

these angles is determined and, therefore, the direction of the magnetic field. The tetragonal lines serve, in a sense, as an internal goniometer. The agreement between these various methods of determining the g factors was good.

The spin Hamiltonian with which the spectrum can be described is given by

$$H = \beta [g_x H_x S_x + g_y H_y S_y + g_z H_z S_z], \quad S = \frac{1}{2}$$

$$g_x = 1.38 \pm 0.01, \quad g_y = 2.85 \pm 0.02, \quad g_z = 2.94 \pm 0.01.$$

It is to be noted that $(g_x + g_y + g_z)/3 = 2.39$ and in the case of the tetragonal symmetry $(g_{11} + 2g_{12})/3 = 2.41$. This close agreement gives strong confirmation that the spectrum observed is indeed caused by the $U^{3+}(f^3)$ ion. Additional confirmation is obtained from the optical spectrum which showed new lines in the regions where the spectrum of U^{3+} —tetragonal symmetry is found.

DISCUSSION

A number of models can explain the observed spectrum. The X axis is pointing to the center of second-nearest neighbor cube. The charge compensation must, hence, be either an F^- ion or a combination of monovalent ion such as Na^+ and F^- ions compensating for

the excess charge of two U^{3+} ions. The possibility of charge compensation by O^{2-} is dismissed, since the orthorhombic spectrum has been seen in crystals in which no evidence of trigonal U^{3+} or U^{4+} has been found.

The most likely possibility is to assume an F^- ion in the second-nearest interstitial position as shown in Fig. 3(a). The anisotropy in the observed spectrum is a little smaller than that of the tetragonal spectrum. The crystal field is smaller and this gives rise to a smaller anisotropy than in the case where the F^- ion is at a tetragonal site, although a still smaller anisotropy would have been expected because of the large U^{3+} — F^- separation in this model. Other possibilities are shown in Figs. 3(b) and 3(a). In this case the combination of a substitutional Na^+ ion in a corner cube, or in an edge cube and an interstitial F^- ion in the adjacent cube can give rise to the distortions observed. These two models can be dismissed since the orthorhombic spectrum is also observed in crystals which have not been co-doped with Na^+ .

ACKNOWLEDGMENT

We are grateful to Dr. B. Schroeder of Solid-State Materials and to W. A. Hargreaves of Optovac Inc. for providing us with some of these crystals.

Neutron Diffraction Investigation of the Magnetic Properties of Compounds of Rare-Earth Metals with Group V Anions

H. R. CHILD, M. K. WILKINSON, J. W. CABLE, W. C. KOEHLER, AND E. O. WOLLAN

Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received 4 March 1963)

The magnetic properties of heavy rare-earth compounds with the NaCl-type structure have been investigated at temperatures between 295 and 1.3°K by neutron diffraction experiments on powdered specimens. All of the nitrides except TmN have a net ferromagnetism at low temperatures, but the diffraction patterns indicate a complicated type of magnetic order. HoP also has an unusual magnetic structure at low temperatures and this structure is presumably stabilized by dipole forces. The other phosphides, antimonides, and arsenides were found to have magnetic ordering transitions to the Mn-O type of antiferromagnetic structure. Low values of the atomic moments and large magnetic anisotropies in the ordered magnetic structures indicate the effects of crystal field interactions at low temperatures.

INTRODUCTION

ALTHOUGH a large amount of research has been performed in recent years on various types of rare-earth compounds, the magnetic properties of these systems are not well understood. In most of these compounds, interpretation of the experimental results has been seriously complicated by crystal distortions or by the presence of other magnetic ions. Consequently, an investigation of the magnetic properties of compounds formed by rare-earth ions and Group V anions was of considerable interest, because these compounds

crystallize in the simple NaCl-type structure and should be more amenable to theoretical analyses.

Only a few experiments of any type have been performed on these compounds, so that there is very little information which is helpful in the understanding of their magnetic properties. The interpretation of the magnetic ordering that exists at low temperatures is based entirely on the neutron diffraction results and on the theoretical calculations by Trammell.^{1,2}

¹ G. T. Trammell, *J. Appl. Phys.* **31**, 362S (1960).

² G. T. Trammell, following paper, *Phys. Rev.* **131**, 932 (1963).

TABLE I. Summary of neutron diffraction results of rare-earth intermetallic compounds.

Compound	a_0 (Å)	T_C (°K)	T_N (°K)	Paramagnetic moment		Ordered magnetic moment		Magnetic axis
				Calculated (μ_B /ion)	Observed (μ_B /ion)	Calculated (μ_B /ion)	Observed (μ_B /ion)	
TbN	4.93	42		9.7	9.7	9.0	6.7, 7.0	[111]
TbP	5.69		9	9.7		9.0	6.2	[111]
TbAs	5.82		12	9.7		9.0	7.7	[111]
TbSb	6.17		14	9.7	9.9	9.0	8.2	[111]
DyN	4.89	26		10.6		10.0	4.8, 7.4	[100]
HoN	4.87	18		10.6	10.8	10.0	6.0, 8.9	[100]
HoP	5.62	5.5		10.6		10.0	8.8	[100]
HoSb	6.13		9	10.6		10.0	9.3	[100]
ErN	4.83	5		9.6	9.4	9.0	3.0, 6.0	
ErP	5.60		3.1	9.6		9.0	5.7	\perp to [111]
ErSb	6.11		3.7	9.6	9.8	9.0	7.0	\perp to [111]
TmN	4.81			No observable magnetic order at 1.3°K				

The first investigations were made on HoN and TbN, and later experiments have included other nitrides, antimonides, phosphides, and arsenides. Although some of the results have been given in other short reports,³⁻⁵ it seemed advisable to include all the results in this article, because some of the original interpretations appear to be incorrect.

EXPERIMENTAL TECHNIQUES

Sample Preparation

All of the rare-earth compounds studied in this investigation have the rocksalt structure, but there is a relatively large variation in the lattice spacing, which significantly affects the magnetic behavior. The changes in lattice spacings are caused primarily by the different sizes of the anions, and the values vary from about 4.9 Å for the nitrides to about 6.1 Å for the antimonides.

The compounds were prepared in polycrystalline form by LaValle⁶ of the Oak Ridge National Laboratory from rare-earth metals which had a spectroscopic purity of about 99.5%. For the nitride samples, the metals were first converted to the hydrides, after which the nitrides were formed by reaction with NH₃. The other compounds were formed by direct reaction of the two elements involved. Quantitative chemical analyses for nitrogen on all of the rare-earth nitrides indicated that the amount of nitrogen in the samples was low and varied from about 94 to 97% of the calculated value. Analyses on other compounds also indicated a slight deficiency in the anion that was present. However, all additional chemical analyses, as well as quantitative checks of the nuclear reflections in the neutron diffraction patterns, suggested that the low values were not primarily the result of anion vacancies in the lattice. They were presumably due mostly to the

presence of small amounts of other rare-earth compounds, such as carbides or oxides, which were formed during the preparation from impurities that were present in the rare-earth metals. The apparent lack of stoichiometry could be directly correlated with the purity of the rare-earth metal, and in one sample of HoP, prepared from very high-purity holmium, the phosphide analysis indicated a phosphorus content which was 99% of the expected value.

Neutron Diffraction Procedures

Since it has been impossible to obtain single crystals of these compounds, all neutron diffraction experiments were performed on powdered specimens. The samples were enclosed in double-jacketed vacuum cryostats at pressures below 10⁻⁶ mm Hg, and measurements were made at sample temperatures from room temperature to 1.3°K. For temperatures above the liquid-helium region, the samples were sealed in a helium atmosphere in aluminum cells which were suspended below the coolant container of the cryostat. A small heater was inserted so that the sample temperature could be raised with respect to that of the coolant, and the temperatures were measured with a calibrated copper-Constantan thermocouple. In the liquid-helium temperature region, the liquid helium was allowed to enter the sample container, and temperatures were obtained by measuring the vapor pressure above the liquid.

Most of the measurements were made on diffractometers located at the ORNL graphite reactor, and the relatively low thermal neutron flux restricted the resolution in the diffraction patterns. However, the precision was adequate for most of the experiments, and those requiring higher precision were later repeated at the Oak Ridge Research Reactor with a diffractometer which gave excellent resolution. Although facilities were available at both installations to apply external magnetic fields to the samples at low temperatures, the latter diffractometer permitted the field to be applied in a direction perpendicular as well as parallel to the scattering vector.

³ M. K. Wilkinson, H. R. Child, J. W. Cable, E. O. Wollan, and W. C. Koehler, *J. Appl. Phys.* **31**, 358S (1960).

⁴ H. R. Child, M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, ORNL Report 3085, 73, 1961 (unpublished).

⁵ M. K. Wilkinson, H. R. Child, W. C. Koehler, J. W. Cable, and E. O. Wollan, *J. Phys. Soc. Japan* **17**, Suppl. BIII, 27 (1962).

⁶ D. E. LaValle, *J. Inorg. Org. Chem.* (to be published).

EXPERIMENTAL RESULTS

General Survey

This investigation has included twelve different compounds, and the results are summarized in Table I. All of the nitrides except TmN have a net ferromagnetism at low temperatures and the Curie points are listed. It was originally believed that these compounds were ferromagnetic with a large amount of ferromagnetic short-range order. However, recent measurements and calculations suggest a more complicated magnetic structure which would fall under the broad classification of ferrimagnetism. HoP is also ferrimagnetic at low temperatures with an unusual type of magnetic order, but all of the other compounds undergo an antiferromagnetic transition at the Néel temperatures which are listed in the table.

Analyses of the paramagnetic diffuse scattering at room temperature were made on several selected compounds. Within experimental error the values of the atomic magnetic moments at this temperature, which was well above the magnetic ordering transitions, were found to be consistent with the calculated values, $g[J(J+1)]^{1/2}$, expected for the free trivalent rare-earth ions. On the other hand, the atomic magnetic moments in the ordered magnetic structures at low temperatures are smaller than the maximum ordered moments, gJ , associated with the ions. These results indicate that the moment values at low temperatures are affected by crystalline field interactions, and calculations by Trammell^{1,2} are consistent with this interpretation.

These calculations show that crystal field effects will reduce the moment values in the magnetically ordered compounds of holmium, erbium, terbium, and dysprosium and that the magnetic moment in the ordered state of TmN will be zero. The calculations are also consistent with the experimentally observed moment directions. They predict that the crystal field interactions will produce a very large magnetic anisotropy with the magnetic moments directed along the edge of the cubic unit cell in the Ho and Dy compounds but along the cube diagonal in the Tb compounds.

Two values based on a simple ferromagnetic structure are given for the magnetic moments that are observed in the ordered nitrides. These values represent the extremes that are possible because of an uncertainty in the background determinations under the coherent reflections. As indicated in the next section, it is now believed that the large values correspond to the atomic moments and that the structures are not simple ferromagnets.

Rare-Earth Nitrides

All of the rare-earth nitrides except TmN were found to have a magnetic ordering transition at low temperatures, and the neutron scattering from the ordered magnetic lattice showed similar characteristics. Figure 1, which gives the diffraction patterns for HoN, is typical of the experimental observations. The pattern at room temperature shows the nuclear reflections superimposed on a very high paramagnetic diffuse

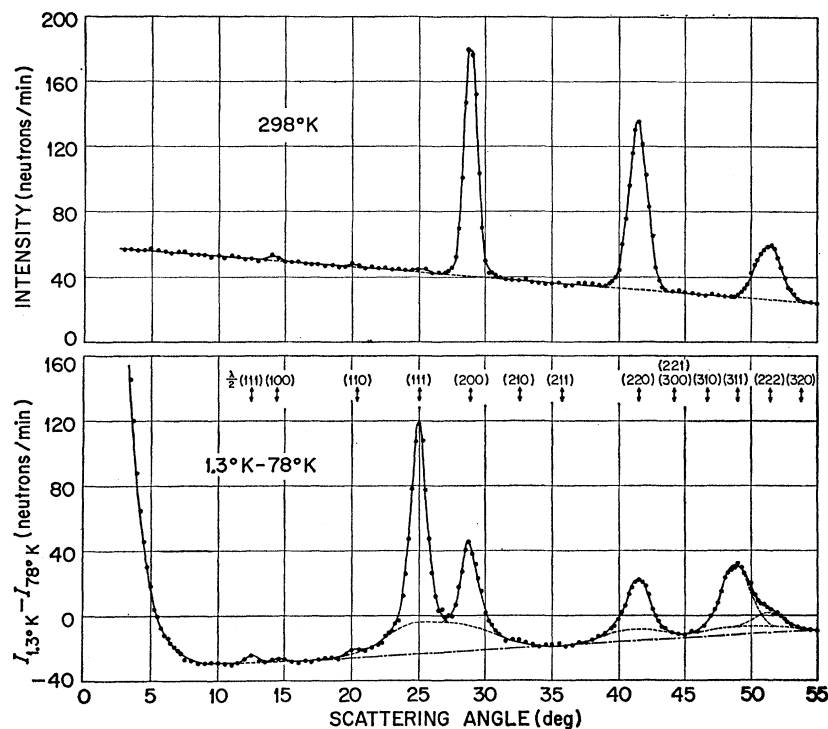


FIG. 1. Neutron diffraction patterns from HoN.

scattering. It is interesting to note that the (111) and (311) nuclear reflections are absent because the nuclear coherent scattering amplitudes of holmium and nitrogen are almost equal. As indicated in Table I, the observed cross section for the paramagnetic scattering is in good agreement with that calculated for the paramagnetic moment of the free Ho^{+3} ion, and the angular variation of the scattering is consistent with the magnetic form factor which was obtained⁷ from investigations on Ho_2O_3 . The lower pattern represents the difference in results obtained at 1.3 and 78°K and thereby shows only the magnetic reflections which appear at low temperatures. These reflections occur at the same positions as the nuclear reflections, thereby indicating a net ferromagnetic moment, and the relative intensities of the reflections correspond to those from a simple ferromagnetic lattice. The results were analyzed on this basis, although the large variations in the diffuse scattering could not be understood.

The very pronounced small-angle scattering and the large increase in diffuse scattering in the angular regions of the reflections indicate the presence of short-range ferromagnetic correlations. However, these effects were characteristic of the diffraction pattern at 1.3°K, which is far below the Curie temperature of 18°K. The small-angle scattering was studied as a function of temperature with well-collimated incident and reflected beams that allowed investigations to scattering angles of one degree. The results are summarized in Fig. 2(a) which shows the small-angle scattering at two angles in excess of the normal background scattering at 10 deg. Figure 2(b) gives the temperature dependence of the (111) magnetic reflection, and the intensities of both curves have been placed on an arbitrary scale to facilitate comparison. It is apparent that the small-angle scattering occurs at temperatures slightly above the Curie point and increases down to the lowest temperature. Consequently, it does not have the characteristics associated with critical magnetic scattering, because the latter has a maximum at the ordering transition temperature. Furthermore, the increase in the development of a short-range-ferromagnetic correlation simultaneously with the development of long-range-ferromagnetic order does not seem reasonable. Therefore, it can only be surmised that the small angle scattering and the corresponding humps in the background near the magnetic reflections result from more than one process. At temperatures above T_c , the normal critical scattering probably occurs and peaks at the transition. However, below T_c , as the critical scattering decreases, additional scattering from another process apparently occurs, and the intensity of this second type of scattering has the same temperature variation as the magnetic coherent scattering. The apparent continuity in scattered intensity as the temperature varies through T_c would, therefore, be accidental.

⁷ W. C. Koehler, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. 110, 37 (1958).

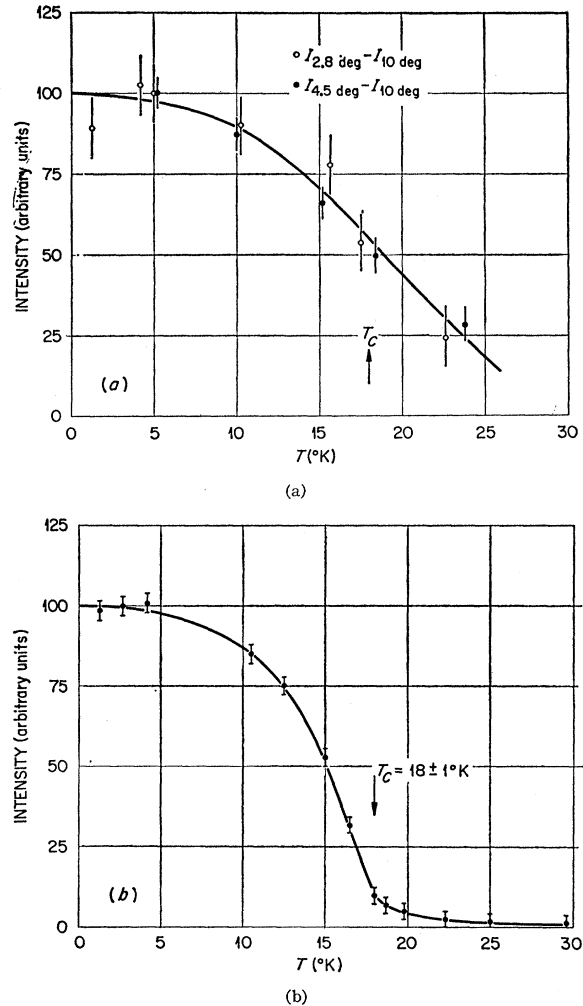


FIG. 2. (a) Temperature variation of small angle scattering from HoN. (b) Temperature variation of (111) magnetic reflection from HoN.

The large variation in the diffuse scattering also caused considerable uncertainty in the calculation of the apparent ferromagnetic moment in HoN at low temperatures. If it is assumed that the long-range magnetic order produces reflections with a resolution comparable to that of the nuclear reflections, then the background must be similar to the one shown by the dotted lines in Fig. 1(b). Calculations based on this assumption give the small moment value listed in Table I. On the other hand, if the large humps in the background are included in the reflections, then the ordered atomic moment corresponds to the large value in the table. This larger value is in good agreement with that obtained from measuring the change in diffuse scattering above and below the ordering transition temperature. Of course, both values are smaller than the maximum ordered moment associated with the Ho^{+3} ion and indicate that the moment value at low temperatures is affected by crystal-field interactions.

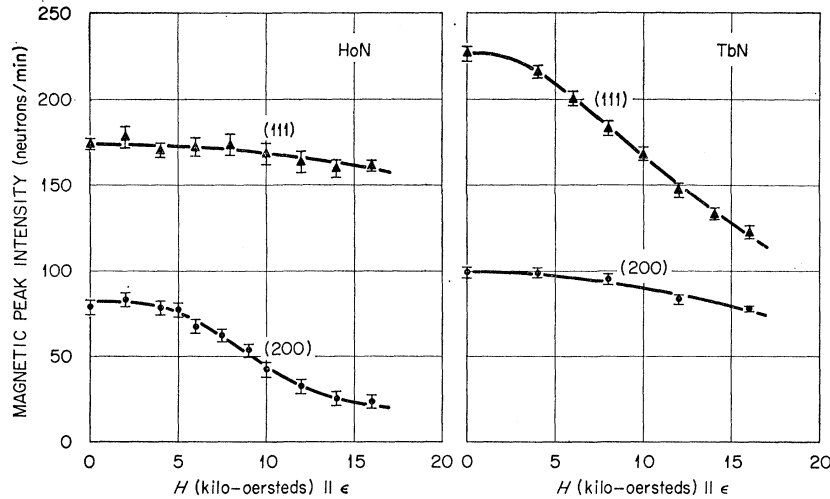


FIG. 3. Variation of magnetic reflections from HoN and TbN in a magnetic field applied in a direction parallel to the scattering vector.

All of the magnetically ordered rare-earth nitrides exhibited this type of diffuse scattering at low temperatures, but the relative sizes of the humps compared to the intensities of the magnetic reflections varied with the rare-earth ion. The effect was the smallest in TbN, and it is seen from the table that the maximum and minimum values for the magnetic moments are not widely different. Although the paramagnetic scattering from TmN was consistent with that expected from the Tm^{+3} ion, no magnetic order or background humping was observed down to 1.3°K.

In a ferromagnetic crystal which has cubic symmetry, it is not possible to determine the direction of the atomic moments from neutron diffraction powder patterns, unless an external field is applied to the sample. The moment directions listed in Table I were obtained by applying a magnetic field parallel to the scattering vector and measuring the relative changes in the intensities of the magnetic reflections. These changes occur as the angle between the direction of the atomic moments is varied with respect to the scattering vector.

The reflections which show the largest decrease in intensity indicate that the easy axis of magnetization is parallel to the scattering vector of those crystal planes. Results of this investigation on HoN and TbN are shown in Fig. 3. The decrease in the (200) reflection from HoN indicates that the moments are directed along the edges of the cubic unit cell and that they can be rotated along a particular cube edge when the field is applied in that direction. There is little or no decrease in the intensity of the (111) reflection with magnetic fields up to 16 kOe. Therefore, it is impossible to rotate the moments to a direction parallel to the cube diagonal with fields of this magnitude, a result which confirms the large magnetic anisotropy predicted by the crystal field calculations. In TbN the same type of study also shows a large magnetic anisotropy, but in this compound the direction of easy magnetization is parallel to the cube diagonal.

The concept of simple ferromagnetic structures in the rare-earth nitrides with the simultaneous existence of some type of unexplained short-range ferromagnetic

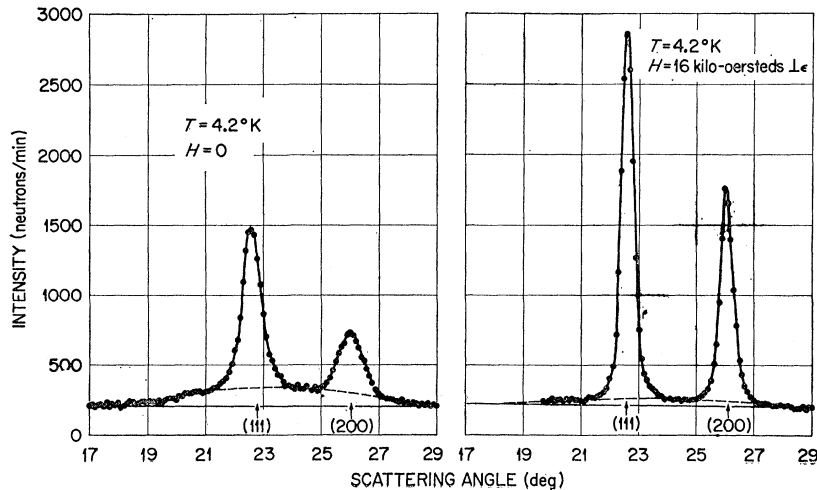


FIG. 4. Comparison of magnetic reflections from HoN in zero magnetic field and in a magnetic field of 16 kOe applied in a direction perpendicular to the scattering vector.

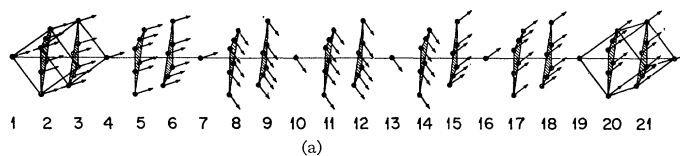
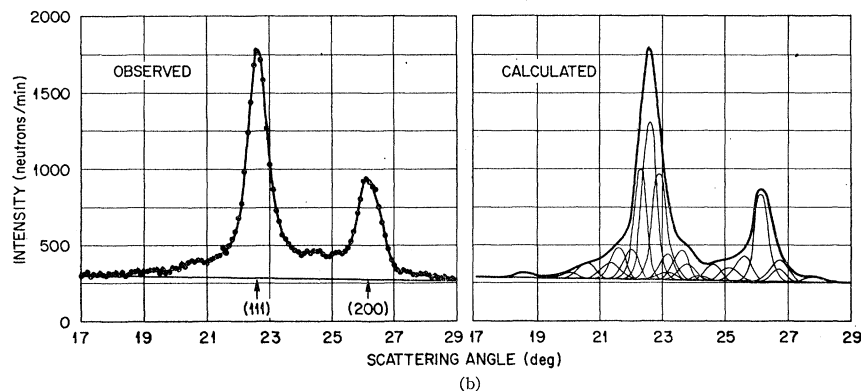


FIG. 5. (a) Possible magnetic structure of HoN below 18°K. (b) Comparison of observed magnetic reflections from polycrystalline HoN with those calculated on the basis of the possible magnetic structure shown in (a). Observed background used as background for calculated reflections.



correlations is difficult to understand, and recent experiments on HoN have given strong indications that this is not the correct interpretation. These experiments, in which samples of HoN were placed in external magnetic fields applied in a direction perpendicular to the scattering vector, have indicated that the magnetic structure is more complex than a simple ferromagnet and that the atomic moment corresponds to the larger value ($8.9 \mu_B$) in Table I. Figure 4, which gives the magnetic scattering at 4.2°K near the (111) and (200) magnetic reflections in zero field and with 16 kOe applied perpendicularly to the scattering vector, shows the observed effects. The intensity of the background hump decreases with the applied field, while the reflections become sharper and their intensity increases. These effects were observed as a function of the magnetic field up to 21 kOe, and the results indicate that saturation would be reached with a field of about 25 kOe. The magnetic intensities of the (111) and (200) reflections, extrapolated to the saturation value, can be explained on the basis of *complete* ferromagnetic long-range order with atomic moments of 8.9 Bohr magnetons directed along the edge of the cubic unit cell. The absolute intensities are in good agreement with the calculations which assume that the moments are re-oriented by the field along the particular cube edge which is most nearly parallel to the applied field. Consequently, these results indicate that the crystal field interactions, which dictate the moment direction, are large compared to 25 kOe, that these interactions reduce the values of the atomic magnetic moments to 8.9 Bohr magnetons, and that additional forces keep these moments from becoming completely aligned in zero magnetic fields. The latter forces, which can be overcome by fields of 25 kOe, presumably lead to a type of magnetic order which causes the unusual scattering that is observed in the background of the diffraction patterns.

Many ordered magnetic structures have been investigated, and the only type of model that has been found to satisfactorily predict the observed effects from HoN is shown in Fig. 5. In this model the value of the individual atomic moments is 8.9 Bohr magnetons and these moments are always directed along one of the cube edges. The arrangement of moments consists of ferromagnetic bands that are perpendicular to the cube diagonal, and the moment direction changes from one cube edge to another at the band edge. Such a structure gives a net ferromagnetism along the cube diagonal and also predicts many satellite reflections around the positions corresponding to the regular ferromagnetic reflections. At the lower part of the figure, the calculated intensities for a polycrystalline specimen are compared with the experimental data, and it is seen that the envelope of the predicted reflections is in satisfactory agreement with the observed results. This particular model, of course, is not a unique structure determination. For example, the variation of the moment direction among the three cube edges may be statistical and not a continuation of the sequence shown in the figure. Furthermore, the seven layers of moments along the cube diagonal may not be a specific value but an average value, and, in fact, a slight variation of this number would probably provide a closer fit to the experimental data. It is merely the intention of the calculations to show that magnetic ordering of this type gives coherent scattering which can account for the observed results. If this type of model is correct, and if there is a regular sequence of the moment directions along the cube edges, then it is likely that the exchange interactions would have favored a spiral moment arrangement in the absence of the large magnetic anisotropy forces. The combination of the anisotropy imposed on the exchange interactions favoring a spiral results in the formation of a retarded spiral structure. Detailed calculations

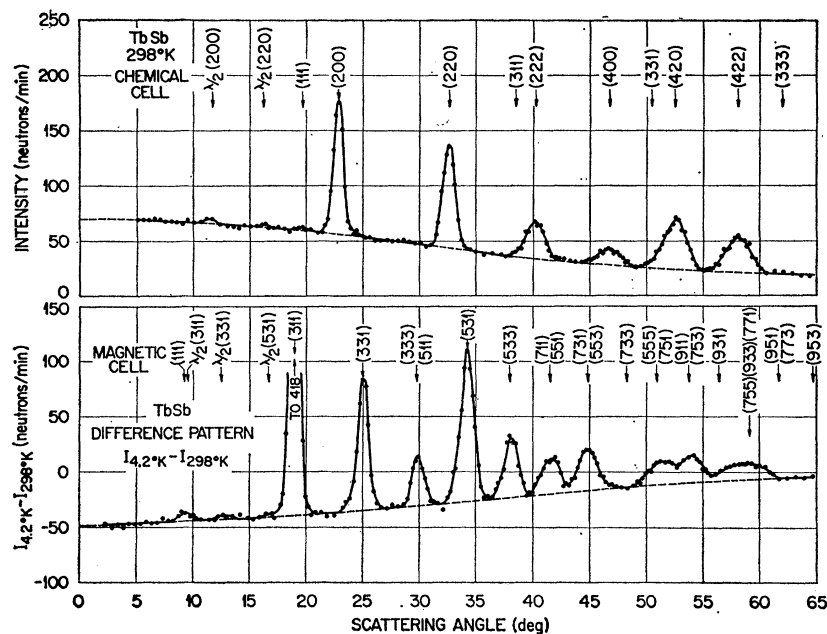


FIG. 6. Neutron diffraction patterns from TbSb.

have not been made for the other rare-earth compounds, but retarded spiral models of this type with different moment orientations could undoubtedly account for the results that have been observed.

Antiferromagnetic Compounds

With the exception of HoP, which is discussed in the next section, all rare-earth compounds except the nitrides become antiferromagnetic at low temperatures, and the Néel temperatures are listed in Table I. The magnetic structures are identical for all of the compounds and correspond to the MnO-type antiferromagnetic arrangement of moments, in which there are ferromagnetic sheets perpendicular to the cube diagonal, and the moment orientation in adjacent sheets is antiparallel. Since the antiferromagnetic structures do not have cubic symmetry, information on the moment direction can be obtained from the powder diffraction patterns in zero applied field. However, in such measurements it is only possible⁸ to determine the relative orientation of the atomic moments with respect to the unique axis of the magnetic lattice. These directions, which are listed in Table I, are seen to be identical to the moment directions of the corresponding rare-earth ions in the nitrides. The low values of the magnetic moments in the ordered structures indicate that crystal field interactions are also important in these compounds, and the correlation of the moment direction with the rare-earth ion is experimental evidence to support Trammell's calculations, which show that the magnetic anisotropy is dictated by the crystal field interactions.

The diffraction patterns from TbSb which are shown in Fig. 6 are typical of those from the antiferromagnetic

compounds. The magnetic reflections in the difference pattern, $I_{4.2^\circ\text{K}} - I_{298^\circ\text{K}}$, do not fall at the same angular positions as the nuclear reflections and require a magnetic unit cell in which each of the axes of the chemical cell is doubled. The absence of the (111) magnetic reflection indicates that the moment direction in TbSb is parallel to the cube diagonal, and the relative intensities of the other reflections confirm this direction.

In the diffraction patterns from the antiferromagnetic compounds, there is no small angle scattering and the magnetic reflections have a shape and resolution comparable to the nuclear reflections. Therefore, the large variations in the background that were observed in the diffraction patterns from the nitrides appear to be directly associated with the magnetic ordering in those compounds. The absence of such background effects removes the ambiguity in the atomic moment determination that was experienced in the nitrides, and the moment values in the magnetically ordered compounds are given in Table I. It is interesting to compare these values as a function of the lattice spacing for antiferromagnetic compounds with the same rare-earth ion. For example, in the terbium compounds, when the distance between rare-earth ions is increased by larger anions, the experimentally observed value of the moment becomes larger and seems to approach the maximum value of $9.0 \mu_B$. This behavior would be expected if the low moment values are caused by crystal field interactions, because the crystal field forces would be reduced as the lattice spacing is increased.

Holmium Phosphide

The three phosphide samples were examined in an effort to obtain a better understanding of the magnetic

⁸ G. Shirane, *Acta Cryst.* 12, 282 (1959).

coupling that exists in these rare-earth compounds. Regardless of the exact type of magnetic structure that exists in the nitrides, it is evident that the magnetic ordering is influenced by strong ferromagnetic interactions. Conversely, the MnO-type antiferromagnetic structure that exists in the antimonides is caused predominantly by antiferromagnetic interactions between second nearest neighbors. On the premise that the relative strengths of these predominant interactions are a function of the distance between rare-earth ions, it appeared quite possible that in the phosphides these distances would be near a critical value where the interactions would closely balance. In such a situation, the magnetic ordering would then be influenced by interactions other than exchange. This condition appears to exist in HoP, and the ordered magnetic lattice below 5.5°K is ferrimagnetic. Figure 7 shows the diffraction patterns from HoP, and it is seen that the magnetic ordering causes ferromagnetic reflections as well as reflections corresponding to an MnO-type antiferromagnetic structure.

The first attempts to determine the magnetic structure of HoP were based on considerations of the four sublattices contained in the magnetic unit cell. Although it was possible to combine ferromagnetic and antiferromagnetic sublattices in a model that would yield the observed reflections, this model was unacceptable for other considerations. It required that the values of the antiferromagnetic moments should be very different from the values of the ferromagnetic moments and that the latter should be much larger than the maximum possible moment for the Ho^{+3} ion. Furthermore, the moment direction in the antiferromagnetic sublattices would be perpendicular to the cube diagonal instead

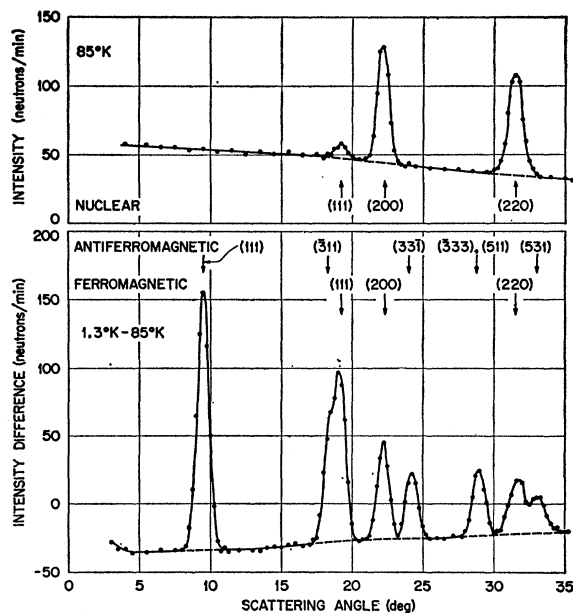


FIG. 7. Neutron diffraction patterns from HoP.

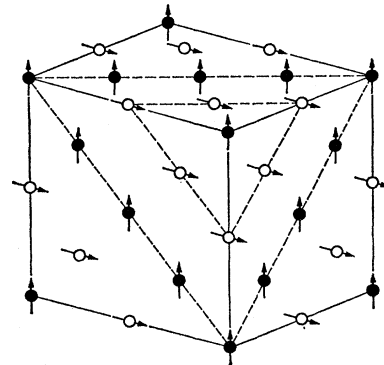


FIG. 8. Magnetic structure of HoP.

of parallel to the cube edges as would be expected from Trammell's calculations and from experimental observations on the other compounds. Of the other models tested, all but one were found to be equally unsatisfactory.

The only magnetic structure with the atomic moments directed along the cube edges, which has been found to account satisfactorily for all of the scattering observations, is shown in Fig. 8. This type of "flip-flop" structure is one in which there are ferromagnetic planes perpendicular to the cube diagonal and adjacent planes have the moment directions at right angles to each other. Therefore, there is a net ferromagnetic component of the moments parallel to the $[110]$ direction and a net antiferromagnetic component perpendicular to that direction. Tests of this model were also made by investigations with an external magnetic field, and results with the field direction parallel to the scattering vector are shown in Fig. 9. The interpretation of such data for a polycrystalline sample is complicated by the presence of two types of magnetic domains. One of these is caused by the unique axis of the magnetic cell, since there are four cube diagonals which can form this axis. However, there are other domains associated with each unique axis, because the ferromagnetic component can be parallel to any one of the face diagonals. Since this complexity exists, a detailed interpretation of the results obtained in an external magnetic field will not be discussed. However, these data have been analyzed and every feature shown in the figure can be explained on the basis of the proposed model with the expected domain transformations.

Although this magnetic structure is very unusual, it is believed to be unique in fitting the various types of neutron scattering results that have been obtained. It seemed possible that the structure might be caused by quadrupole interactions, but calculations by Trammell² showed that such interactions could not stabilize this configuration. However, his calculations proved that if the magnetic anisotropy requires the moment direction to be parallel to the cube edges, then this "flip-flop" structure can be stabilized by dipole forces

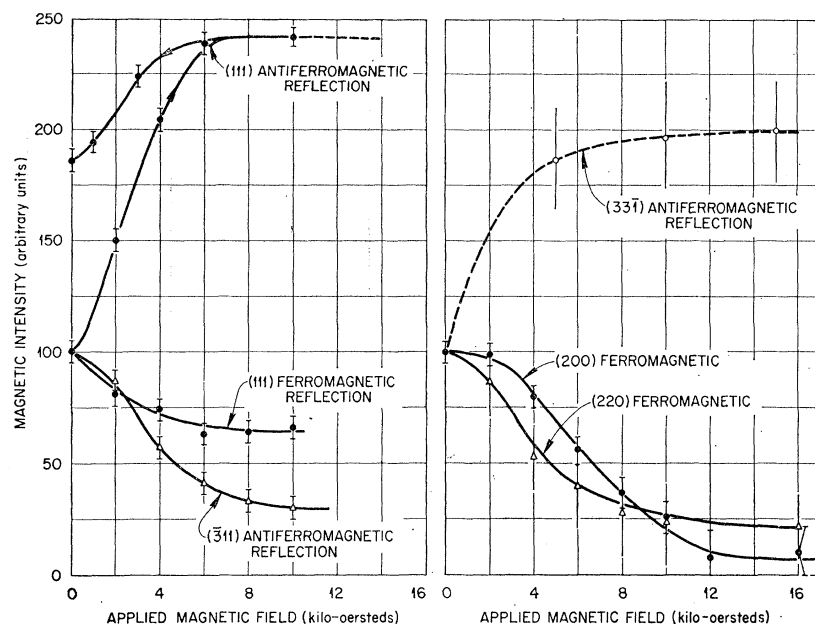


FIG. 9. Variation of magnetic intensities from HoP with magnetic field applied along scattering vector.

when the antiferromagnetic interactions are slightly larger than the ferromagnetic interactions. The assumption of a large magnetic anisotropy is predicted by the crystal field calculations, and, of course, it has been confirmed experimentally for both HoN and HoSb. Consequently, there appears to be little doubt that this unusual magnetic structure exists in HoP and that it is the result of dipole interactions.

As Trammell has shown² the normal MnO-type antiferromagnetic structures observed in ErP and TbP are not inconsistent with this interpretation. In TbP the magnetic dipole energy of the antiferromagnetic structure is large, but the antiferromagnetic interactions are presumably sufficiently greater than the ferromagnetic interactions that the dipole forces cannot affect the magnetic ordering. ErP has a smaller interatomic spacing than HoP, which would suggest that the ferromagnetic interactions more closely approach the antiferromagnetic interactions than those in HoP. However, the Mn-O type structure is a stable antiferromagnetic configuration for dipole forces when the moment direction is perpendicular to the cube diagonal as it is in the Er compounds of this series.

DISCUSSION

The neutron diffraction results show that compounds containing rare-earth ions and Group V ions, which crystallize in the rocksalt structure, undergo magnetic ordering at low temperatures and that the type of magnetic ordering appears to vary with the interatomic distances. The nitrides have the smallest distance between atoms, and the magnetic structure is apparently the result of strong ferromagnetic interactions. The antimonides have the largest lattice spacing, and

these compounds order in the MnO-type antiferromagnetic structure, which requires a predominant antiferromagnetic interaction between next-nearest neighbor magnetic ions. The phosphides have interatomic distances that seem to be close to a critical value where the predominant exchange interactions balance. Consequently, the magnetic ordering in the phosphides is influenced by weaker interactions, and in HoP, a very unusual type of magnetic structure is stabilized by dipole forces.

If the magnetic order in the rare-earth nitrides corresponded to simple ferromagnetism, the magnetic structures of all of these compounds could be correlated with the assumption that nearest neighbor and next-nearest neighbor exchange interactions are predominant. This correlation would merely require that there is a ferromagnetic interaction between nearest neighbors, an antiferromagnetic interaction between next-nearest neighbors, and that the ferromagnetic interaction decreases more rapidly when the distance between magnetic ions is increased by larger anions. However, with the more complicated magnetic structures that are believed to exist in the nitrides, the picture of magnetic exchange interactions becomes more complex. The proposed bands of ferromagnetism certainly suggest that some of the important exchange interactions extend over distances that are much farther than those between second nearest neighbors. Since these compounds have been found to possess relatively high electrical conductivities,⁹ it is possible that such long-range exchange interactions would take place through the conduction electrons.

⁹ J. F. Miller and R. C. Himes, in *Rare Earth Research*, edited by E. V. Kleber (The Macmillan Company, New York, 1961), p. 232.

The results of the neutron diffraction investigations have definitely indicated the importance of crystal field interactions in determining the magnetic properties of these compounds at low temperatures. In all of the magnetic structures, the atomic magnetic moments were found to be smaller than the maximum values associated with the trivalent rare-earth ions, whereas the moments contributing to the paramagnetic scattering at room temperature were consistent with values for the trivalent ions. Furthermore, there was a large magnetic anisotropy in all of the magnetic structures, and a specific moment direction was associated with a particular rare-earth ion. As shown in the following paper, both effects are due to crystal field interactions, and the experimental observations are in good agreement with the theoretical predictions. Since the theoretical calculations are based on the cubic symmetry of the compounds, it was of interest to determine if there were any structural changes below the magnetic ordering transition. X-ray observations¹⁰ on HoN down to 6°K were unable to detect any departure from the cubic symmetry of the lattice to an accuracy of about one part in five thousand. Similar measurements have not been made on the other compounds.

Although the moment direction in the magnetic structures of the holmium compounds has been listed as the [100] direction, slightly better agreement with the observed intensities is obtained when there is a

small tilt of the moments (of the order of 5°) with respect to the cube edge. This effect was first noticed in the "flip-flop" structure of HoP, where the best fit of the experimental data produced a model in which the ferromagnetic component of the moments was about 5% larger than the antiferromagnetic component. Subsequent inspection indicated that the best agreement with the HoSb results was obtained when the moments made a slightly larger angle with the cube diagonal than that between the [100] and [111] directions. Should this tilt of the moments from the cube edge be real, then there must be second-order effects that modify the crystal field interactions and produce this small change in direction. Similar deviations in the listed moment directions for the terbium and erbium compounds were not evident, but very slight changes would not exceed the experimental accuracy of the observations.

ACKNOWLEDGMENTS

The authors are particularly indebted to D. E. LaValle for the preparation of the samples used in this investigation, many of which had not been prepared previously in either the purity or quantity that these experiments required. They also wish to express their appreciation to H. L. Yakel and R. M. Steele for x-ray analyses of the samples and to G. T. Trammell for many helpful discussions on the theoretical implications of this research.

¹⁰ We are indebted to H. L. Yakel for these observations.