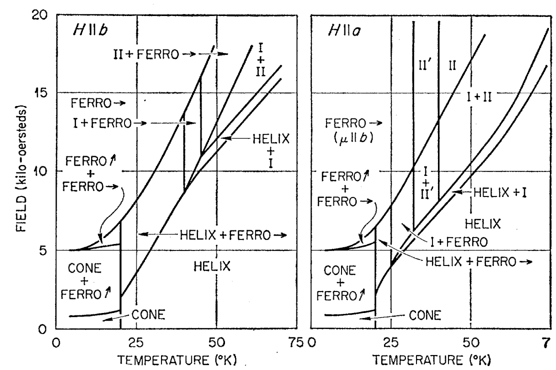

FIG. 8. Schematic *H-T* phase diagrams for single-crystal holmium.

magnetic contribution indicating that the net moment has a component perpendicular to the field direction. Above 42°K the induced moment is parallel to the field. The oscillatory structure of which the satellite is characteristic is the intermediate state II. The intensity-temperature curve for the satellite extends only to 58°K because, at higher temperatures, it was not possible, with the field available, to transform the structure completely to Fan-II.

From data such as those just described, and from the Ames magnetization data, the schematic phase diagrams shown in Fig. 8 were deduced. The left-hand side of the diagram refers to **H** ‖ *b*. Above 45°K the transformation, helix to ferromagnet, takes place via two intermediate phases as discussed above, and there are three plateaus in the magnetization curve. Between 39 and 45°K the intermediate phase II is not observed. The transformation to the ferromagnet takes place through intermediate phase I. In this temperature range the magnetization curves show two plateaus. Between 20 and 39°K a single transformation occurs. Below 20°K, the transition is from the cone to an out-of-plane ferromagnet to a *b*-axis ferromagnet.

On the right is a phase diagram for **H** ‖ *a*. Above 40°K there is a net magnetization parallel to the field direction but there are only the two intermediate phases I and II, hence only two kinks in the magnetization curves. Between 33 and 40°K two intermediate phases are again observed but there is a small component of the magnetization normal to the field direction. This is designated as II′. In the range 25 to 33°K, the substance passes through an intermediate phase I to the *b*-axis ferromagnet, and again there are two kinks in the magnetization curves. From 20–25°K there is a single transition to the *b*-axis ferromagnet and below 20°K the situation is as for the field parallel to *b*.

Mixed phase regions are indicated because lines from several phases are observed simultaneously in the diffraction patterns.

Finally, in Fig. 9 are shown the wave number-temperature relations measured in the two intermediate states. (The wave number for the more intense third harmonic of phase I is plotted.) For completeness, the virgin-state results are included as well. With the

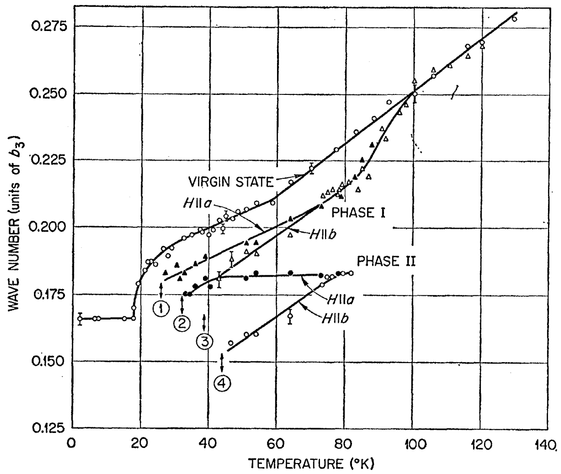

FIG. 9. Variation of wave number with temperature in various magnetic configurations of holmium. The numerals 1 and 2 indicate the appearance of intermediate phase I and II, respectively, for $H \parallel a$, and 3 and 4 the appearance of phase I and II with $H \parallel b$. The virgin-state curve is shown for comparison.

magnet available for the experiment, the start of the transformation to phase II could be brought about below about 80°K, and to phase I below about 100°K. The influence of the field on the magnetic structure first becomes directionally dependent below about 75°K. With $\mathbf{H} \parallel a$, the wave number in phase II is constant at $0.182b_3$ to about 40°K, at which temperature phase II′ develops. The wave number changes from $0.182b_3$ at 40°K to $0.175b_3$ at 33°K. The numeral 2 in the figure marks the temperature below which the oscillatory phase II′ is no longer observed. In the intermediate phase I, the wave number of the third harmonic decreases to a value of $0.182b_3$ at the critical point indicated by the numeral 1 at 25°K.

With $\mathbf{H} \parallel b$, the slopes of the curves in the two phases are nearly the same, and the rate of decrease of wave vector with decreasing temperature is more rapid than for $\mathbf{H} \parallel a$. The critical points for the disappearance of phase I and phase II are marked by the integers 3, and 4, at 39 and 45°K, respectively.

The complex magnetization process of holmium, some details of which have been deduced from neutron diffraction and classical magnetization measurements clearly reflects the complex interplay between exchange energy, anisotropy energy, magneto-elastic effects, and magnetic potential energy. It is not surprising that all the details of the process are not given correctly by the theory in its present form. Indeed, it is a triumph of the theory that so many of its features are correctly described.

4. The Remanent State

At several stages of this study, some very pronounced hysteresis effects were observed. At low temperatures, in particular, the remanent magnetization was found to be a considerable fraction of the saturation magnetization. We describe briefly the results of experiments designed to study the remanent state.

In general, a magnetic field of the order of 20 kOe, sufficient to saturate or nearly saturate the specimen, was applied parallel to an a or b direction in the basal plane. The field was then reduced to zero, and the intensity distribution near several important reciprocal lattice points was studied. In Fig. 10(a) are shown the data obtained in the virgin state for a (110) reflection; in Fig. 10(b) in the residual state after the field had been applied parallel to its scattering vector, and Fig. 10(c), in the residual state after magnetization normal to its scattering vector, all at a temperature of 4.2°K.

As expected, there is an enhancement of the (110) reflection in the remanent state compared to the virgin state which enhancement is greater for the b axis magnetization than for magnetization along a. The peak intensities of the satellites are reduced from the virgin-state values and the lines are quite broad and appear to be superimposed upon a very broad diffuse maximum centered at the nuclear position. In contrast to the magnetization process, during which the satellite intensities decrease in intensity without appreciable change in position, the satellites of the remanent state have one or more components which correspond to wave numbers smaller than the virgin-state value, as well as to the virgin-state value itself. The latter is indicated by arrows in the figure.

Measurements have been made in various fields decreasing in magnitude from the maximum mag-

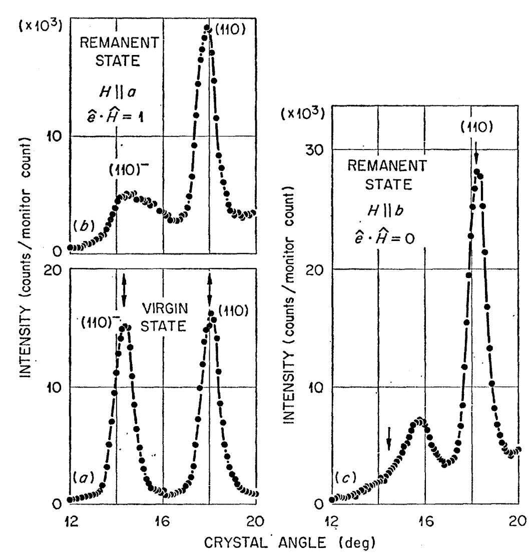

FIG. 10. Intensities near (110) in the remanent state. In 10(b) a field had been applied parallel to $\hat{e}_{110}$ and turned off. In 10(c) the field was applied perpendicular to $\hat{e}_{110}$. The virgin-state pattern is shown for comparison in 10(a). A considerable intensity remains in the (110) nuclear peak, and the satellite distribution is markedly different from that of the virgin state.

netizing field, and in these fields patterns very similar to those of Fig. 10 were found.

Thus, while magnetization from the virgin state takes place directly from the helix, on demagnetization the system relaxes to an average configuration which has some of the properties of intermediate phase I. Reversal of the field and continuation of the cycle never reproduced the helical configuration. Once formed, the residual state configuration could be eliminated only by warming the sample above 25°K.

Another set of observations is illustrated in Fig. 11. For this series of measurements the crystal was prepared in a remanent state corresponding to Fig. 10(b) and then the region of reciprocal space parallel to b_3 in the neighborhood of (002) was studied. The remanent-state pattern is shown in Fig. 11(b), and is to be compared with the virgin-state data in Fig. 11(a). In this case the (002) reflection shows a magnetic contribution and this implies a net moment in the basal plane. As before the satellite lines are broadened and reduced in peak intensity.

With the crystal so oriented, one further experiment was carried out in which the field was applied parallel to the c axis, i.e., to the scattering vector for the (002) reflection. As shown in Fig. 11(d) the peak intensity of the (002) reflection dropped off with increasing field, whereas the peak intensity in the satellite increased slightly. Both effects appeared to saturate near 10 kOe. A scan of the pertinent angular region in a field of 15 kOe is illustrated in Fig. 11(c). As shown there, the (002) reflection had nearly, but not quite, been reduced to its virgin-state value.

It is clear from the data of Fig. 10(b) and Fig. 11(b) that the residual state configuration following magnetization parallel to an a direction has some oscillatory character and a net magnetic moment in the basal plane. As indicated by the breadth of the lines and by the diffuse maxima upon which they are found, there is no single well-defined wave number in the relaxed state, but rather there is a distribution of wave numbers so that the remanent state configuration is a relatively disordered one.

A few observations were made for decreasing fields

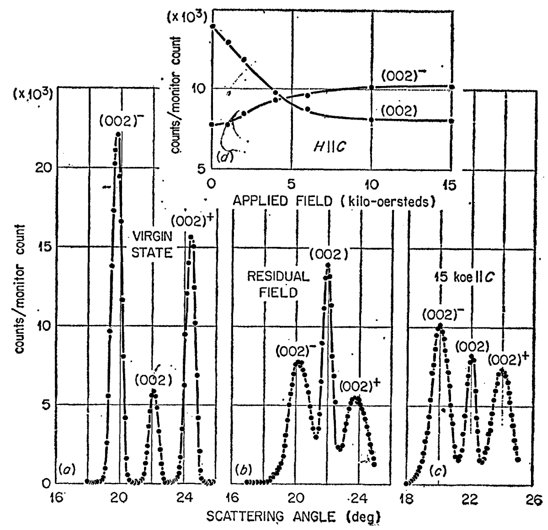

FIG. 11. Effect of a magnetic field on the remanent intensities near (002). Fig. 11(a) is a scan at 4.2°K over the (002) and its satellites $(002)^{\pm}$. Fig. 11(b) is a scan over the same region after a magnetic field had been applied parallel to an a-direction and reduced to zero. The satellites are much broader, and a considerable magnetic intensity remains in the (002) reflection. Fig. 11(c) is a scan in a field of 15 kOe applied parallel to the c direction following the operation of 11(b) some reduction of the (002) intensity and an increase and sharpening of the satellites is observed. In 11(d) these changes are followed as a function of the field.

at temperatures higher than 4.2°K, and the results show that hysteresis is connected with intermediate phase I, and not with phase II. Similar observations were made by Strandburg, Legvold, and Spedding.

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