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Neutron Diffraction Study of the Magnetic Structure of $BaNiF_4$

D. E. Cox
Brookhaven National Laboratory, Upton, New York 11973*

AND

M. Eibschütz, H. J. Guggenheim, and L. Holmes
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

The orthorhombic compounds $BaMF_4$ (M = Mn, Fe, Co, or Ni) have recently been found to undergo antiferromagnetic transitions at low temperatures. Susceptibility measurements on $BaNiF_4$ reveal that a broad maximum occurs at about 150°K similar to that observed in a number of layer-type structures. As the temperature is lowered, $\chi_{\|}$ along b decreases rapidly, while $\chi_{\perp}$ goes through a shallow minimum around 50°K. At 77°K, no magnetic order can be detected in powder neutron diffraction patterns of $BaNiF_4$, but at 4.2°K there are magnetic peaks which can be indexed on a unit cell doubled along the b and c directions ($A2_1am$ orientation). The magnetic structure consists of puckered (010) sheets within which the moments are coupled antiparallel to neighboring moments about 4-Å apart. However, the crystal structure is such that the net interaction between adjacent sheets is zero, and ordering in the b direction depends upon interactions between second nearest sheets 14-Å apart. This is very similar to the situation in K_2NiF_4 and pronounced two-dimensional behavior is therefore to be expected. The moments are directed along the b axis and the ordered moment is about 2.0 μ_B per Ni ion. The magnetic symmetry is actually monoclinic, and the simplest magnetic space group is $P_{2a}2_1$.

INTRODUCTION AND EXPERIMENTAL DETAILS

The isostructural family of mixed fluorides $BaMF_4$, where M is one of the divalent transition metal ions Mn, Fe, Co, or Ni, have recently been shown to possess a number of interesting magnetic and electrical properties. The Co and Ni compounds are ferroelectric,[1] and all four are piezoelectric and exhibit antiferromagnetic behavior at low temperatures.[2,3] The present paper describes the results of a magnetic susceptibility and neutron diffraction study of $BaNiF_4$, which reveals that pronounced two-dimensional magnetic behavior is to be expected in this material.

The crystal structure of these compounds has been found to be orthorhombic.[4] It may be described essentially as a sequence of heavily puckered (010) layers of distorted MF_6 octahedra with Ba ions in between. The transition metal ions within the layers are about 4-Å apart and form M–F–M configurations which are quite close to being linear. The centers of the puckered layers are separated by slightly more than 7 Å in the b direction.

The samples of $BaNiF_4$ were prepared by melting BaF_2 and NiF_2 in an atmosphere of HF. Single crystals were obtained by the horizontal zone-melting method. Susceptibility measurements were made on single crystals with a vibrating sample magnetometer at temperatures between 1.4° and 300°K and fields of up to 14.5 kOe. Powder neutron data were obtained at 4.2° and 77°K with neutrons of wavelength 1.125 Å.

RESULTS AND DISCUSSION

Susceptibility curves are shown in Fig. 1. The data are qualitatively very similar to those reported for the two-dimensional antiferromagnet K_2NiF_4.[5] A broad maximum occurs at about 150°K, and the susceptibility along the b axis decreases rapidly at lower temperatures. In the perpendicular plane there is a shallow minimum at about 50°K. The material is isotropic at high temperatures and in the a–c plane at low temperatures to within about 6%.

The 77°K neutron data revealed no peaks of magnetic origin. All the reflections could be indexed on the basis of the chemical cell ($a = 5.77_5$ Å, $b = 14.36_9$ Å, $c = 4.13_9$ Å; A 2_1am orientation). Intensity calculations made with the parameters found for $BaZnF_4$[4] gave only fair agreement. Therefore, although the crystal structure is relatively complicated with twelve variable positional parameters, a least-squares refinement of the 77°K data utilizing 21 observations was attempted. The final parameter values were as follows [all atoms in 4(a) positions $x, y, 0$]. Ba: −0.037, 0.147, 0; Ni: 0.0, 0.414, 0; F(1): 0.287, 0.475, 0; F(2): 0.201, 0.300, 0; F(3): −0.255, 0.329, 0; F(4): 0.023, 0.917, 0; the weighted R factor being 0.061. Standard errors were approximately 0.01 and 0.003 for the x and y parameters respectively. The final values are not much different from those of $BaZnF_4$, but must be regarded as rather tentative in view of the limited amount of data.

At 4.2°K, a number of small additional peaks were observed in the neutron pattern which could be indexed with a unit cell doubled in the b and c directions. The simple collinear magnetic arrangement depicted in Fig. 2 was found to account for the observed intensities very satisfactorily. The spin direction lies along the b axis, as demonstrated by the susceptibility data, and the ordered moment is 1.9_6 μ_B per Ni ion, with an estimated possible error of 0.2 μ_B. The experimental Ni^{2+}

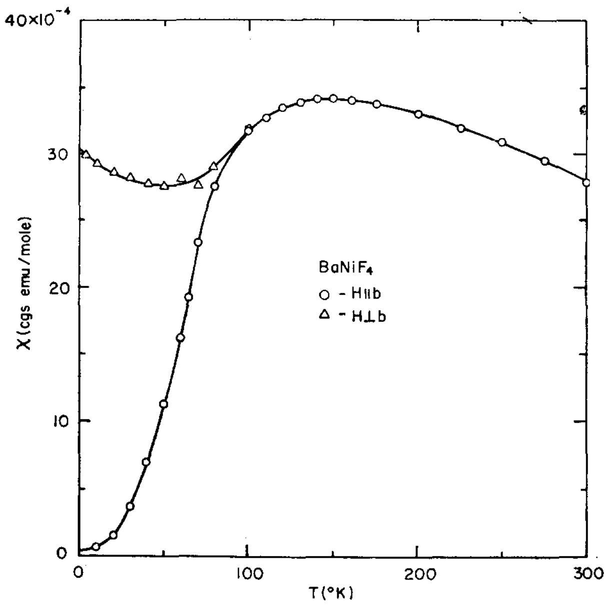

FIG. 1. Single-crystal susceptibility data for $BaNiF_4$.

form factor determined for NiO by Alperin[6] was used in these calculations. Observed and calculated intensities are listed in Table I.

The magnetic symmetry of this structure is actually not orthorhombic, but monoclinic. There are two equivalent magnetic cells which can be derived by doubling either the *a* or the *c* axis of the primitive monoclinic cell which is related to the face-centered orthorhombic cell by the following transformation: $\mathbf{a}_m = -\frac{1}{2}(\mathbf{b}_0 - \mathbf{c}_0)$, $\mathbf{b}_m = \mathbf{a}_0$, $\mathbf{c}_m = \frac{1}{2}(\mathbf{b}_0 + \mathbf{c}_0)$. The simplest magnetic space group would then be $P_{2a}2_1$. However, there was no indication in the neutron patterns of any changes in the nuclear peaks which might reflect a lowering of the symmetry.

It is clear that the maximum in the susceptibility curves at 150°K cannot correspond to the onset of long-range three-dimensional order. The parallel situation in structures of K_2NiF_4 type has been discussed by Lines[7] in terms of a two-dimensional model and investigated in considerable detail by Birgeneau *et al.*[8] A closer look at the structure in Fig. 2 strongly suggests that this is also applicable to $BaNiF_4$. Within the puckered (010) layers a given moment is coupled antiparallel to four nearest neighbors: two at a distance of 4.1 Å, and two at 3.8 Å. These intralayer exchange interactions are probably quite strong, since they involve Ni–F–Ni configurations which are not far from being linear. However, it is evident that a given moment within the layer centered at $y=0.5$, for example, has equal numbers of parallel and antiparallel crystallographically equivalent neighbors in adjacent layers centered at $y=0$ and $y=1$. The net interaction between adjacent layers is therefore zero just as in K_2NiF_4. Ordering in the *b* direction is determined by interactions between next nearest layers which are about 14-Å apart. The doubling of the cell perpendicular to the layers is analogous to the situation in Ca_2MnO_4[9]; it seems reason-

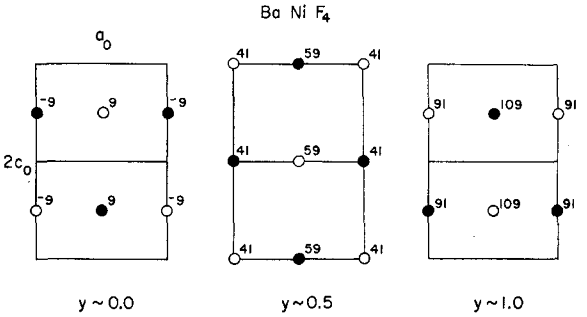

FIG. 2. Magnetic structure of $BaNiF_4$ showing three successive (010) layers. Open and closed circles depict oppositely directed moments along the *b* axis. Small numerals denote height in units of 0.01 b. Only Ni ions are shown.

TABLE I. Comparison of observed and calculated nuclear (I_N) and magnetic (I_M) intensities for $BaNiF_4$. Atomic positions as in text. μ(Ni) taken as 1.96 μ_B.

h	*k*	*l*	I_N(calc) 77°K	I_M (calc) 4.2°K	*I* (obs) 4.2°K	*I* (obs) 77°K
0	$\frac{1}{2}$	$\frac{1}{2}$	···	7	8	···
0	2	0	54	···	52	53
0	$\frac{3}{2}$	$\frac{1}{2}$	···	20	16	···
0	$\frac{5}{2}$	$\frac{1}{2}$	···	11	289	216
1	$\frac{1}{2}$	$\frac{1}{2}$	···	62		
1	2	0	223	···		
1	$\frac{3}{2}$	$\frac{1}{2}$	···	21	18	···
0	1	1	237	···	263	265
0	$\frac{7}{2}$	$\frac{1}{2}$	···	4	73	65
1	$\frac{5}{2}$	$\frac{1}{2}$	···	1		
0	4	0	66	···		
1	1	1	166	···	169	165
0	3	1	1	···	2	2
1	$\frac{7}{2}$	$\frac{1}{2}$	···	1	211	210
1	4	0	226	···		
0	$\frac{9}{2}$	$\frac{1}{2}$	···	1	<5	···
2	0	0	28	···	27	25
1	3	1	48	···	48	46
0	$\frac{1}{2}$	$\frac{3}{2}$	···	···		
2	$\frac{1}{2}$	$\frac{1}{2}$	···	1	129	123
2	2	0	120	···		
0	$\frac{3}{2}$	$\frac{3}{2}$	···	4		
1	$\frac{9}{2}$	$\frac{1}{2}$	···	3		
2	$\frac{3}{2}$	$\frac{1}{2}$	···	8	7	···
0	$\frac{11}{2}$	$\frac{1}{2}$	···	0	22	···
0	$\frac{5}{2}$	$\frac{3}{2}$	···	6		
2	$\frac{5}{2}$	$\frac{1}{2}$	···	11		

able to expect that some of the other BaMF$_4$ compounds might not show a doubling in this direction by analogy with K$_2$NiF$_4$.

Neutron studies of some of the other compounds of this type, and as a function of temperature, are being undertaken.

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Neutron Diffraction Measurement of the Effective Magnetic Moment of Ni^{2+} in KNiF$_3$*

M. T. HUTCHINGS
Brookhaven National Laboratory, Upton, New York 11973
AND
H. J. GUGGENHEIM
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

Two main effects reduce the apparent moment associated with a cation in an ordered antiferromagnet. Covalency tends to spread the moment onto the adjacent anions resulting in a loss due to cancellation at the ligand,[1] and the nature of the antiferromagnetic ground state gives rise to zero point deviations from fully aligned spins.[2] The latter effect has proved very difficult to measure experimentally with accuracy. In principle the moment associated with the cation may be measured using neutron diffraction by extrapolation of the magnetic Bragg peak intensities to forward scattering. The present measurements were carried out on an ideal antiferromagnet, KNiF$_3$, in order to test the current theories of covalency and spin deviations. The magnitude of both effects may be predicted in this compound [1,2] as the covalency parameters are known from NMR work.[3] From powder diffraction at 4.2°K we find a value of 1.495(±0.020) for $[g\langle S_z\rangle_0 f(\tau_{111})/F_{200}]$ giving a value of 0.851(±0.050) for the effective value of $\langle S_z\rangle_0$. The error in $\langle S_z\rangle_0$ here includes both the random error of the experiment (0.011), and possible systematic errors (0.039) due to the uncertainties in the current values of the Ni^{2+} g factor, the form factor, and the nuclear scattering lengths. This value for $\langle S_z\rangle_0$ may be compared with 0.803 calculated using the molecular orbital theory of covalency and spin wave theory, and 0.832 calculated using covalency parameters determined from a configuration interaction approach[4] and perturbation calculations of the spin deviation.[5] The experiments thus confirm the order-of-magnitude of the theoretical prediction, but the current systematic errors preclude an exact test of the theoretical approach at the present time. The measurements illustrate the difficulties in obtaining precise values of either covalency parameters or the spin deviation using this technique.

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