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Neutron Diffraction Investigations of the Magnetic Ordering in Rare Earth Nitrides

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Neutron diffraction investigations on HoN and TbN at low temperatures show that both compounds become ferromagnetic with Curie temperatures of about 18°K and 43°K, respectively. Although the paramagnetic scattering is consistent with moment values calculated for the free trivalent rare earth ions, the observed ferromagnetic moments are lower than the calculated values and indicate the effect of crystalline field interactions. Diffraction patterns from both compounds at 1.3°K show considerable ferromagnetic short-range-order scattering with characteristics which are different from those associated with critical magnetic scattering.

THE number of magnetically-ordered systems of rare earth ions which have been investigated is relatively small, and most of these systems have been complicated by crystal distortions or by the presence of other magnetic ions. Since all the rare earth elements form nitrides which possess the simple NaCl-type structure and might be amenable to relatively easy theoretical analyses, it was of interest to investigate the existence of magnetic ordering in these compounds at low temperatures. The first investigations were performed on HoN and TbN, and this report contains the preliminary results which were obtained.

The compounds were prepared[1] from rare earth metals which had a spectroscopic purity of about 99.5%. The metals were first converted to the hydrides after which the nitrides were formed by reaction with NH_3 at temperatures from 850° to 1100°C. Quantitative chemical analyses for nitrogen indicated that only about 95% of the desired amount was present in the samples. Additional analyses suggest that this low value is not the result of nitrogen vacancies in the nitride lattice but is due to the presence of small amounts of rare earth oxides and carbides formed during the preparation from oxygen and carbon which were present in the metals.

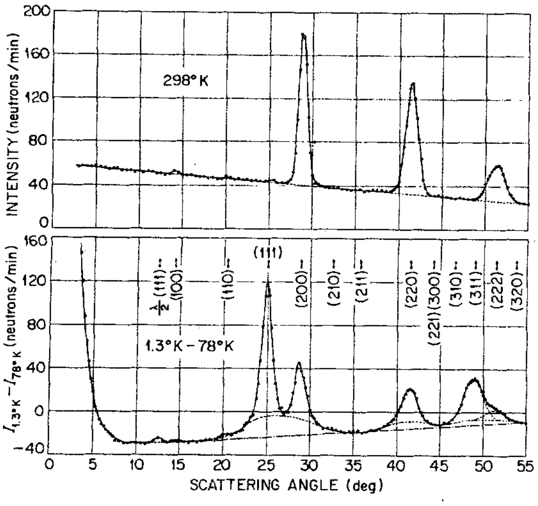

FIG. 1. Neutron diffraction patterns from HoN.

Neutron diffraction investigations have been performed on powdered specimens of both compounds at temperatures from 298°K to 1.3°K, and Fig. 1 shows diffraction patterns obtained from HoN. The pattern at room temperature shows the nuclear reflections superimposed on a very high paramagnetic diffuse scattering. The observed cross section of this paramagnetic scattering is in good agreement with that calculated for the paramagnetic moment (10.6 Bohr magnetons) of the free Ho^{+3} ion, and the angular variation of the scattering is consistent with the magnetic form factor which was obtained from investigations[2] on Ho_2O_3. Ferromagnetic reflections were observed in the diffraction patterns from HoN at liquid-helium temperatures, and these reflections are shown in Fig. 1b, where the data represent the difference in results obtained at 1.3°K and 78°K. It is interesting to note that the (111) and (311) magnetic reflections actually occur at positions where nuclear reflections would be expected, but the latter are missing because the nuclear scattering amplitudes of holmium and nitrogen are almost equal. The intensity of the (111) magnetic reflection was studied as a function of temperature, and it was found to exhibit a Brillouin-type dependence with a Curie temperature about 18°K. The very pronounced small-angle scattering and the large increase in diffuse scattering in the angular regions of the reflections are characteristic of the diffraction pattern at 1.3°K and indicate the presence of a short-range ferromagnetic correlation at temperatures far below the magnetic transition temperature. This small-angle scattering, which has been studied with well-collimated incident and reflected beams at scattering angles to one degree, occurs at temperatures above the Curie point and increases with decreasing temperatures down to 1.3°K. Therefore, it does not have the characteristics associated with critical magnetic scattering, and the mechanism for producing it is not yet understood.

The large variation in the diffuse scattering causes considerable uncertainty concerning the calculation of the ferromagnetic moment in the ordered lattice at low temperatures. However, if it is assumed that the long-range ferromagnetic order produces reflections with a

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[1] We are very much indebted to D. E. LaValle, ORNL, for preparing these samples.

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

resolution comparable to the nuclear reflections, then the background must be similar to that shown by the dotted lines in Fig. 1(b), and the ferromagnetic moment is about 6.8 Bohr magnetons per holmium ion. If the large humps in the background are included in the reflections, a value of about 8.6 Bohr magnetons per holmium ion is obtained. Since either calculation gives a moment which is smaller than the maximum ordered moment (10.0 μ_B) associated with the Ho^{+3} ion, these results indicate that the moment value is affected by crystalline field interactions. Recent calculations by Trammell[3] of the energy levels which result from these interactions are consistent with this interpretation. His calculations also predict that the magnetic moments in the ordered lattice are directed along the edges of the cubic unit cell and that relatively large energies are required to move them from this direction. This prediction was verified experimentally by measurements of the (200) and (111) magnetic intensities when a magnetic field was applied parallel to the scattering vectors of the corresponding reflecting planes. The magnetic contribution to the (200) reflection was almost eliminated by a magnetic field of 16 koe, but there was little effect on the (111) intensity by a field of this value. These results indicate that moderate magnetic fields can turn the atomic moments from one cube edge to another, but these fields are not sufficiently strong to rotate the moments to a direction parallel to the cube diagonal.

The neutron diffraction results from TbN are similar to those which were obtained from HoN. At room temperature, the paramagnetic scattering is consistent with that calculated for the trivalent Tb ion, and at low temperatures the compound becomes ferromagnetic with a Curie point about 43°K. Although the diffraction patterns from TbN at 1.3°K show a ferromagnetic short-range-order scattering similar to that observed from HoN, the intensity of this scattering is smaller. Therefore, there is less difficulty in obtaining the size of the ferromagnetic moment from the magnetic reflections, and these calculations give a value of 7.0 μ_B per Tb ion. This value is also lower than the maximum ordered moment (9.0 μ_B) associated with the Tb^{+3} ion and indicates the effect of the crystalline field. Investigations of the intensities of the magnetic reflections in an external magnetic field suggest that in TbN the direction of easy magnetization is parallel to the cube diagonal.

Additional experiments will be performed on HoN and TbN to investigate the nature of the small angle scattering from these compounds and to obtain a better magnetic form factor associated with the 4*f* electrons in these ions. Neutron scattering experiments will also be performed on the other rare earth nitrides which have sufficiently small absorption cross sections to permit analysis by this technique.

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[3] G. T. Trammell (private communication).

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Direct Cation-Cation Interactions in Primarily Ionic Solids*

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It is pointed out that there is considerable experimental evidence for direct cation-cation interactions in several primarily ionic solids containing transition-element cations with outer-electron configuration nd^m, where $m \leq 5$. Competitive indirect (cation-anion-cation) interactions are dominant if $m=5$. Nevertheless, if cation-occupied octahedra share a common face, as in the corundum and NiAs-type structures, the direct (cation-cation) interactions may also significantly influence the physical properties of the material. If octahedral-site cations have $m \leq 3$, the cation-anion-cation interactions are weak and cation- -cation interactions may be dominant. The consequences of cation- -cation interactions are described and shown to be quite distinct from those of cation-anion-cation interactions so that the dominant mechanism can usually be distinguished. Data for several illustrative materials are presented.

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THE purpose of this paper is to point out some of the electric, magnetic, and crystallographic consequences to be associated with cation- -cation (no anion intermediary) interactions in primarily ionic crystals and to review the experimental data on several compounds that appear to illustrate the importance of these effects.

Cation- -cation interactions are induced by the overlap of partially filled *d* orbitals of neighboring transition-element cations. In the illustrative examples of this effect, the interacting cations are located in octahedral (or distorted octahedral) interstices of an anion sublattice, so that cation- -cation interactions are possible if cation-occupied octahedra share either a common face or a common edge. In a cubic structure, crystalline

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