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Neutron Diffraction Study of the Magnetic Properties of Rare-Earth-Iron Perovskites*

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A neutron diffraction study has been made of the magnetic properties of the rare-earth-iron perovskites, $NdFeO_3$, $HoFeO_3$, and $ErFeO_3$, at temperatures ranging from 955° to 1.25°K.The iron ions in each of these compounds undergo a transition to an antiferromagnetic configuration in which each moment has six oppositely directed moments at nearest neighbor distances. The Néel temperatures are 760°K, 700°K, and 620°K, respectively, for the compounds of Nd, Ho, and Er. The moment directions in $HoFeO_3$ and $ErFeO_3$ are parallel and antiparallel to the orthorhombic [100] direction at room temperature: at 43°K the moments are found to be in a $(1\bar{1}0)$ plane. In $HoFeO_3$ the iron-ion moments at 1.25°K are parallel to [001]; in $ErFeo_3$ at the same temperature they are parallel to [110]. The magnitudes of the ordered iron moments at temperature saturation are 4.5_7, 4.6_0, and 4.6_2 Bohr magnetons in $NdFeO_3$, $HoFeO_3$, and $ErFeO_3$, respectively. In the liquid helium temperature range, magnetic ordering transitions of the rare-earth ions in $HoFeO_3$ ($T_N=6.5$°K) and $ErFeO_3$ ($T_N=4.3$°K) are observed. The Er^{+3} ion moments form a nearly ideal antiferromagnetic configuration in which a chain of parallel moments is surrounded by four chains of oppositely directed moments at nearest neighbor distances. In this compound the Er^{+3} ion moments are parallel and antiparallel to [001] and at 1.25°K have a magnitude of 5.8 Bohr magnetons. In $HoFeO_3$ the ions are ordered in a distorted antiferromagnetic configuration in which, at 1.25°K, each Ho^{+3} moment with magnitude of 7.5 Bohr magnetons, makes an angle, in the (001) plane, of about 27° with the [010] direction so as to produce a net ferromagnetic moment of 3.4 Bohr magnetons per $HoFeO_3$ molecule parallel to [100].

I. INTRODUCTION

Earlier neutron diffraction studies on perovskite-like compounds ABO_3[1–3] have been restricted to those having nonmagnetic A site ions. The present work is concerned with rare-earth-iron perovskites in which both A and B site ions possess magnetic moments. In this case there is the complicating factor of interactions between unlike magnetic ions.

It has proved convenient to divide the paper into three main sections, the first of which has to do with the magnetic ordering of the iron-ion spin systems in the compounds $NdFeO_3$, $HoFeO_3$, and $ErFeO_3$ at high temperatures. In the second section the neutron data relative to the magnetic ordering of rare-earth-ion moments at low temperatures are treated. The analysis in this temperature region is somewhat more involved, for, in certain cases, both ionic systems are magnetically ordered. In the third section the diffraction results are discussed in reference to the complex macroscopic magnetic properties of these compounds.

II. SAMPLE PROPERTIES AND PROCEDURES

The rare-earth-iron perovskite samples were prepared and analyzed by methods similar to those described previously for $LaFeO_3$.[3] Within the limits of powder x-ray diffraction techniques the orthoferrites of Nd, Ho, and Er were found to be isostructural with $GdFeO_3$, the structure of which has been determined by Geller[4] from single crystal x-ray data. In the orthorhombic unit cell are four distorted simple perovskite cubes. The iron ions are in parameterless special positions within the limits of detection of the data but significant displacements from ideal positions are found for the gadolinium ions and for the two sets of nonequivalent oxygen ions. The most probable space group is P_{bnm}. Geller and Wood[5] and Bertaut and Forrat[6] have shown that the orthoferrites of La, Ce, Pr, Nd, Sm, and Eu are all isostructural with $GdFeO_3$ with varying degrees of distortion. Recent studies by Forrat[7] indicate that compounds of the heavier rare earths including Ho and Er are also isostructural with $GdFeO_3$.

The results of chemical analyses and room-temperature x-ray diffraction measurements[8] are collected in Table I, where lattice parameters of $LaFeO_3$ and $GdFeO_3$ are included for comparison. The relative distortions in the orthoferrite series as measured by the deviations of the pseudocell parameters from their ideal values may be seen in the last columns of the table.

Neutron diffraction data were collected at temperatures ranging from 955°K to 1.25°K with the samples in briquet form or as finely divided powders according to experimental expediency. Extended diffraction patterns were taken at one or more elevated temperatures, at room temperature, at 77°K or at 43°K, at 4.2°K, and at 1.3°K. Limited regions of the patterns were studied as well at intermediate temperatures.

In this study the nuclear intensities observed for $HoFeO_3$ and $ErFeO_3$, in particular, were found to be in fair agreement with predictions based on Geller's

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* The work herein reported was presented in part to the International Union of Crystallography, Montreal, Canada, July, 1957.

[1] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

[2] U. H. Bents, Phys. Rev. **106**, 225 (1957).

[3] W. C. Koehler and E. O. Wollan, J. Phys. Chem. Solids **2**, 100 (1957).

[4] S. Geller, J. Chem. Phys. **24**, 1236 (1956).

[5] S. Geller and E. Wood, Acta Cryst. **9**, 563 (1956).

[6] E. F. Bertaut and F. Forrat, J. phys. radium **17**, 129 (1956).

[7] F. Forrat, thesis, Institute Fourier, Universite de Grenoble (unpublished).

[8] We are indebted to Dr. H. L. Yakel for these measurements.

TABLE I. Analytical and x-ray diffraction data for rare-earth perovskites.

Sample	Total iron (wt. %) obs	Total iron (wt. %) calc	Tetravalent iron percentage of total iron	Lattice parameters (A^0) Orthorhombic P_{bnm} a_1	a_2	a_3	Monoclinic $a_1=a_3$	a_2	β
$LaFeO_3$[a]				5.556	5.565	7.862	3.932	3.931	90.2
$NdFeO_3$	21.1	22.5	6.1	5.450	5.587	7.761	3.902	3.880	91.4
$GdFeO_3$[b]				5.346	5.616	7.668	3.877	3.834	92.8
$HoFeO_3$	22.4	20.8	5.4	5.282	5.592	7.606	3.846	3.803	93.3
$ErFeO_3$	19.9	20.6	2.0	5.252	5.576	7.579	3.830	3.790	93.4

[a] Yakel (reference 8), Geller and Wood (reference 6).
[b] Geller (reference 5).

positional parameters for $GdFeO_3$. These parameters were adopted as a first approximation for the analysis of the magnetic scattering data.

III. IRON-ION SPIN SYSTEM

1. Spin Configuration

It is convenient to consider together the results of the high-temperature experiments for the several samples since the neutron diffraction patterns of $NdFeO_3$, $HoFeO_3$, and $ErFeO_3$ all exhibit magnetic reflections characteristic of the antiferromagnetic configuration already reported for $LaFeO_3$. A typical set of data is illustrated in Fig. 1 in which are shown portions of diffraction patterns obtained for $ErFeO_3$ at room temperature and at 955°K. At the higher temperature the pattern consists of the coherent nuclear reflections of $ErFeO_3$ superposed upon the angularly dependent paramagnetic scattering background which at this temperature is contributed to by both the erbium and the iron ions. In the room-temperature pattern additional coherent reflections appear at the (011) (101) and at the (013) (103) (211) (121) positions. The indices here and in subsequent discussions refer to the orthorhombic crystallographic unit cell.

The magnetic unit cell can clearly be chosen in a number of ways, but an approximate unit cell which is appropriate to the chemical unit is one for which $a_1=a_2=\sqrt{2}a_0$; $a_3=2a_0$ where a_0 is the ideal cubic lattice period. With this cell, only reflections for which $H_1+H_2=2n+1$; $H_3=2n+1$ are observed. The configuration inferred from these indicial relations in the

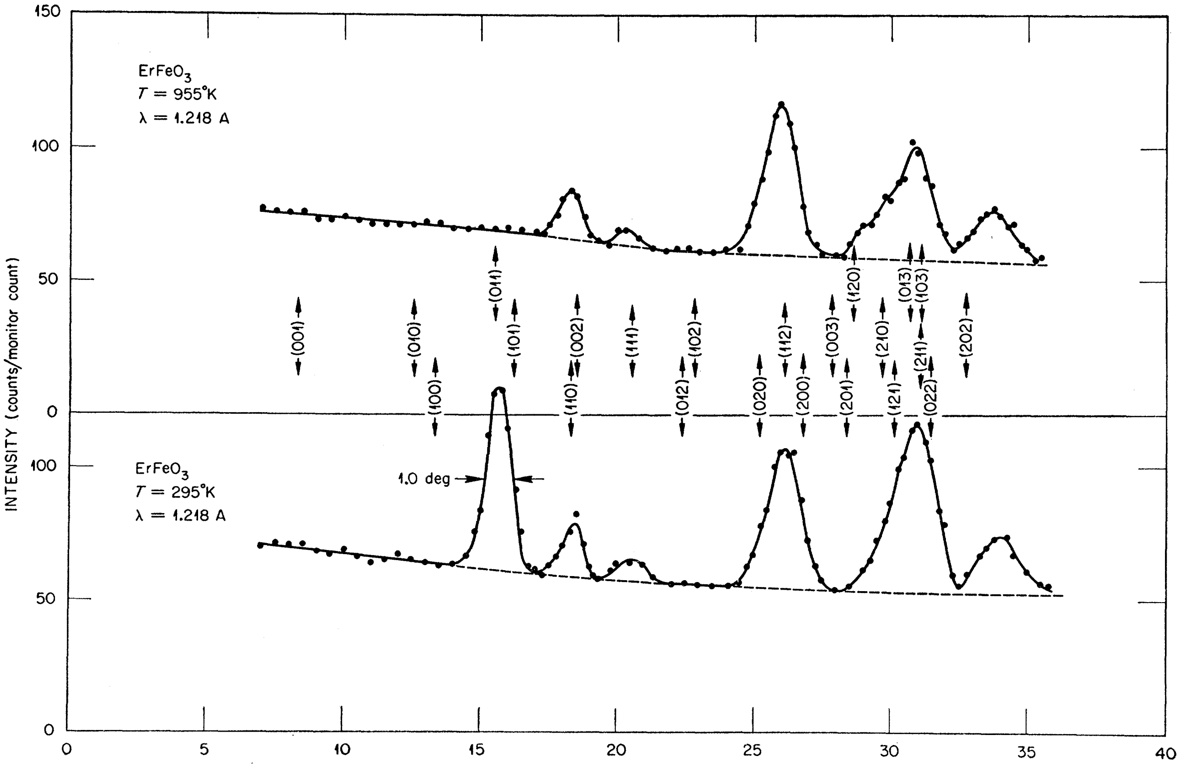

FIG. 1. High-temperature neutron diffraction data for $ErFeO_3$.

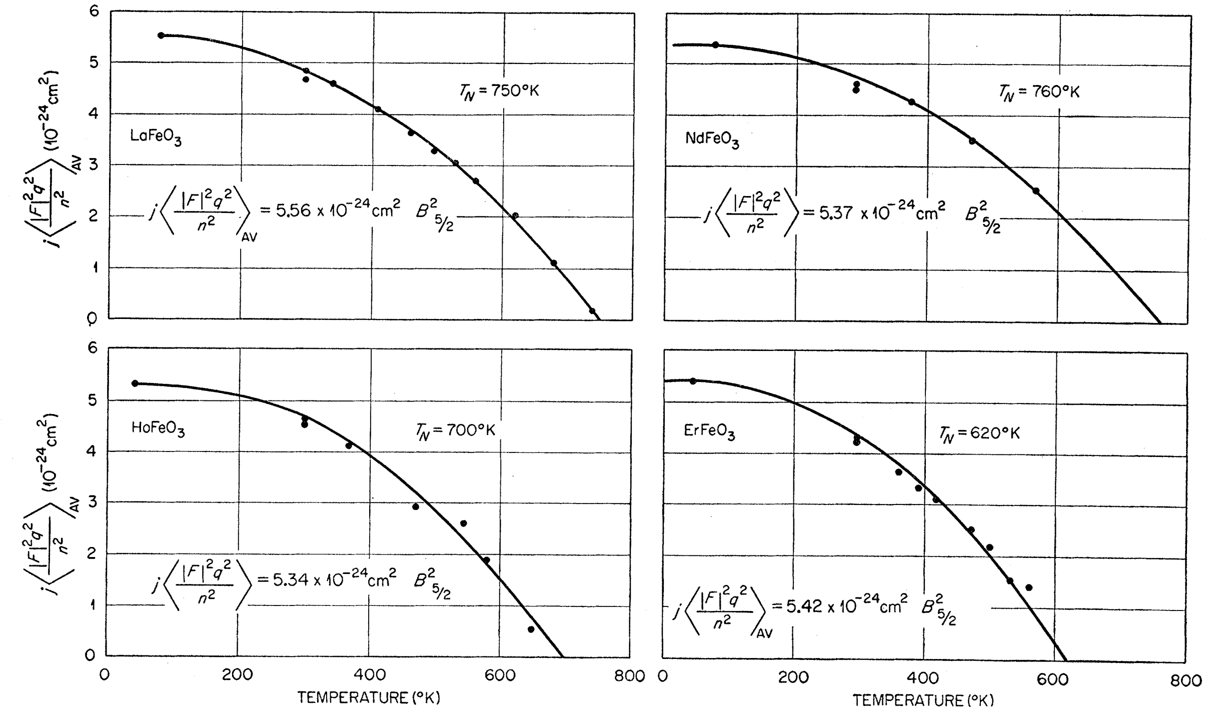

FIG. 2. Temperature dependence of (011, 101) magnetic reflection of rare-earth orthoferrites. The Néel temperatures are obtained by extrapolation.

G-type antiferromagnetic configuration,[1] or, the simple cubic ($\pi\pi\pi$) configuration.[9]

2. Néel Temperatures

The Néel temperature for ordering of the iron-ion moments was determined from the temperature dependence of the first strong magnetic reflection in each case, and the results of the measurements are shown in Fig. 2. The solid curves are calculated from the Brillouin function corresponding to spin $\frac{5}{2}$ and the intercepts of these curves with the temperature axes are taken as the transition temperatures. As shown in the figure, these are 750°K, 760°K, 700°K, and 620°K, respectively, for $LaFeO_3$, $NdFeO_3$, $HoFeO_3$, and $ErFeO_3$.

3. Magntic Moments

The moments of the iron ions in the antiferromagnetically ordered configurations were calculated from the $j(F/n)^2\langle q^2\rangle_{\text{Av}}$ values measured at 43°K where the spin systems are effectively temperature saturated. When the total intensity in the (011) (101) group is measured, $\langle q^2\rangle_{\text{Av}}$ has the value $\frac{2}{3}$ irrespective of the moment direction[10] and one needs only the iron form factor to obtain the effective moments. For this purpose we have chosen an average of published form factor data[11] with which moment values of 4.6_5, 4.5_7, 4.6_0, and 4.6_2 Bohr magnetons were found for the Fe^{+3} ions in the orthoferrites of La, Nd, Ho, and Er, respectively. It may be noted that these values are significantly smaller than the expected values of 5.0 Bohr magnetons.

4. Moment Direction

The line splitting in the neutron diffraction patterns of $LaFeO_3$ and of $NdFeO_3$ are sufficiently small that the equivalent reflections in a powder line are nearly exactly superposed; in such a case no information regarding the moment direction relative to the crystal axes can be obtained. In the patterns of $HoFeO_3$ and of $ErFeO_3$, however, some of the smaller angle lines which are free of interference from nuclear intensity are sufficiently split by the crystalline distortions that a partial resolution of their components can be effected. From estimates of their relative intensities one can infer the spin direction in the crystal in favorable cases. By this means the following results have been obtained:

At room temperature, for both $HoFeO_3$ and $ErFeO_3$

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[9] H. A. Gersch and W. C. Koehler, J. Chem. Phys. Solid **5**, 180 (1958).

[10] Strictly speaking $\langle q^2\rangle_{\text{Av}}$ is not exactly $\frac{2}{3}$ for the true structure because of the crystallographic distortions. The maximum error made by neglecting the distortions is of the order of 1% in the moment values and this is taken into account in the above tabulation.

[11] C. G. Shull and E. O. Wollan, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. II, p. 210.

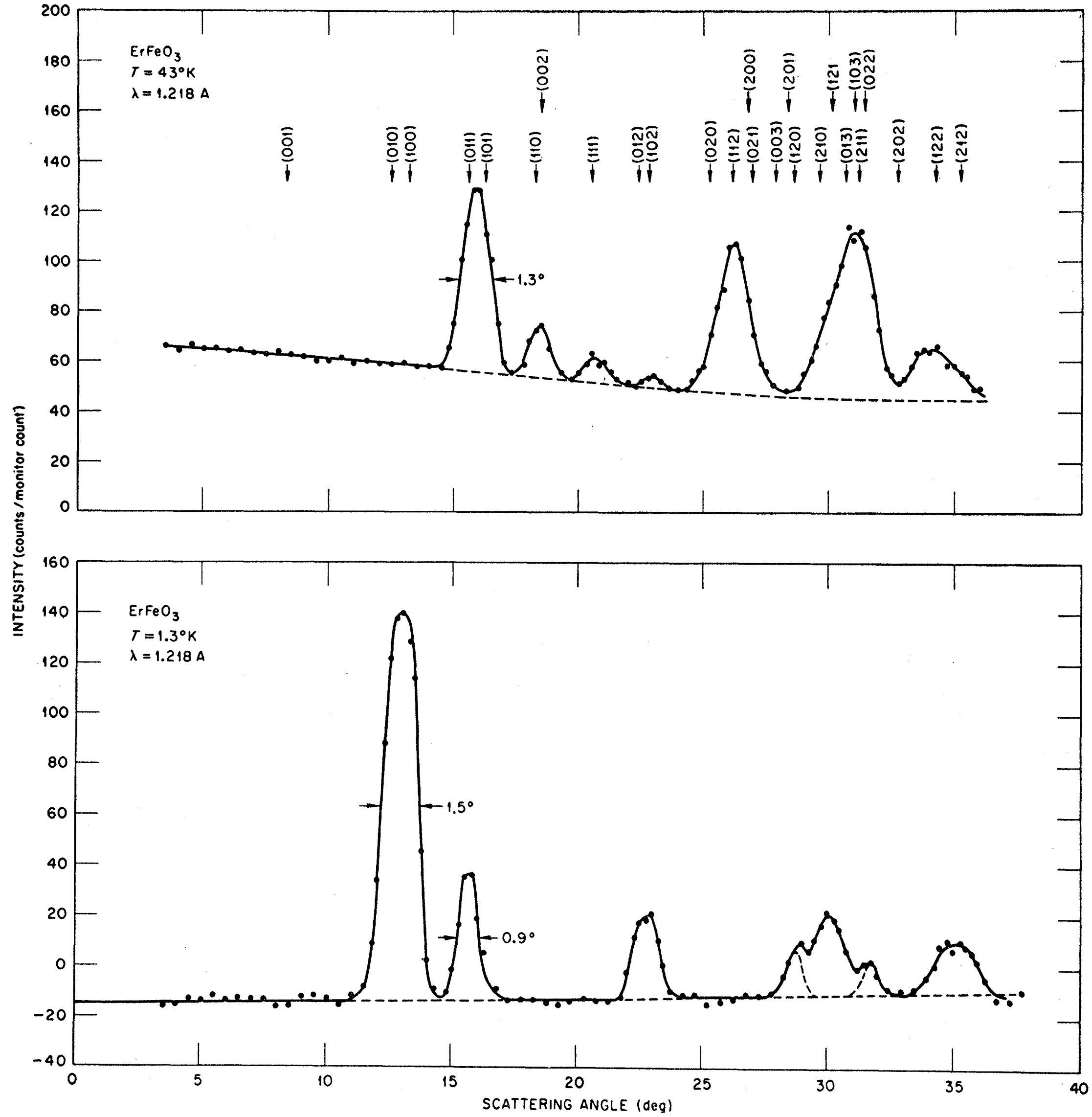

FIG. 3. Neutron diffraction data for $ErFeO_3$ at low temperatures. The upper curve is the diffraction pattern observed at 43°K. The (011, 101) reflection is considerably broader at this temperature than at room temperature indicating a change in the relative intensities of its components. The lower curve is a temperature difference pattern and shows only those diffraction effects which have developed between 1.3°K and 43°K. The breadth of the (010, 100) reflection indicates that both components have appreciable contributions. In the (011, 101) line only the (011) has an appreciable intensity.

the (011) is approximately three times as intense as the (101). It follows that the direction of antiferromagnetism, at room temperature is parallel or nearly parallel to the [100] direction.

At 43°K, for both compounds, the two components are approximately equally intense. At this temperature the moments must lie in a $(1\bar{1}0)$ plane. Thus between the two temperatures there has occurred a change in the direction of antiferromagnetism. At very low temperatures, as is shown in succeeding sections, it is possible to specify the directions within the $(1\bar{1}0)$ plane more precisely.

IV. MAGNETIC ORDERING IN THE RARE-EARTH-ION SYSTEMS

In the liquid helium temperature range, evidence for magnetically ordered configurations of the rare earth ions has been obtained for $HoFeO_3$ and $ErFeO_3$. Such evidence is illustrated for $ErFeO_3$ in Fig. 3. In the upper half of the figure is displayed a portion of the diffraction pattern obtained at 43°K and this consists of the coherent nuclear reflections and the coherent magnetic reflections arising from the antiferromagnetic arrangement of iron-ion moments all superimposed upon the paramagnetic scattering background of the erbium ions.

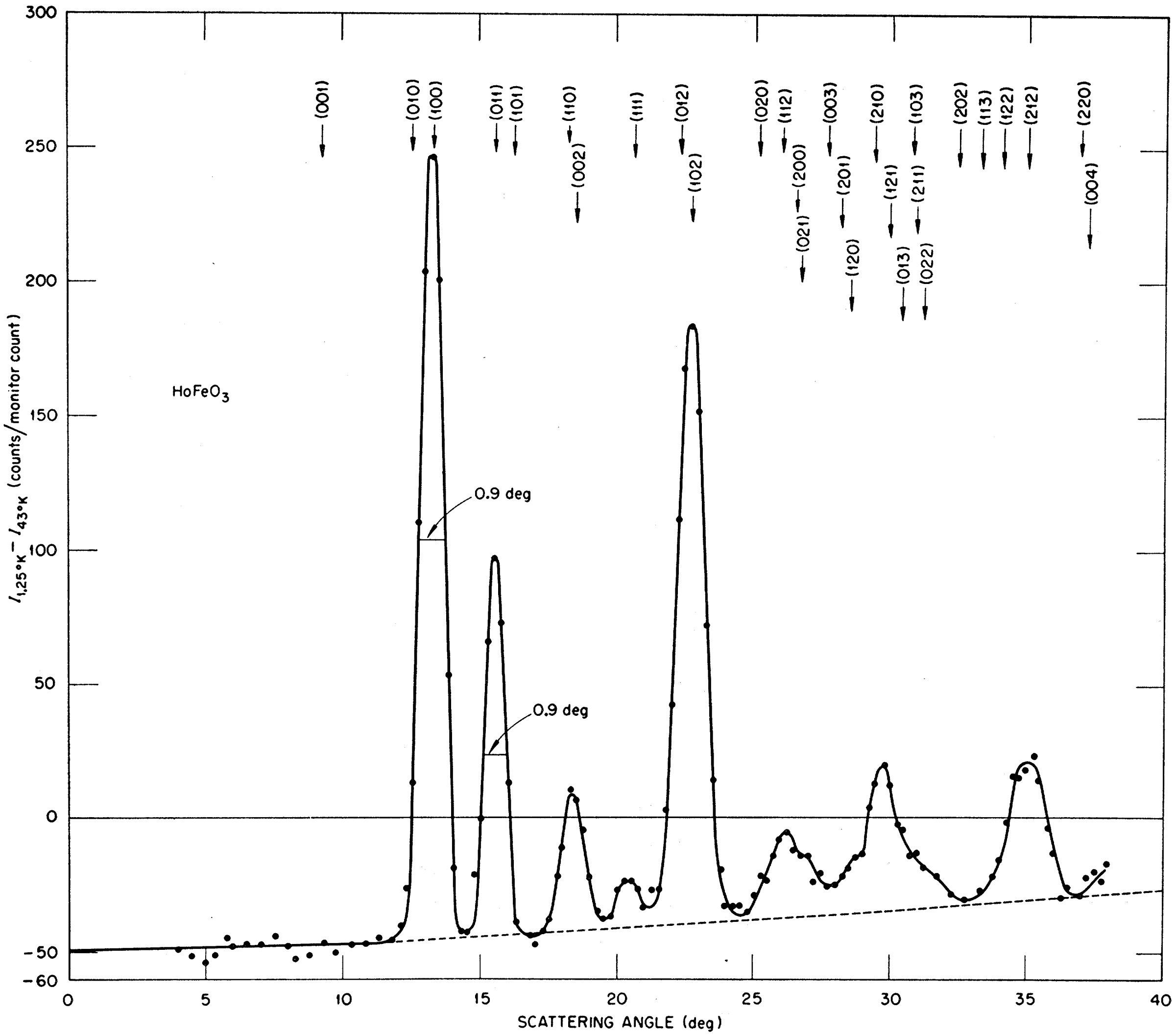

FIG. 4. Temperature difference pattern of HoFeO$_3$ $I(1.3°K)-I(43°K)$. Of the (010, 100) group the major contribution is from the (100); of the (011, 101) group the (011) predominates.

In the lower half of the figure is shown the difference pattern derived from the 43°K pattern and from data obtained at 1.25°K. The difference pattern displays those coherent scattering effects which have developed at the lower temperature. Since the iron-ion spin system is essentially saturated at 43°K, and since the temperature factors are not expected to change appreciably from 43°K to 1.25°K, the reflections observed in the difference pattern are attributed to magnetic ordering of the erbium ions. One may also find intensity variations if there have occurred parameter shifts between the two temperatures or if further changes in iron-ion moment direction have taken place. The ordering of the erbium ion moments is further evidenced by the dimunition of the paramagnetic scattering which is shown in the difference pattern as a negative background. A similar set of data for the same two temperatures is shown in Fig. 4 for HoFeO$_3$. In both patterns the line breadths of a few of the strong magnetic reflections are indicated, and these will be referred to in subsequent discussions.

1. Configurations and Moment Directions

We note first that considerable information relative to the approximate configurations and orientations of the rare-earth-ion moments can be obtained essentially by inspection of the diffraction patterns.

In both cases there are observed strong magnetic reflections with indices, referred to the orthorhombic chemical cell, with $H_1+H_2=2n+1$, $H_3=2n$. There are, in addition, in both sets of data other and generally weaker reflections with $H_1+H_2=2n+1$, $H_3=2n+1$ which are superimposed upon the magnetic reflections characteristic of the iron-ion spin system. From these observations one is led to a configuration of moments which is essentially the *C*-type antiferromagnetic configuration in which a chain of parallel moments is surrounded by four chains of oppositely directed moments at nearest neighbor distances.

For an ideal *C*-type arrangement with ions on simple cubic lattice sites and with moments which have a single axis of alignment, there are three possible directions which may be taken by the line of parallel moments. For each arrangement, only those reflections corresponding to the first category mentioned above would be observed and with powder data alone no distinction between the three configurations could be made. In the orthoferrites of Ho and Er, however, the rare earth ions are displaced from the ideal positions, and as a result of these displacements additional classes of reflections will be found in the diffraction patterns depending upon the orientation of the unique direction of the configuration.

A priori, the direction of the line of like spins in the orthoferrites may be parallel to orthorhombic [110], [$1\bar{1}0$], or [001] directions and the corresponding configurations, in the nomenclature of an earlier paper, are $(0\pi\pi)$, $(\pi 0\pi)$, and $(\pi\pi 0)$, respectively.[9] When the rare-earth-ion displacements are taken into account, it is only the $(\pi\pi 0)$ configuration, with its unique direction parallel to the a_3 axis, that is consistent with the observations, for only this configuration predicts nonzero intensities for reflections of the class $H_1+H_2=2n+1$ and $H_3=2n+1$.

With the approximate configuration established we may next, by comparing the relative intensities of the (010, 100) and (012, 102) reflections,[12] ascertain to a fair degree of certainty the moment directions of the Ho^{+3} and Er^{+3} ions. Consider first the pattern of $\mathrm{ErFeO_3}$. The measured (010, 100)/(012, 102) intensity ratio is 1:0.18 and, as indicated by the breadth of the line, both the (010) and (100) components make sizeable contributions to the first reflection. These two observations require that the moment be parallel or nearly parallel to the orthorhombic a_3 axis and hence to the unique configuration direction. For $\mathrm{HoFeO_3}$ the corresponding observed intensity ratio is 1:0.96, but in this case, as may be seen from the line breadth, most if not all of the intensity in the first peak is due to the (100) reflection. With these intensity ratios it is necessary that the Ho^{+3} ion moments be parallel or nearly parallel to the orthorhombic [010] direction and hence perpendicular to the unique configuration direction.[13]

2. $\mathrm{ErFeO_3}$

We consider next the quantitative aspects of the low-temperature data and take up first the results for $\mathrm{EeFeO_3}$.

Quite generally the magnetic structure amplitude for a magnetic reflection $(H_1H_2H_3)$ may be written as a vector sum, over the magnetic unit cell

$$\mathbf{F}=\textstyle\sum_j p_j \mathbf{q}_j \exp 2\pi i(H_1x_j+H_2y_j+H_3z_j), \tag{1}$$

in which the ion at $(x_jy_jz_j)$ has a magnetic scattering amplitude p_j given by

$$p_j=(e^2\gamma/2mc^2)\mu_j f_j, \tag{2}$$

where μ_j is the magnitude of the magnetic moment on the jth site, f_j is the corresponding amplitude form factor, and $\mathbf{q}_j$ is defined by

$$\mathbf{q}_j=\mathbf{e}(\mathbf{e}\cdot\boldsymbol{\kappa}_j)-\boldsymbol{\kappa}_j, \tag{3}$$

with $\mathbf{e}$ the unit scattering vector for the set of planes $(H_1H_2H_3)$, and $\boldsymbol{\kappa}_j$ the moment direction of the ion on the jth site. All other symbols have their usual significance.

The intensity in a given reflection $(H_1H_2H_3)$ is proportional to $(\mathbf{F}\cdot\mathbf{F}^*)$ but, for comparison with powder data $(\mathbf{F}\cdot\mathbf{F}^*)$ must be averaged over the various planes which contribute to the powder line. If it is assumed that for each set of ions in the orthoferrites there is a single scattering amplitude and a single alignment direction, a considerable simplification of Eq. (1) results.

It will be recalled[4] that in the rare-earth-iron perovskites the Fe^{+3} ions are found in special positions $4b$: $(\frac{1}{2}00;\ 0\frac{1}{2}0;\ \frac{1}{2}0\frac{1}{2};\ 0\frac{1}{2}\frac{1}{2})$ and the rare-earth ions in special positions $4c$: $\pm(xy\frac{1}{4};\ \frac{1}{2}-x,\ \frac{1}{2}+y,\ \frac{1}{4})$ of the space group P_{bnm}. If we denote by p_A and p_B the magnetic scattering amplitude of the rare-earth ions on the *A* sites and of the iron ions on the *B* sites, and if the moment directions of the rare-earth ion at $(xy\frac{1}{4})$ and of the iron ion at $(\frac{1}{2}00)$ are given by the unit vectors $\boldsymbol{\kappa}_A$ and $\boldsymbol{\kappa}_B$, respectively, then the expression (1) above may be written

$$\mathbf{F}=p_AR_A\mathbf{q}_A+p_BR_B\mathbf{q}_B, \tag{4}$$

where R_A and R_B are algebraic sums over the *A* sites or over the *B* sites of the form

$$R=\textstyle\sum_j \varphi_j \exp 2\pi i(H_1x_j+H_2y_j+H_3z_j), \tag{5}$$

in which φ_j is (± 1) depending upon the spin configuration (*G* or *C*) approximate to the particular set of sites.

Values of $\langle\mathbf{F}\cdot\mathbf{F}^*\rangle_{\mathrm{Av}}$ are then readily calculated and can be expressed in terms of the positional parameters of the rare-earth ions, the amplitudes p_A and p_B, and the moment directions $\boldsymbol{\kappa}_A$ and $\boldsymbol{\kappa}_B$. As we have already remarked, the iron ions scatter only into reflections with $H_1+H_2=2n+1$, $H_3=2n+1$; the rare-earth ions, however, because of their nonzero parameters scatter into all classes of reflections. The geometrical part, *R*, of the

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[12] See for example Fig. 18 of reference 1, but note that cubic (110) and (112) correspond to orthohombic (010, 100) and (012, 102), respectively.

[13] The above discussion is based on the premise that the rare-earth ions in the two compounds have but a single axis of alignment. From subsequent quantitative analysis it follows that this is very nearly the case for $\mathrm{ErFeO_3}$. In $\mathrm{HoFeO_3}$, however, the configuration of Ho^{+3} ion moments deviates markedly from the ideal one and the statement that the moments are parallel to [010] must be reinterpreted accordingly.

TABLE II. Comparison of observed and calculated magnetic intensities $ErFeO_3$.[a]

Index	P_{obs} (neutrons/min) $P_{1.25^0}$	$P_{diff.}$	$P_{calc.}$ (neutrons/min) $\lvert Fe\rvert^2$	$\lvert Er\rvert^2$	ErFe	Total	
001	nil	nil	0	0	0	0.00	
010			0	475	0		
	990±20	980±20				952	
100			0	477	0		
011*		210±15	215	60.6	121	397	
	620±20						598
101		0±20	201	0	0	201	
110*			0	0.82	0		
	85±10	nil				0.82	
002			0	0	0		
111*	40±10	nil	0	6.5	0	6.5	
012			0	82.9	0		
	170±10	175±10				181	
102			0	97.9	0		
020*			0	0	0		
112			0	0.36	0		
	355±15	nil				0.36	
200			0	0	0		
021			0	0	0		
003		nil				0	
201						8.01	
120						88.4	
210						126.4	
121		330±15				76.4	
013							326
						−14.6	
103						0	
211						41.3	
022						0	
202						0	
		nil					1.7
113						1.7	
122						79.0	
		180±15					197
212						117.8	
220						2.04	
		nil					2.0
004						0	

[a] Reflections designated by (*) have contributions from nuclear scattering or from the iron-ion spin system or both.

structure amplitude for the erbium ion configuration is largest when $H_1+H_2=2n+1$, $H_3=2n$ and the intensities of the reflections $H_1+H_2=2n+1$, $H_3=2n+1$ depend upon the relative orientation of κ_A and κ_B.

The intensities of the magnetic reflections in $ErFeO_3$, as measured in the diffraction pattern at 1.25°K and from the difference pattern of Fig. 3, are listed in the second and third columns of Table II. The intensities of the reflections with $H_1+H_2=2n+1$, $H_3=2n$ were first reduced to absolute values of p_{Er}^2 with the aid of the calculated structure factors. For this purpose the $GdFeO_3$ parameters, $x=-0.018$ $y=0.06$,[4] were used, and κ_{Er} was taken parallel to the a_3 axis. These values of p_{Er}^2 are plotted as a function of $\sin\theta/\lambda$ in Fig. 5 in which the solid curve is the experimentally determined differential scattering cross section for Er^{+3} in Er_2O_3,[14] normalized in the forward direction to $p_{Er}^2=2.5\times10^{-24}$ cm^2 as suggested by the first two reflections which are relatively insensitive to the exact parameter values chosen. Since the third point, which depends more sensitively on the parameters, falls within ten percent of the curve, it is indicated that the parameters used are approximately correct.

With $p_{Er}^2=2.5f_{Er}^2\times10^{-24}$ cm^2, with the $GdFeO_3$ parameters, and with κ_{Er} parallel to [001] the intensities for all reflections except those to which the iron-ion spin system contributes were calculated and the results are summarized in Table II. Magnetic reflections with $H_3=2n$ were not observed in the diffraction patterns and the intensities predicted for them are unmeasurably small.

It remains now to examine the reflections of the class $H_1+H_2=2n+1$, $H_3=2n+1$. The structure factors for reflections of this type have in general three terms: they have contributions from the iron ions alone, from the rare-earth ions alone, and from a cross term involving both types of ions. Only the first of these reflections, the (011, 101), is well resolved, but from its intensity one can deduce that the iron-ion moments are approximately parallel and antiparallel to the [110] direction at 1.25°K. The structure factors for these two reflections, given for reference to the following discussion, are

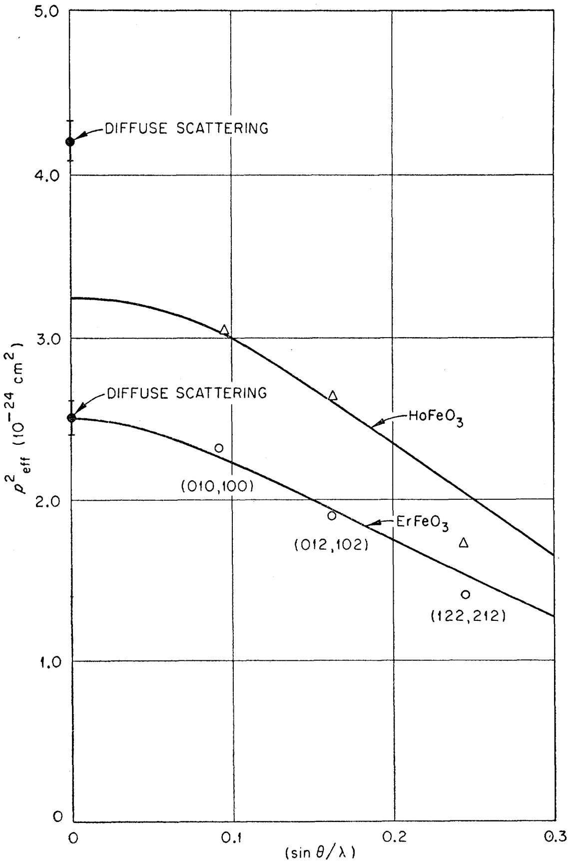

FIG. 5. Comparison of coherent and diffuse scattering measurements for $HoFeO_3$ and $ErFeO_3$.

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[14] W. C. Koehler and E. O. Wollan, Phys. Rev. 92, 1380 (1953).

$$\begin{aligned}\langle \mathbf{F}\cdot\mathbf{F}^*\rangle_{011} &= 16[p_{\mathrm{Er}}^2 \sin^2 2\pi y\langle q_{\mathrm{Er}}^2\rangle + p_{\mathrm{Fe}}\langle q_{\mathrm{Fe}}^2\rangle \\ &\quad + (2p_A p_B \sin 2\pi y m_2)/(b_2^2+b_3^2)a_3 \\ &\quad \times (m_1^2a_1^2+m_2^2a_2^2+m_3^2a_3^2)^{\frac{1}{2}}] \\ \langle \mathbf{F}\cdot\mathbf{F}^*\rangle_{101} &= 16p_{\mathrm{Fe}}^2\langle q_{\mathrm{Fe}}^2\rangle, \end{aligned} \tag{6}$$

in which $\mathbf{b}_1\mathbf{b}_2\mathbf{b}_3$ is the vector set reciprocal to $\mathbf{a}_1\mathbf{a}_2\mathbf{a}_3$, and $m_1m_2m_3$ are the components of a lattice vector parallel to $\boldsymbol{\kappa}_{\mathrm{Fe}}$.

As we have shown in the discussion of the iron-ion spin system, the total intensity of the (101, 011) reflection at 43°K is very nearly independent of the direction of antiferromagnetic alignment. Similarly at 1.25°K the total contribution of the iron ions alone to this reflection is independent of moment direction. Since the iron-ion spin system is temperature saturated at 43°K and since for any reasonable parameters the nuclear intensity in these reflections is small, the excess intensity at 1.25°K over that at 43°K is attributed to scattering by the erbium ions.

Now if one calculates the erbium ion contribution to this powder line, one finds a nonzero intensity only for the (011); further the intensity which is predicted without the cross term is only about one-third of that observed. Thus it is necessary to include the cross term in such a way as to give a sizeable positive contribution. This is achieved only if the vector $\boldsymbol{\kappa}_{\mathrm{Fe}}$ has an appreciable component in the [010] direction.

The vector $\boldsymbol{\kappa}_{\mathrm{Fe}}$ is further restricted in direction by the observation that the intensity in the (011, 101) reflection in the difference pattern, which is due almost entirely to the (011), is equal within the errors of observation to the difference in total intensity as measured at 1.25°K and 43°K. If $\boldsymbol{\kappa}_{\mathrm{Fe}}$ had deviated appreciably from the $(1\bar{1}0)$ plane in the temperature range from 43°K to 1.25°K, there would have been a redistribution of the intensity in the (011) and (101) reflections, and a (101) reflection would have been observed in the difference pattern, contrary to observation. From the magnitude of the intensity of the (011) reflection, one concludes that the $\boldsymbol{\kappa}_{\mathrm{Fe}}$ cannot have an appreciable component parallel to the a_3 axis and it is therefore parallel or nearly so to the [110] direction.

It has also been observed that the intensity distribution between the (011) and (101) reflections is essentially the same at 4.2°K, which is just below the Er^{+3} ion transition temperature as at 43°K.

With the [110] direction for $\boldsymbol{\kappa}_{\mathrm{Fe}}$ and with $p_{\mathrm{Fe}}^2 = 1.56f_{\mathrm{Fe}}^2\times10^{-24}$ cm^2 (based on results of Sec. III.3 above), the intensities of the remaining reflections of this class were calculated and these are summarized in Table II also. For comparison the intensities observed at 1.25°K are given together with the intensities measured in the difference pattern in the first part of the table. In the latter part only the difference pattern intensities are given. It will be noted that negative terms may appear in this part of the table of calculated intensities since the iron-ion contribution at 43°K is subtracted off. The intensity agreement is quite satisfactory.

The magnetic structure proposed for $\mathrm{ErFeO_3}$ at 1.25°K is illustrated in Fig. 6.[15]

It has been noted above that the development of coherent magnetic reflections in the diffraction pattern of $\mathrm{ErFeO_3}$ in the liquid helium temperature range is accompanied by a reduction in the diffuse scattering level, and in special cases this reduction can be interpreted quantitatively. For the rare-earth ions studied here an approximate "conservation of cross section" between the coherent and incoherent scattering applies.[16] As a consequence of this conservation one may obtain an independent measure of the coherent scattering amplitude of the ordered erbium moments from the difference in the differential scattering cross sections measured at a temperature which is low compared to the transition temperature and at a high temperature. For $\mathrm{ErFeO_3}$ the 43°K−1.25°K difference cross section leads to a value for p_{Er}^2 in the forward direction which is (fortuitously) in exact agreement with that obtained from the coherent scattering data and this serves as a check on the proposed structure.

3. $\mathrm{HoFeO_3}$

As described in the section above on configurations and moment orientations, the arrangement of Ho^{+3} ion moments in $\mathrm{HoFeO_3}$ is approximated by a *C*-type or s c ($\pi\pi0$) antiferromagnetic configuration. A detailed analysis of the diffraction data reveals, however, that the configuration is not ideally antiferromagnetic but that there is associated with it a net magnetic moment. We consider now the observations which are pertinent to this point.

The first of these is the presence in the difference pattern of relatively strong (110, 002) and (111) reflections. For an ideal moment configuration, as a few calculations readily show, these reflections are expected to be unmeasurably weak and indeed they were not observed for $\mathrm{ErFeO_3}$. We have already emphasized that within the limits of detection of powder x-ray diffraction methods no phases other than the holmium iron perovskite were detected. Moreover the intensities of these reflections are temperature dependent, and have the same temperature dependence below 4.2°K as the strong (100) reflection. It is highly improbable that these diffraction effects can be due to an impurity phase which was undetected in the x-ray diffraction patterns; because of possible contaminants

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[15] The configurations of one or both sets of ions must depart to a slight extent from the ideal configurations envisaged here. Discussion on this point is deferred to the final section of the paper.

[16] The argument follows directly from the treatment of neutron scattering by rare-earth ions given by G. T. Trammell, Phys. Rev. **92**, 1387 (1953) and depends on the assumption that the neutron energy is very high compared to the ordering temperature and to the crystal field splitting energy.

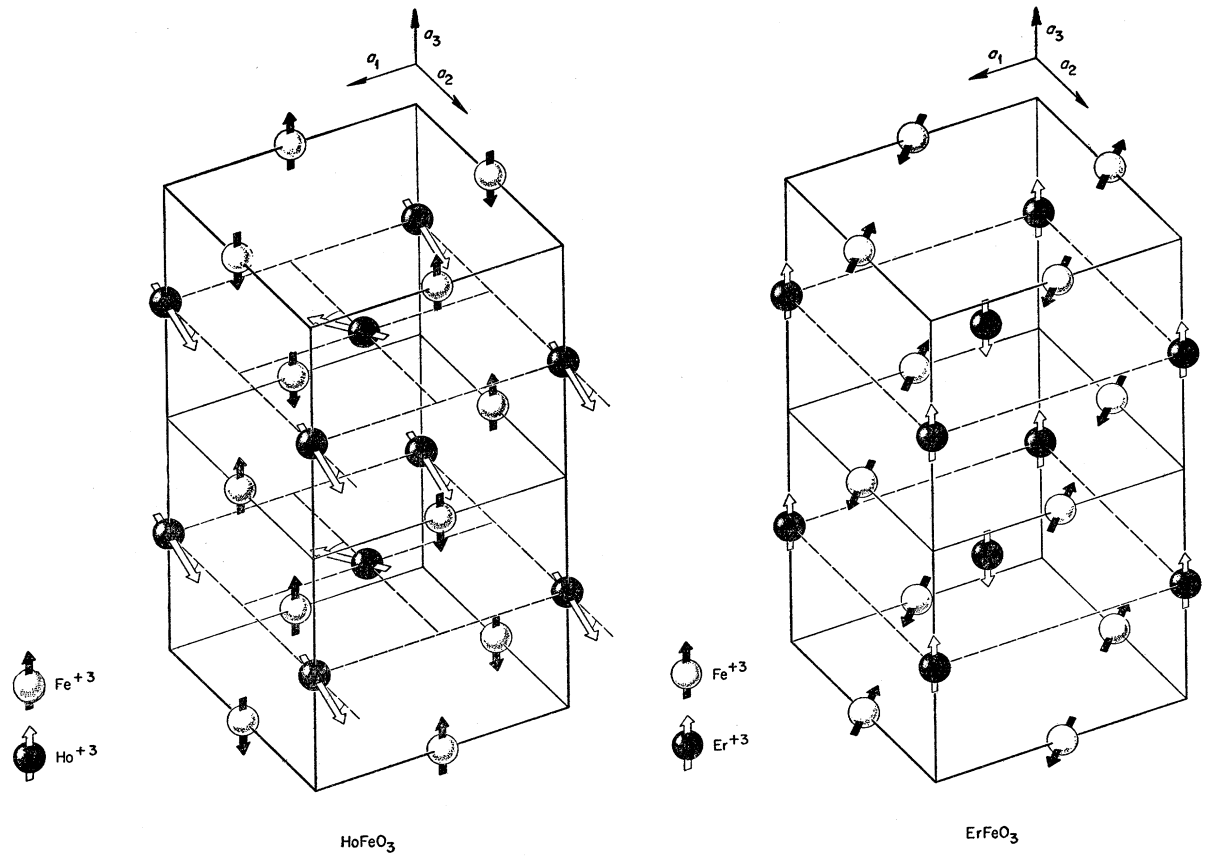

FIG. 6. Proposed magnetic structures for $HoFeO_3$ and $ErFeO_3$ at 1.3°K. The structures shown are highly idealized. The displacements of the rare-earth ions from special parameterless positions and the nonequivalence of their anion surroundings (not shown) are significant to the nonideal antiferromagnetic configurations of these compounds.

unreacted oxide phases can be eliminated since Fe_2O_3 is antiferromagnetic at much higher temperatures, and Ho_2O_3, in the absence of external fields, exhibits only short-range order type scattering.[17] The most probable impurity is Ho-Fe garnet but the magnetic structure one infers from the magnetization data[18] for this compound does not predict intensity at the scattering angle corresponding to the (110, 002) reflection. These lines are therefore attributed to $HoFeO_3$.

A second datum pertinent to this discussion is the value $p_{Ho}{}^2=(4.2\pm0.15)\times10^{-24}$ cm^2, which was measured in the near forward direction from the diffuse scattering difference cross section. The significance of this result is apparent when one carries out an analysis of the reflections of the class $H_1+H_2=2n+1$, $H_3=2n$ in the manner described above for $ErFeO_3$. If one assumes an ideal configuration with the Ho^{+3} ion moments parallel to [010] one finds that the intensities of the three resolved reflections of this class are fairly well fitted by the Ho^{+3} ion differential cross section for paramagnetic scattering,[19] although, as illustrated in Fig. 5, the third point deviates from the curve rather more than the corresponding point for $ErFeO_3$. The extrapolation to zero scattering angle, however, yields a value of $p_{Ho}{}^2=3.25\times10^{-24}$ cm^2 which is twenty percent lower than the value obtained from the diffuse scattering analysis.

One cannot bring these two numbers into agreement by a simple change of the moment direction of an ideal configuration. To demonstrate this one has only to examine the $\langle q\rangle_{Av}{}^2$ values for the (010, 100) reflection. Disregarding for the moment the fact that most of the intensity is found in the (100) reflection, the average value of q^2 for the composite reflection is equal to $\frac{1}{2}$, approximately, for any moment directions which are normal to the a_3 axis, and any component of the moment direction parallel to a_3 makes $\langle q\rangle_{Av}{}^2$ larger. In order to bring the two $p_{Ho}{}^2$ values into agreement it is necessary that $\langle q\rangle_{Av}{}^2$ for (010, 100) be smaller by about 20% than its minimum allowed value.

Further, the first two strong coherent reflections,

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[17] W. C. Koehler, E. O. Wollan, M. K. Wilkinson, and J. W. Cable, Bull. Am. Phys. Soc. **2**, 1927 (1957).

[18] R. Pauthenet, Compt. rend. **243**, 1499 (1956).

[19] W. C. Koehler, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. **110**, 37 (1958).

(010, 100) and (012, 102) are, as in $ErFeO_3$, relatively insensitive to the positional parameters so that it is unlikely that this discrepancy can be accounted for on the basis of shifts in the positions of the holmium ions.

Finally, since there is no evidence for a magnetic unit cell which is larger than the chemical unit, and in view of the relative intensity relationships already described, we are led to the conclusion that the configuration of Ho^{+3} ion moments in $HoFeO_3$ is not the ideal ($\pi\pi0$) configuration. Departures from ideality may occur if the several holmium ions in the unit cell have different magnetic moments (and therefore different scattering amplitudes), different axes of alignment, or both.

If the ions have different moments but the same axis of alignment then, as we have shown above, that axis must be close to the [010] direction. In this case the p^2 value derived from the coherent (010, 100), (012, 102), etc. intensities in the manner illustrated in Fig. 5 will be a measure of the square of the average moment[20] $(\sum_{j=1}^{n} \mu_j/n)^2$, and the value obtained from the diffuse scattering will give the average squared moment $[(1/n) \sum_{j=1}^{n} \mu_j^2]$. If, instead the ions all have the same moment but different axes of alignment, the analysis of the above mentioned coherent intensities yields the average squared projection of the moments on the a_2 axis and the diffuse scattering analysis yields the magnitude of moment itself. In either of these two cases one may construct configurations in which the net, macroscopic magnetic moment per unit cell is or is not equal to zero, and each gives rise to a characteristic set of diffraction effects. Of these only those arrangements in which there is a net magnetic moment are consistent with the intensity observed in the (110, 002) reflection.

From the observations outlined above we have been led to consider in detail two structural models and these are defined in Table III. In the first model each Ho^{+3} ion is assumed to have the same scattering amplitude p, but the ions have the different moment directions indicated. The net magnetic moment $\boldsymbol{\sigma}$ is normal to the a_2 axis. In the second model two types of holmium ion moments are assumed corresponding to scattering amplitudes p_1 and p_2 and the [010] direction is taken as the axis of alignment of the moments. The direction of $\boldsymbol{\sigma}$ is parallel to [010] in this case.

TABLE III. Models assumed for Ho^{+3} ion moments in $HoFeO_3$.

Site	$p_j\boldsymbol{\kappa}_j$	
	I[a]	II
$x, y, \frac{1}{4}$	$p(l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3)/\lvert\mathbf{A}_L\rvert$	$p_1\mathbf{a}_2/a_2$
$, \bar{y}, \frac{3}{4}$	$p(l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3)/\lvert\mathbf{A}_L\rvert$	$p_1\mathbf{a}_2/a_2$
$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}$	$p(l_1\mathbf{a}_1-l_2\mathbf{a}_2+l_3\mathbf{a}_3)/\lvert\mathbf{A}_L\rvert$	$-p_2\mathbf{a}_2/a_2$
$\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{4}$	$p(l_1\mathbf{a}_1-l_2\mathbf{a}_2+l_3\mathbf{a}_3)/\lvert\mathbf{A}_L\rvert$	$-p_2\mathbf{a}_2/a_2$

[a] l_1, l_2, l_3 are components of a vector $\mathbf{A}_L$.

TABLE IV. Observed and calculated difference pattern intensities $HoFeO_3$ (43°K−1.25°K).

	P_{calc} (neutrons/min)						
	Model I				Model II		P_{obs}
Index	$\boldsymbol{\sigma}\parallel\mathbf{a}_1$		$\boldsymbol{\sigma}\parallel\mathbf{a}_3$		$\boldsymbol{\sigma}\parallel\mathbf{a}_2$		(neutrons/min)
001	0		0		0		nil
010	0		0		0		0
		1137		1137		1137	
100	1137		1137		1137		1160±25
011	457		457		457		500±20
		528		466		467	
101	71		9		10		
110	88		254		135		
		238		254		285	230±20
002	150		0		150		
111	105		80		70		90±20
012	416		416		416		
		1092		1092		1092	1115±30
102	676		676		676		
020	34		34		0		
112	151		112		171		
200	57	307	57	260	57	236	230±30
021	65		57		8		
003	0		0		0		
201	39		39		39		
120	29		42		41		
210	215		232		232		
121	0		−27		−28		
		430		431		412	463±50
013	−8		−8		−8		
103	−8		1		2		
211	124		126		120		
022	39		26		14		
202	22		46		69		∼0
113	40		19		28		
122	90	432	101	442	106	451	390±30
212	302		322		317		
220	2		58		11		
		29		58		38	∼0
004	27		0		27		

General expressions for the magnetic structure factors have been obtained starting with Eq. (1) above, but the results are somewhat long and will not be given here. We note, however, that the intensities of the powder reflections are in general influenced by the direction of $\boldsymbol{\sigma}$ and also, for reflections of the class $H_1+H_2=2n+1$, $H_3=2n+1$, by the orientation of the axis of alignment of the iron-ion spin system.

The calculations of the intensities for the two models are given in Table IV and these are based on the following quantities which were established from preliminary iterative computations: (1) positional parameters $x=-0.025$ $y=0.065$ for both models; (2) $p_{\mathrm{Ho}}^2=4.1\times10^{-24}$ cm² in the forward direction and $l_2^2a_2^2/A_L^2=0.79$ for Model I; $(p_1^2+p_2^2)/2=4.1\times10^{-24}$ cm² and $[(p_1+p_2)/2]^2=0.79[(p_1^2+p_2^2)/2]$ in the forward direction for Model II; (3) $p_{\mathrm{Fe}}^2=1.53\times10^{-24}$ cm² in the forward direction for both models.

A comparison of the intensities calculated for the three cases with those observed does not permit an unambiguous determination of the direction of the net ferromagnetic moment. The intensity agreement for all three cases, while generally less good then one can expect, is considered to be satisfactory in view of

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[20] See, for example, reference 1.

the many parameters which enter into the calculations. One can infer, however, from the recently reported measurements of Bozorth and Kramer[21] that the net magnetization is parallel to [100]. Thus Model I with $\boldsymbol{\sigma}_0$ parallel to the a_1 axis is proposed as the low-temperature magnetic structure of $HoFeO_3$. This structure is illustrated in Fig. 6 also.

4. Transition Temperatures

The intensity of the first strong reflection (010, 100) in each of the compounds $HoFeO_3$ and $ErFeO_3$ was measured as a function of temperature in the temperature range below 4.2°K. The Néel temperatures, obtained in the usual way, were found to be 6.5°K and 4.3°K, respectively, for $HoFeO_3$ and $ErFeO_3$. In both compounds the magnetic intensities are essentially temperature saturated at 1.25°K.

5. Rare-Earth-Ion Moments

From the observations of the preceding sections, values of the moments of the magnetically ordered rare-earth ions can be obtained. For $ErFeO_3$ the data are interpreted in terms of an ordered magnetic moment per erbium ion of 5.8 Bohr magnetons. For $HoFeO_3$, as we have already pointed out, the interpretation depends upon the structural model which is assumed, but we can now eliminate Model II from further consideration. With Model I as a basis of discussion, each Ho^{+3} ion has the same magnetic moment of 7.5 Bohr magnetons but the moment directions of the ions make angles of about 27° with the a_2 axis and the deviations from exact alignment are such that there is a net magnetic moment, normal to the a_2 axis of, 3.4 Bohr magnetons per holmium ion.

Since these values are based on very low-temperature data, they represent very nearly the moment values at temperature saturation and it is significant that they are substantially lower than the saturation moments of the free ions which are 10.0 and 9.0 Bohr magnetons, respectively, for Ho^{+3} and Er^{+3}.

6. $NdFeO_3$

The diffraction patterns of $NdFeO_3$ observed in the liquid helium temperature range showed no evidence, either in the coherent reflections or in the diffuse scattering for magnetic ordering of the Nd^{+3} at temperatures down to 1.3°K. From the sensitivity of the observations, an upper limit of 0.5 Bohr magnetons for the ordered moment of Nd^{+3} in $NdFeO_3$ was set.

V. POSSIBLE DEPARTURES FROM IDEAL CONFIGURATIONS IN THE IRON-ION SPIN SYSTEMS

The neutron diffraction patterns of the compounds studied all exhibit very weak but measurable coherent peaks which correspond to the (010, 100) and/or (012, 102) reflections at temperatures which are high compared to 4.2°K. These effects have already been displayed without comment in Figs. 1 and 4 in which the diffraction patterns of $ErFeO_3$ are shown. In this case the (012, 102) is observed at 43°K but not at room temperature and similar effects were observed for $HoFeO_3$. In the pattern for $NdFeO_3$ both (010, 100) and (012, 102) were found to be present below about 570°K.

Reflections of this type are forbidden by the space group P_{bnm}, and by arguments analogous to those presented with the low-temperature observations on $HoFeO_3$ it is improbable that they are due to impurities. The high temperatures at which they are observed makes it necessary to attribute them to magnetic scattering from the iron-ion spin systems, but as we have emphasized reflections of this class are forbidden for an ideal *G*-type configuration. The presence of such reflections in the diffraction patterns implies that the configurations are nonideal.

In view of the very limited data available (one line in some cases) and the very low intensities, we have not considered it feasible to attempt a detailed explanation of these effects. Since the intensities are so low, however, the deviations from ideal alignment must be small and the conclusions of the preceding sections will remain valid.

VI. SUMMARY AND DISCUSSION

Magnetic properties of rare-earth-perovskite-type compounds have been measured in a number of laboratories.[22] These investigations have revealed the existence of a weak or parasitic ferromagnetism with a Curie temperature ranging from about 750°K in $LaFeO_3$ to about 625°K in $YbFeO_3$. At room temperature the magnitude of the parasitic magnetization $\boldsymbol{\sigma}_0$ is very low for all compounds studied: a typical value is $0.05\mu_B$ per molecule of rare-earth orthoferrite. In addition, in those cases where single crystals have been studied, a complex dependence with temperature of the anisotropy of $\boldsymbol{\sigma}_0$ has been found.

In this section of this paper a discussion of the neutron diffraction results relative to the macroscopic measurements is presented. Frequent reference will be made to the single crystal data for $HoFeO_3$ and $ErFeO_3$ obtained by Bozorth and his collaborators.

It has been suggested that the weak ferromagnetism of the rare-earth perovskites be attributed to imperfections in an otherwise perfect antiferromagnetic configuration of iron-ion moments[23]: the close corre-

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[21] R. M. Bozorth and V. Kramer, *Colloque International de Magnétisme, Grenoble, 1958* [Suppl. J. phys. radium **20**, 329 (1959)].

[22] H. Forestier and G. Guiot-Guillain, Compt. rend. **230**, 1844 (1950); **235**, 48 (1952). R. Pauthenet and P. Blum, Compt. rend. **239**, 33 (1954); R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956); M. A. Gilleo, J. Chem. Phys. **24**, 1239 (1956); R. M. Bozorth, V. Kramer, and J. P. Remeika, Phys. Rev. Letters **1**, 3 (1958); H. Watanabe, J. Phys. Soc. Japan **14**, 511 (1959); R. C. Sherwood, J. P. Remeika, and H. J. Williams, J. Appl. Phys. **30**, 217 (1959). See also reference 21.

[23] L. Néel, Compt. rend. **239**, 8 (1954).

spondence between Curie points and Néel temperatures of the rare-earth orthoferrites supports this view. One may further infer that the moment directions of the iron ions deviate from exact alignment from the observation that the direction of the parasitic magnetization σ_0 and the direction of antiferromagnetic alignment κ_{Fe} are mutually perpendicular in $HoFeO_3$ and $ErFeO_3$ at room temperature. (σ_0 is parallel to [001],[21] κ_{Fe} to [100].) If there were, for example, a rigidly determined direction of antiferromagnetism but different sublattice magnetizations one would expect σ_0 to be parallel to κ_{Fe}.

There are some interesting relations between the quantities σ_0 and κ_{Fe} in the liquid nitrogen temperature region. For example, for $ErFeO_3$ Bozorth et al. found a region between about 40°K and 80°K in which σ_0 was unmeasurably small. One will recall that it is in this temperature range that a change in the direction of κ_{Fe} was observed. Such changes of the magnitude of σ_0 with changes in direction of κ_{Fe} are similar to those observed in α-Fe_2O_3 and may be amenable to a treatment such as that of Dzyaloshinsky.[24] Indeed Bozorth[25] has suggested such an explanation for the weak magnetism of the orthoferrites which correctly correlates the directions of σ_0 and κ_{Fe} at room temperature. It may be pointed out, however, that if the weak "forbidden" reflections mentioned in Sec. V above are in fact due to deviations from exact alignment of the iron-ion spin systems, they are not consistent with Bozorth's model, for on that model the (010, 100) and (120, 210) reflections should be absent.

At very low temperatures the ferromagnetization is influenced and contributed to by the approximately antiferromagnetically ordered system of rare-earth ion moments. In $HoFeO_3$, according to Bozorth and Kramer, σ_0 becomes parallel to [100] below about 60°K and its magnitude increases rapidly with decreasing temperature attaining a value of $3.0\mu_B$ at 1.3°K. In the liquid helium temperature range it is necessary to attribute this large ferromagnetization to the rare earth ion configuration primarily, rather than the iron-ion spin system in order to account satisfactorily for the diffuse scattering by $HoFeO_3$. (See Sec. IV above.) Moreover, it is impossible to obtain a moment of $3\mu_B$ from a highly distorted antiferromagnetic configuration of iron-ion moments without markedly reducing the intensity of the (101, 011) reflection. In fact, this reflection increases its intensity at low temperatures.

For $ErFeO_3$ the parasitic magnetization attains a maximum value of about $0.5\mu_B$ parallel to [100] at about 4.5°K and then decreases at lower temperatures. Since both the iron and erbium ion moment systems may be contributing more or less equally to σ_0 in this temperature range, complicated effects are not unexpected.

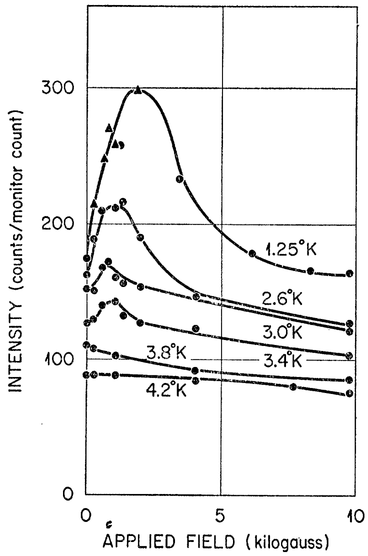

FIG. 7. Field and temperature dependence of (010, 100) magnetic reflection in $ErFeO_3$.

Consider now the measurements[21] of the magnetizations of $HoFeO_3$ and $ErFeO_3$ at very low temperatures and as a function of direction in the crystal. At the lowest temperature reached, 1.3°K, and in weak fields the direction of minimum susceptibility is [001] for $HoFeO_3$ and [010] for $ErFeO_3$. One might ordinarily infer from these observations that the moments of the Ho^{+3} ions are more nearly parallel to [001] and of the Er^{+3} ions to [010] than to other directions whereas κ_{Ho} is more nearly [010] and κ_{Er} more nearly [001].

In high fields the largest magnetization is observed parallel to these directions, e.g., parallel to the direction of approximate alignment. In $ErFeO_3$ the magnetization parallel to [001] increases precipitously beyond a critical field and approaches a saturation value of $5.7\mu_B$ at 1.3°K. This value is very close to the ordered moment of $5.8\mu_B$ deduced from the diffraction experiments. It is indicated that the Er^{+3} ion configuration is metamagnetic in the sense that the antiferromagnetic coupling is readily broken down when a field is applied parallel to the direction of parallel moments.

In $HoFeO_3$ it appears, since σ_0 is easily rotated from [100] to [010] that the moment system first sets itself perpendicular to a field applied parallel to [010]. With increasing fields the moments tend to be aligned parallel to the field.

A few observations have been made in the course of this study concerning the effect of an applied magnetic field on the scattering by $ErFeO_3$ at low temperatures. Most of the measurements were made on the strong (010, 100) powder reflection and this was chosen because of its low multiplicity. Even with polycrystalline samples, the neutron diffraction technique permits of directional selectivity since only those crystallites in the sample which are properly oriented for Bragg reflection contribute to the scattered intensity. If the multiplicity is high, however, a considerable

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[24] I. Dzyaloshinsky, J. Chem. Phys. Solids 4, 241 (1958).

[25] R. M. Bozorth, Phys. Rev. Letters 1, 362 (1958).

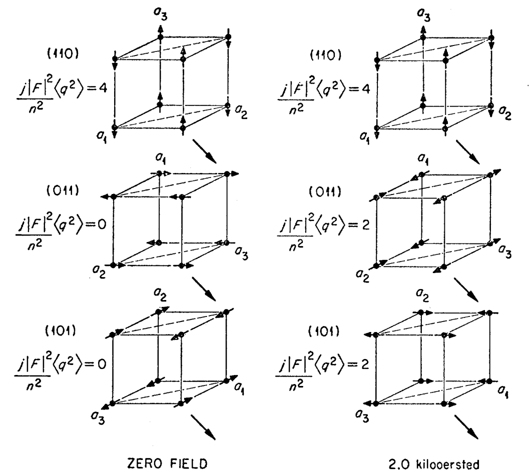

FIG. 8. Possible mechanism for field induced transitions in $ErFeO_3$. For convenience, the indices are referred to an undistorted cubic unit cell.

averaging over direction occurs, and there is a corresponding loss of detail.

In these experiments fields up to 10.0 kilo-oersteds were applied parallel to the scattering vector for the (010, 100) powder reflection at various temperatures in the liquid helium range. The results are summarized in Fig. 7. One notes a pronounced intensity maximum at low temperature. One also notes the general slow decrease of the intensity, excluding the broad peak, with increasing fields at all temperatures.

An interpretation of these observations is illustrated by the sketches of Fig. 8. It is convenient in this discussion to disregard the crystallographic distortions and to index the reflections relative to a cell which is twice as long on each edge as the ideal perovskite unit. The a_3 axis of the orthorhombic unit and of the cubic unit coincide and the (010, 100) orthorhombic indices are replaced by (110) cubic indices. The [001] direction is still the axis of like spins. In the figure are depicted three of twelve equally probable reflecting orientations of crystallites in a polycrystalline sample. The heavy arrow denotes the scattering vector, and the field direction. In zero field only those crystallites oriented as in the top sketch, or those rotated around a_3 by intervals of 90° scatter coherently into the (110) powder reflection. In the orientations shown in the lower two sketches the structure factors for (011), and (101) are zero identically as long as a_3 is the unique axis of the configuration. We have seen that the direction [001] is the easy axis of magnetization. When the field is applied as in (*a*) there is no component of it which is parallel to a_3 so that to a first approximation the field applied to a crystallite in orientation (*a*) will produce no effect. Consider now the same field direction relative to the laboratory but now applied to crystallites oriented as in (*b*) and in (*c*). In these cases there is a component of the field parallel to a_3 and one expects that with sufficiently high fields the antiferromagnetic arrangement will be decoupled and the system will approach magnetic saturation.

Depending upon the relative strengths of the exchange and anisotropy energies the transformation may proceed directly or via an intervening state in which the antiferromagnetic spin systems sets itself perpendicular to the direction of the field.[26]

If the transformation proceeds directly no intensity change in the (110) powder reflection will be observed because the structure factors for (011) and (101) will still be zero. If in the transformation the moments are simply rotated into the plane normal to a_3 there will again be no change of intensity so long as the a_3 axis continues to be the unique axis of the configuration.

In order to bring about the observed increase of intensity it is necessary that an intensity contribution be obtained from those crystallites oriented as in (*b*) and (*c*) which in zero field have zero structure factors. This can be achieved only if there is a rearrangement of the configuration as well as a change in moment direction; i.e., a structural domain[27] transformation such that for crystallites oriented as at (*b*), a_1 becomes the unique axis, and/or for crystallites oriented as at (*c*) a_2 becomes the unique axis. A possible arrangement which fits the observed 1:2 intensity ratio is shown in the second set of diagrams.

One may thus account for the intensity maximum in Fig. 7. With increasing fields the moments in the crystallites which are not of orientation (*a*) approach saturation and the intensity falls to essentially the zero field value because the contributions to the antiferromagnetic reflection from (*b*) and (*c*) oriented crystallites have disappeared. The contribution from the (*a*) oriented crystallite is only slightly affected by a field applied normal to its alignment direction as reflected by the slow decrease in intensity in high fields.

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It is a pleasure to acknowledge the cooperation of Dr. F. H. Spedding in making available to us sufficient quantities of pure rare-earth oxides to enable this work to be carried out.

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[26] L. Néel ("Les électrons dans les métaux," R. Stoops, Editor, Brussels, 1955, p. 251), Report to the 10th Solvoy Congress, 1954.

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