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Recent Magnetic Neutron Scattering Investigations at Oak Ridge National Laboratory

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A brief summary is given of recent neutron diffraction investigations at the Oak Ridge National Laboratory on rare-earth metals and intermetallic compounds.

Introduction

During the past few years, various types of magnetic substances have been investigated by neutron diffraction at the Oak Ridge National Laboratory. These investigations include iron-group compounds such as $FeBr_2$, $FeCl_2$, $CoBr_2$, $CoCl_2$, and $CrCl_3$, which show a metamagnetic behavior and have antiferromagnetic structures consisting of ferromagnetic sheets of moments aligned antiparallel, MnI_2, which has a helical-type of antiferromagnetic order, and $MnCl_2$ and $FeCl_3$, which have complex antiferromagnetic structures that are not yet understood. Current investigations also include alloy systems of the 3*d* and 4*d* transition metals, and some of the experiments will be discussed in another paper at this Conference.[1] However, the largest effort in recent months has been directed toward rare-earth metals and compounds, and this review will be limited principally to brief discussions of these investigations.

Rare-earth intermetallic compounds

Since interpretation of experimental results on many rare-earth compounds has been complicated by crystal distortions or by the presence of other magnetic ions, investigations have been performed on rare-earth intermetallic compounds which crystallize in the simple NaCl-type structure and should be more amenable to theoretical analyses. The first investigations[2] were made on HoN and TbN, and later experiments have included other nitrides, antimonides, phosphides, and arsenides. The results of these investigations are summarized in Table I.

All of the nitrides except TmN become ferromagnetic at low temperatures, but the diffraction patterns in the ferromagnetic state show scattering effects that are indicative of short-range ferromagnetic correlations. This scattering, which exists at temperatures far

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		
				Calculated (μ_B/ion)	Observed (μ_B/ion)	Calculated (μ_B/ion)	Observed (μ_B/ion)	Magnetic Axis
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	
HoN	4.87	18		10.6	10.8	10.0	6.0, 8.9	[100]
HoP	5.62	5.5		10.6		10.0		
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	⊥to[111]
ErSb	6.11		3.7	9.6	9.8	9.0	7.0	⊥to[111]
TmN	4.81	No observable magnetic order at 1.3°K						

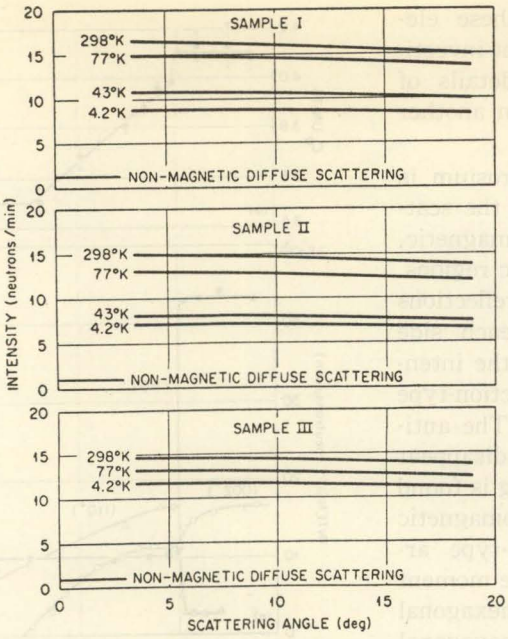
below the Curie points, does not have the characteristics associated with critical magnetic scattering, and the mechanism for producing it has not been established. Therefore, there is considerable uncertainty in the calculations of the ferromagnetic moments, and two values are given in Table I. The small values correspond to the long-range order which produces reflections with a resolution comparable to the nuclear reflections, and the large values were obtained by including the short-range order scattering in the magnetic reflections. Although values for the paramagnetic moments that were obtained from the paramagnetic scattering are in good agreement with those calculated for the free trivalent ions, the ferromagnetic moments are smaller than the maximum ordered moments associated with the ions. These results indicate that the moment values at low temperatures are affected by crystalline field interactions, and calculations by Trammell[3] are consistent with this interpretation. These calculations show that crystal field effects will reduce the moment values in HoN, TbN, and ErN and that the magnetic moment in the ordered state of TmN will be zero. These calculations also indicate 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 HoN and along the cube diagonal in TbN. Experiments in external magnetic fields have verified these moment directions, and fields of 21 kilo-oersteds were not able to rotate the moments from the cube edges in HoN. However, magnetic fields of this magnitude were able to overcome the short-range correlations and produce complete long-range ferromagnetic order corresponding to the large value of the atomic moment. These results suggest that crystal field interactions reduce the atomic moments in the rare-earth nitrides to the large values listed in Table I and that other weaker interactions prevent the moments from attaining complete long-range ferromagnetic order.

The other rare-earth intermetallic compounds also exhibit magnetic ordering at low temperatures. However, all of them except HoP become antiferromagnetic with an MnO-type antiferromagnetic structure in which ferromagnetic sheets of moments exist along the cube diagonal and adjacent ferromagnetic planes are antiparallel. The size and orientation of the atomic moments indicate that crystal field interactions are also important in these compounds. Since there were no observable short-range-order effects from the antiferromagnetic structures, these effects in the nitrides are probably associated with their ferromagnetic behavior.

With the assumption that nearest neighbor and next-nearest neighbor exchange interactions are predominant, the magnetic structures can be correlated with the same types of exchange interactions. This correlation requires 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. These conditions would predict a critical value of the lattice spacing in which the ferromagnetic and antiferromagnetic interactions are equal, and the magnetic ordering would then be influenced by interactions other than exchange. The magnetic ordering in HoP, which has a lattice spacing near the critical value, is consistent with this interpretation. HoP becomes ferrimagnetic below 5.5°K and the magnetic structure appears to be an unusual type, which can be stabilized by dipole forces.

Rare-earth metals

No significant determinations have yet been made of the magnetic structures which exist at low temperatures in elements belonging to the first half of the rare-earth series. However, the available data indicate different magnetic ordering properties from those of the heavy rare-earth metals. Preliminary single-crystal measurements have shown that neodymium is antiferromagnetic at 4.2°K, but the structure is sufficiently complex that it has not been established. Investigations[4] on polycrystalline cerium have determined that the hexagonal-close-packed phase becomes antiferromagnetic at 12.5°K and have suggested a magnetic structure consisting of ferrimagnetic layers stacked along the hexagonal axis, but the weak intensities of the antiferromagnetic reflections prevented a



TEMP PHASE PERCENTAGES

	NORMAL fcc	hcp	COLLAPSED fcc
(°K)	(%)	(%)	(%)
298	100		
77	10	80	10
43	5	55	40
4.2	5	45	50

(°K)	(%)	(%)	(%)
298	75	25	
77	57	35	8
43	8	40	52
4.2	5	40	55

(°K)	(%)	(%)	(%)
298	10	90	
77	10	87	3
4.2	8	84	8

Fig. 1. Diffuse Neutron Scattering from Cerium

definite structure determination.

The investigations of cerium were undertaken primarily to determine if the anomalous behavior in specific heat[5] and magnetic susceptibility[6] measurements at low temperatures could be correlated with the various crystallographic phases and to determine if this behavior corresponded to a change in the electronic structure of the cerium atoms. Three samples, which were carefully prepared to give different concentrations of the three low temperature phases, were examined at various temperatures, and analyses were made of the diffuse scattering. A summary of the results is shown in Fig. 1, and it is apparent that the presence of the collapsed face-centered cubic phase is accompanied by a large decrease in the diffuse scattering. Almost all of the diffuse scattering from cerium is paramagnetic scattering, and the data can be explained satisfactorily if the atoms in the normal f.c.c. and h.c.p. phases have one $4f$ electron in the $^2F_{5/2}$ state and the atoms in the collapsed f.c.c. phase do not have a magnetic moment. When the collapsed f.c.c. phase is formed, the $4f$ electron is presumably transferred to the conduction band, giving the cerium atoms a tetravalent character and leaving them with no unpaired electrons.

The rare-earth metals in the second half of the series exhibit unusual magnetic properties and in general there are two temperature regions of magnetic order. Single crystal neutron diffraction measurements have now been made on many of these metals and this report will summarize the investigations on Dy[7], Ho[8], and Er[9], which allowed the

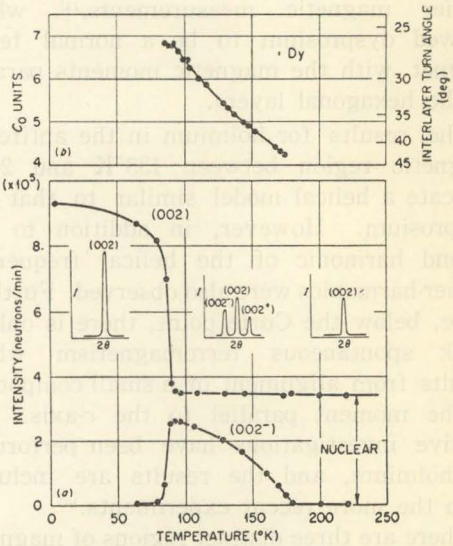


Fig. 2. Temperature Dependence of the (002) and (002−) Reflections and of the Magnetic Unit Cell Dimension for Dysprosium.

major structure characteristics of these elements to be determined. More recent investigations, which emphasize specific details of the structures, will be presented in another paper at this Conference.[10]

The magnetic behavior of dysprosium is indicated in Fig. 2 (a), which shows the scattered neutron intensity in the paramagnetic, antiferromagnetic, and ferromagnetic regions. Below 179°K antiferromagnetic reflections appear as satellite reflections on each side of the (002) nuclear reflection, and the intensities increase with a Brillouin-function-type dependence down to about 90°K. The antiferromagnetic reflections begin to disappear at 90°K, and ferromagnetic scattering is found in the (002) reflection. The antiferromagnetic structure corresponds to a helical-type arrangement of the moments with the moment orientation perpendicular to the hexagonal c-axis. The moments within a hexagonal layer are aligned in ferromagnetic sheets with a specific angle of rotation between moments in adjacent layers, and the variation of this angle with temperature is shown in Fig. 2 (b). Very weak reflections, corresponding to second harmonics of the helical frequency, were observed in the antiferromagnetic region below about 150°K, but reflections for higher order harmonics were not present within the limit of detection. In the ferromagnetic region, the neutron diffraction results confirmed earlier magnetic measurements,[11] which showed dysprosium to be a normal ferromagnet with the magnetic moments parallel to the hexagonal layers.

The results for holmium in the antiferromagnetic region between 133°K and 20°K indicate a helical model similar to that for dysprosium. However, in addition to the second harmonic of the helical frequency, higher harmonics were also observed. Furthermore, below the Curie point, there is only a weak spontaneous ferromagnetism which results from alignment of a small component of the moment parallel to the c-axis. Extensive investigations have been performed on holmium, and the results are included with the more recent experiments.[10]

There are three distinct regions of magnetic order in erbium, and Fig. 3 (a) shows the intensities of representative reflections which indicate the magnetic behavior. Satellite reflections, corresponding to magnetic order with a single sinusoidal variation along the c-axis, occur at 80°K, but, unlike helical structures, there are no reflections of the $(00l^{\pm})$-type between 80°K and 53°K. The structure in this temperature region consists of ferromagnetic sheets of moments in the hexagonal layers with the moment direction parallel to the c-axis and the moment amplitude modulated sinusoidally. The presence of $(00l^{\pm})$-type satellite reflections below 53°K signifies the formation of a helical structure from the components of the moment perpendicular to the c-axis. Finally, at 20°K, the structure becomes a ferromagnetic helix, in which the components of the moments parallel to the c-axis are ferromagnetic while the perpendicular components remain in a helical arrangement. Fig. 3 (b) shows dimensions for the magnetic cell along the c-axis, and the only variation in cell dimensions occurs between 53°K and 20°K as the helical structure develops. Small reflections, corresponding to the third harmonic of the frequency which modulates the moment amplitude parallel to the c-axis, were also observed in this intermediate temperature region, and these reflections indicate a change

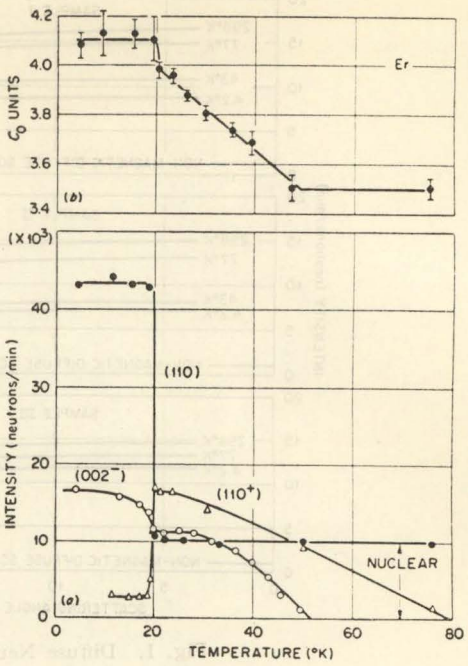


Fig. 3. Temperature Dependence of the (110), (110+) and (002−) Reflections and of the Magnetic Unit Cell Dimension for Erbium.

in the modulation from sinusoidal to one approaching a square wave.

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DISCUSSION

R. J. Elliott: Is the stabilization of the HoN order by quadrupole-quadrupole interaction rejected because it gives the wrong order, or because it is estimated to give too small an effect?

M. K. Wilkinson: Calculations by Trammell have shown that for a [100] moment direction both the ferromagnetic structure and the simple MnO-type antiferromagnetic structure have lower quadrupole energies than the structure observed.

C. J. Gorter: Have you information on the dependence of the antiferromagnetic moments on the temperature, corresponding to a variation of entropy? Does it correspond with theory?

M. K. Wilkinson: In the case of Dy, where the spin arrangement is the helical type, the temperature dependence of the measured intensity corresponds to changes in the ordered moment and the variation is similar to a Brillouin function. In the case of Ho, this is also true. But in Er, where a sinusoidal modulation of the moments occurs first and this structure is followed by a different type of order, in which the modulation starts to square off, it is very difficult to measure the changes in specific moment values.