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Magnetic Structure of the Two-Dimensional Antiferromagnet $BaCoF_4$

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The results of magnetic-susceptibility and neutron-diffraction measurements on $BaCoF_4$ show behavior characteristic of a two-dimensional antiferromagnet. The material is highly anisotropic and exhibits two magnetic phases, *A* and *B*, both of which order in three dimensions at the same temperature, $T_N = (69.6 \pm 0.1)$ °K. The magnetic structure consists of puckered (010) layers of moments within which nearest neighbors are coupled antiparallel. The ordering of the moments 14 Å apart in the *b* direction is antiparallel in phase *A* and parallel in phase *B*. The moments are directed along [100]. If the Co^{2+} moment is assumed to be the same for both phases, then the ordered moments have a magnitude of $(3.4 \pm 0.2)\mu_B$ at 4.7 °K.

I. INTRODUCTION

Properties characteristic of two-dimensional magnetic behavior are to be expected in $BaCoF_4$ from the nature of the crystal structure.[1,2] In this there are puckered layers of CoF_6 octahedra, with an interlayer separation (7 Å) which is almost double the separation of the Co^{2+} ions within the layer (4 Å). Magnetic studies in the isomorphous compounds $BaMF_4$ (M = Mn, Fe, Ni) have revealed pronounced two-dimensional magnetic behavior.[3] We report here the results of magnetic-susceptibility and neutron-diffraction studies which have been undertaken to clarify the nature of the magnetic ordering in $BaCoF_4$.

The compound has been assigned the orthorhombic space group $C_{2v}^{12} - A2_1am$ with four formula units per unit cell[1] ($a_0 = 5.8519_3$ Å, $b_0 = 14.628_2$ Å, and $c_0 = 4.2102_3$ Å at 298 °K).[2] The structure[2] consists of distorted CoF_6 octahedra sharing corners to form puckered sheets perpendicular to the [010] direction. The sheets are separated by nonmagnetic Ba^{2+} ions. Within the sheets there are nearly linear Co-F-Co-F configurations parallel to the *c* axis and zig-zag Co-F-Co-F configurations which are parallel to the *a* axis and have a Co-F-Co angle of 146.5°.[2] The dominant feature of the crystal structure (shown in Fig. 1) is the presence of largely "isolated" layers of magnetic Co^{2+} ions.

II. EXPERIMENTAL

The samples were synthesized from the melts of high-purity BaF_2 and CoF_2 in an atmosphere of HF. Single crystals of $BaCoF_4$ were obtained by means of the horizontal-zone-melting method. The general direction of growth was parallel to the *b* axis. The crystals have excellent (010) cleavage planes, and are transparent and a uniform violet in color. Magnetic-susceptibility measurements were made with a vibrating-sample magnetometer. Approximately 200-mg samples were mounted free of strain (i.e., not glued) in the magnetometer, and χ was measured as a function of temperture between 1.4 and 300 °K. Neutron-diffraction data were obtained both on a powder sample and a sin-

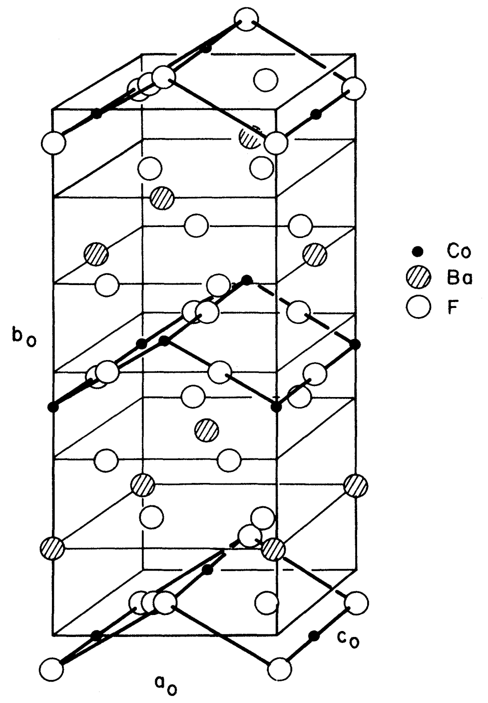

FIG. 1. Idealized picture of the structure of $BaCoF_4$.

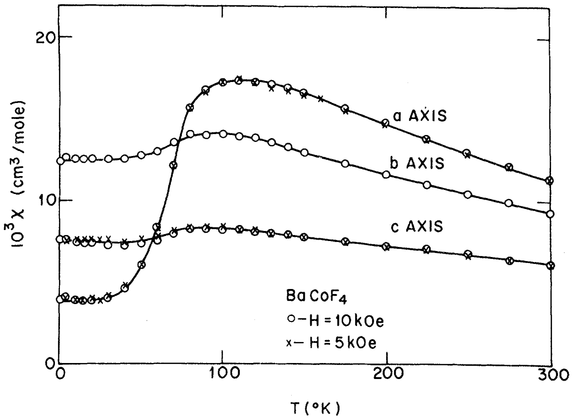

FIG. 2. Magnetic susceptibility χ along the three crystal axes in BaCoF$_4$.

gle crystal with dimensions 3 × 6 × 8 mm with neutrons of wavelengths 1.03 and 1.20 Å, respectively, at temperatures between 4.7 and 80 °K.

III. RESULTS AND DATA ANALYSIS

A. Magnetic Susceptibility

The magnetic-susceptibility curves for crystals of BaCoF$_4$ are shown in Fig. 2. The χ curves display broad maxima at (110 ± 10) °K for $H \parallel a$ and at 90 ± 10 °K for $H \perp a$. All three curves have maximum slope at the same temperature, $T' \approx 70$ °K. Along the a axis, χ decreases to an apparent Van Vleck limit, $\chi_{vv} = (4.0 \pm 0.5) \times 10^{-3}$ cm/mole, at 1.4 °K. Except for the anisotropy in the (100) plane, which is due to the orthorhombic symmetry, the behavior is similar to the anisotropic two-dimensional antiferromagnets, K$_2$CoF$_4$ and Rb$_2$CoF$_4$.[4] No evidence was found of a field-dependent χ, as has been reported[5] by Zorin *et al.*, as shown by the points at 5 and 10 kOe in Fig. 2.

B. Magnetic-Structure Determination

Powder-neutron-diffraction data at 80 and 4.7 °K are shown in Fig. 3. The nuclear data are con-

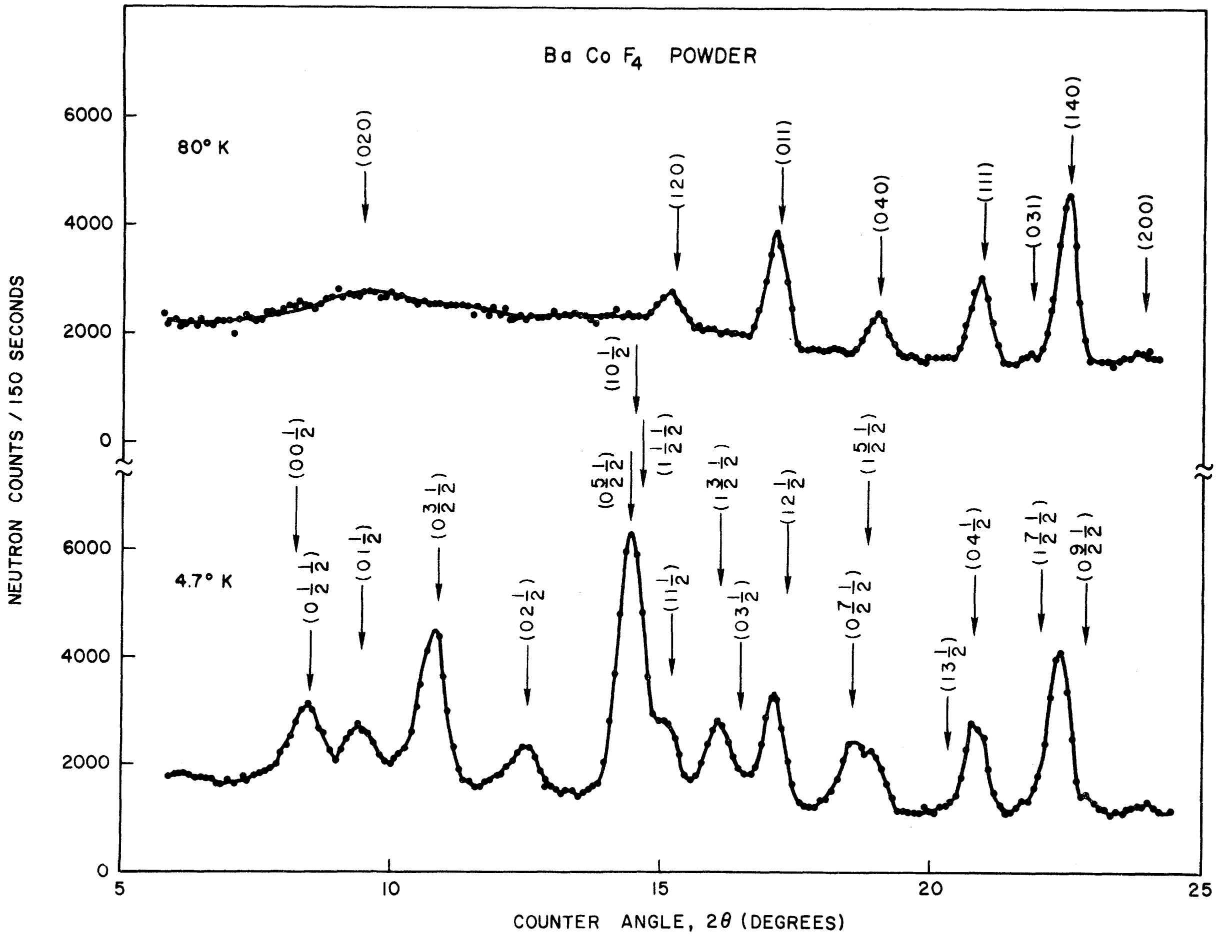

FIG. 3. Neutron-diffraction patterns from a powder sample of BaCoF$_4$ at 80 and 4.7 °K. All peaks are indexed in terms of the chemical cell.

TABLE I. Comparison of observed and calculated nuclear and magnetic intensities for a powder sample of $BaCoF_4$ at 4.7 and 80 °K based on atomic positions from Ref. 2, assuming spin direction along a and Co^{2+} moment $3.3\mu_B$.

$h\ k\ l$	I_{calc}		I_{obs} (4.7 °K)	I_{obs} (80 °K)
$0\ \frac{1}{2}\ \frac{1}{2}$	32.1		58.2	...
$0\ 1\ \frac{1}{2}$	31.4	35.1	33.8	<5.0
$0\ 2\ 0$	3.7			
$0\ \frac{3}{2}\ \frac{1}{2}$	139.7		152.3	...
$0\ 2\ \frac{1}{2}$	49.3		41.9	...
$1\ 0\ \frac{1}{2}$	14.7	284.6	307.1	26.3
$0\ \frac{5}{2}\ \frac{1}{2}$	131.8			
$0\ \frac{1}{2}\ \frac{1}{2}$	84.3			
$1\ 1\ \frac{1}{2}$	22.7			
$1\ 2\ 0$	31.1			
$1\ \frac{3}{2}\ \frac{1}{2}$	44.4	77.1	62.5	...
$0\ 3\ \frac{1}{2}$	32.7			
$0\ 1\ 1$	76.7	83.1	91.0	89.5
$1\ 2\ \frac{1}{2}$	6.4			
$0\ \frac{7}{2}\ \frac{1}{2}$	65.0	113.6	101.2	30.9
$1\ \frac{5}{2}\ \frac{1}{2}$	3.4			
$0\ 4\ 0$	45.1			
$1\ 3\ \frac{1}{2}$	0.1	68.6	84.1	64.1
$0\ 4\ \frac{1}{2}$	12.0			
$1\ 1\ 1$	56.5			
$0\ 3\ 1$	4.2	174.0	57.5	141.4
$1\ \frac{7}{2}\ \frac{1}{2}$	7.7			
$1\ 4\ 0$	145.9			
$0\ \frac{9}{2}\ \frac{1}{2}$	16.2			
$2\ 0\ 0$	2.0	8.2	5.3	<5.0
$1\ 4\ \frac{1}{2}$	6.2			
$1\ 3\ 1$	61.8	264.8	325.3	231.1
$0\ \frac{1}{2}\ \frac{3}{2}$	2.4			
$2\ \frac{1}{2}\ \frac{1}{2}$	0.5			
$2\ 2\ 0$	145.8			
$2\ 1\ \frac{1}{2}$	0.7			
$0\ 5\ \frac{1}{2}$	1.6			
$0\ 1\ \frac{3}{2}$	2.8			
$0\ \frac{3}{2}\ \frac{3}{2}$	15.8			
$1\ \frac{9}{2}\ \frac{1}{2}$	28.1			
$2\ \frac{3}{2}\ \frac{1}{2}$	5.2			
$0\ 2\ \frac{3}{2}$	7.0		5.4	...
$1\ 2\ \frac{1}{2}$	2.9		1.3	...
$0\ \frac{11}{2}\ \frac{1}{2}$	0.4			
$1\ \frac{1}{2}\ \frac{3}{2}$	36.0			
$0\ \frac{5}{2}\ \frac{3}{2}$	23.2	91.2	138.6	...
$2\ \frac{5}{2}\ \frac{1}{2}$	12.0			
$1\ 5\ \frac{1}{2}$	10.6			
$1\ 1\ \frac{3}{2}$	9.1			

sistent with the room-temperature crystallographic space group.[1,2] The 80 °K neutron data revealed no peaks of magnetic origin. At 4.7 °K two sets of magnetic peaks are observed. The first of these sets is of the type $(h, \frac{1}{2}k, \frac{1}{2}l)$ with k and l odd integers, showing that the magnetic unit cell is doubled along the b and c axes, as in the isostructural compounds $BaNiF_4$ and $BaFeF_4$.[3] The second set of magnetic reflections is of the type $(h, k, \frac{1}{2}l)$ with l an odd integer, consistent with a magnetic unit cell which is doubled only along the c direction. Intensity calculations reveal that in both cases the moments are directed along the a axis, and we conclude that there were two distinct coexisting magnetic phases, A and B. The B phase has not previously been observed in the $BaMF_4$ series. Thus $BaCoF_4$ behaves in a fashion analogous to that of Rb_2MnF_4.[6]

A least-squares refinement of the data gives satisfactory agreement for the magnetic structures depicted in Fig. 4. Best agreement with the observed intensities for the two sets of peaks is obtained if the spin direction is along the a axis. If the Co^{2+} moment is assumed to be the same for both structures, the relative proportion of the A and B phases is about 3 : 1 and the Co^{2+} moment is $(3.3 \pm 0.2)\mu_B$. The theoretical form factor[7] was used in these calculations. Observed and calculated powder-nuclear and magnetic intensities at 80 and 4.7 °K are given in Table I. (All the indices in the table are based on the chemical cell.) Intensity calculations were made using the 25 °C positional parameters from Keve *et al.*[2] and zero-temperature factors. The weighted R factors

$$R_w = [\sum w(I_{obs} - I_{calc})^2/\sum w(I_{obs})^2]^{1/2}$$

for the 80 and 4.7 °K data are 16.5% and 16.3%, respectively. In each structure there is antiferro-

TABLE II. Observed and calculated magnetic intensities for a single crystal of $BaCoF_4$ at 4.7 °K, assuming spin direction along a and Co^{2+} moment of $3.4\mu_B$. The last four reflections are nuclear ones.

$h\ k\ l$[a]	I_{calc}	I_{obs}	Phase
$0\ \frac{1}{2}\ \frac{1}{2}$	12.6	17.4	A_I [b]
$0\ 1\ \frac{1}{2}$	94.0	87.8	B[c]
$0\ \frac{3}{2}\ \frac{1}{2}$	187.9	194.8	A_{II}
$0\ 2\ \frac{1}{2}$	198.4	196.6	B
$0\ \frac{5}{2}\ \frac{1}{2}$	90.8	85.8	A_I
$0\ 3\ \frac{1}{2}$	180.2	180.1	B
$0\ \frac{7}{2}\ \frac{1}{2}$	162.0	147.4	A_{II}
$0\ 4\ \frac{1}{2}$	87.5	94.0	B
$0\ \frac{1}{2}\ \frac{3}{2}$	8.7	16.2	A_{II}
$0\ 1\ \frac{3}{2}$	26.9	28.4	B
$0\ \frac{3}{2}\ \frac{3}{2}$	22.8	23.1	A_I
$0\ 2\ \frac{3}{2}$	72.1	70.9	B
$0\ \frac{5}{2}\ \frac{3}{2}$	97.4	98.6	A_{II}
$0\ 3\ \frac{3}{2}$	79.5	77.1	B
$0\ 2\ 0$	8.6	15.8	Nuclear
$0\ 1\ 1$	162.7	165.3	Nuclear
$0\ 4\ 0$	212.3	190.5	Nuclear
$0\ 3\ 1$	11.3	15.6	Nuclear

[a] Indexed on the chemical cell.

[b] Phase A $(a, 2b, 2c)$ [A_I $k + l = 4n + 2$, A_{II} $k + l = 4n$; the indices hkl for these conditions correspond to the magnetic cell].

[c] Phase B $(a, b, 2c)$.

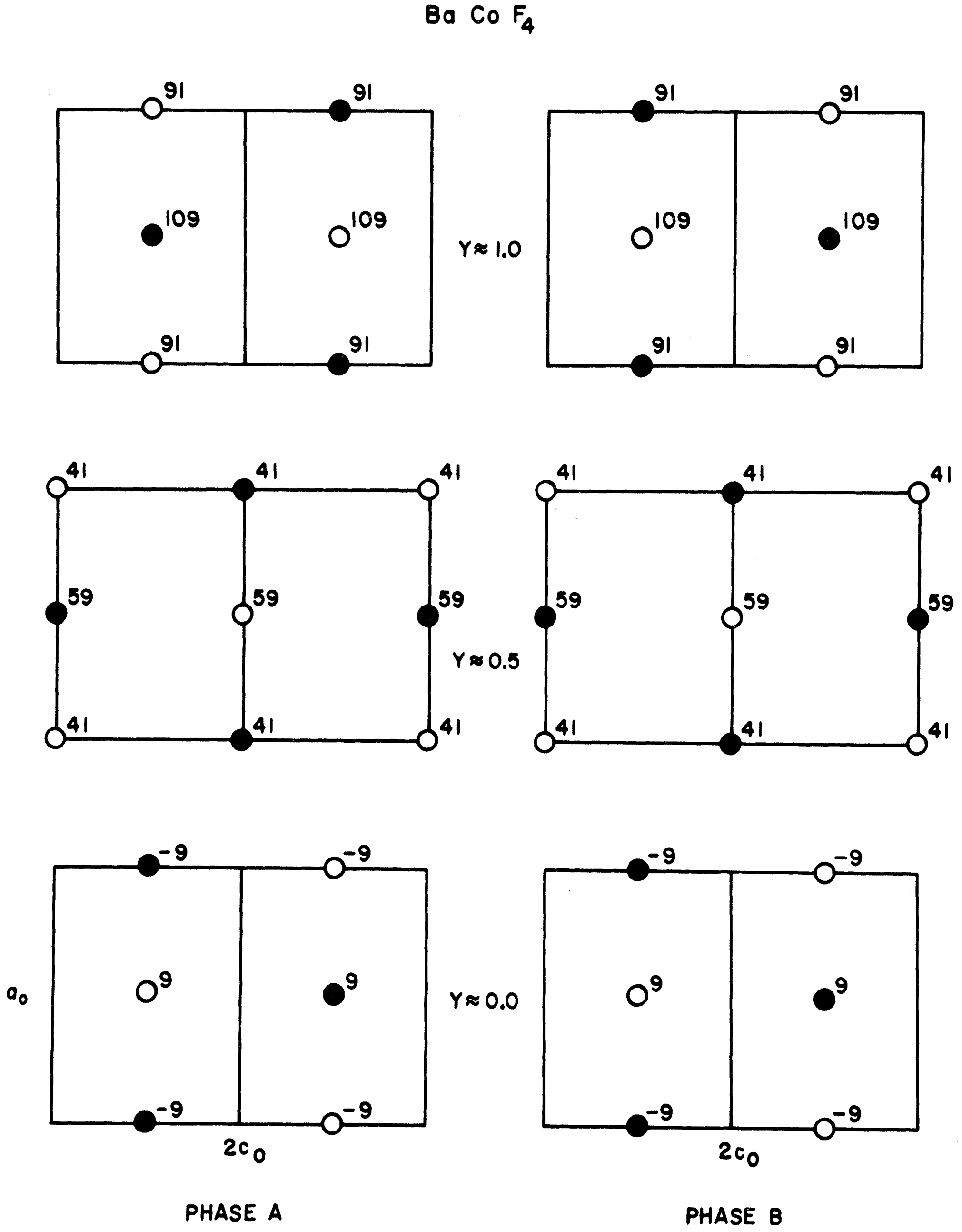

FIG. 4. Magnetic structure of phase *A* and *B* in $BaCoF_4$. Open and closed circles represent oppositely directed moments. Spin axis is along [100] direction in both cases. Only Co^{2+} ions are shown.

magnetic coupling within sheets in the *ac* planes, but the stacking of the sheets in the *b* direction differs in exactly the same way as in K_2NiF_4 and Ca_2MnO_4.[8] The net interaction between nearest-neighbor sheets 7 Å apart is zero, as a given moment has two parallel and two antiparallel equivalent neighbors in the adjacent sheets. However, Co^{2+} neighbors 14 Å apart along the [010] direction have their moments *parallel* in phase *B*, and *antiparallel* in phase *A*. Within the puckered (010) sheets a given magnetic moment is coupled antiparallel to four nearest neighbors, two at a distance of 3.9 Å and two at a distance of 4.2 Å. The intralayer exchange interactions are probably strong, since they involve Co-F-Co configurations which are not far from being linear.

Single-crystal neutron data were also collected at 80 and 4.7 °K. The data confirm the magnetic

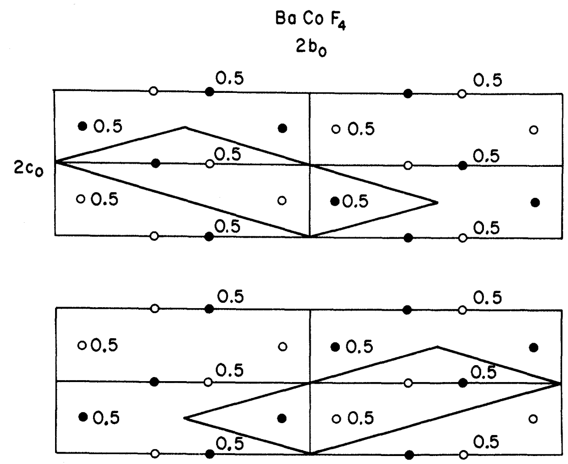

FIG. 5. Magnetic structure of phase A of $BaCoF_4$. Open and closed circles represent oppositely directed moments. Spin axis is along [100] direction. The two settings of the monoclinic unit cell shown correspond to the two magnetic domains of phase A. Only the Co^{2+} ions are shown.

structures proposed above, i.e., the simultaneous existence of the two magnetic phases in the same sample. In this case the A/B is about 9 : 11. The different ratios observed in the powder and in the single crystal can be explained using the model proposed by Birgeneau *et al.*[6] Apparently, the net coupling between the sheets is so weak that the two phases have about equal energy, so that local microscopic phenomena (e.g., strain, impurities, dislocations) will determine which phase appears in a given region of the sample. The single-crystal intensities were corrected for absorption. A least-squares fit to the data yields a Co^{2+} moment in the single crystal of $(3.4 \pm 0.2)\mu_B$. Observed and calculated single-crystal magnetic intensities at 4.7 °K are given in Table II. Also in Table II are listed four nuclear intensities which were used in order to obtain an instrumental scaling constant. These indicate that at least in this intensity range extinction effects are relatively minor. The R factor is 0.055 and the R_w factor is 0.115.

The good agreement between I_{obs} and I_{calc} in Tables I and II confirms that the arrangement in Fig. 4 is indeed correct, and also that the moments are directed along the a axis, rather than the b axis, as observed in the isostructural compounds $BaMF_4$ (M = Mn, Fe, Ni). The value of the magnetic moment $(3.4\mu_B)$ is close to the spin-only value of $3\mu_B$.

The magnetic symmetry of phase A 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: $a_m = -\frac{1}{2}(b_0 - c_0)$, $b_m = a_0$, $c_m = \frac{1}{2}(b_0 + c_0)$. There are two equivalent spin arrangements (domains) corresponding to the monoclinic cell. These are illustrated in Fig. 5, which also shows the two settings of the monoclinic cell. The domains are labeled A_{I} and A_{II} in Table II and they correspond to the following allowed systematic reflections: $A_{\text{I}}: k + l = 4n + 2$ and $A_{\text{II}}: k + l = 4n$. (Note that the indices hkl for the above conditions are based on the orthorhombic magnetic cell.) The ratio of the two domains $A_{\text{I}} : A_{\text{II}}$ in the single crystal was found to be 4 : 11. The simplest magnetic Shubnikov space group is $P_{2a}2_1$. The B phase remains orthorhombic and the most probable magnetic space group is $P_{2c}2_1ab$.

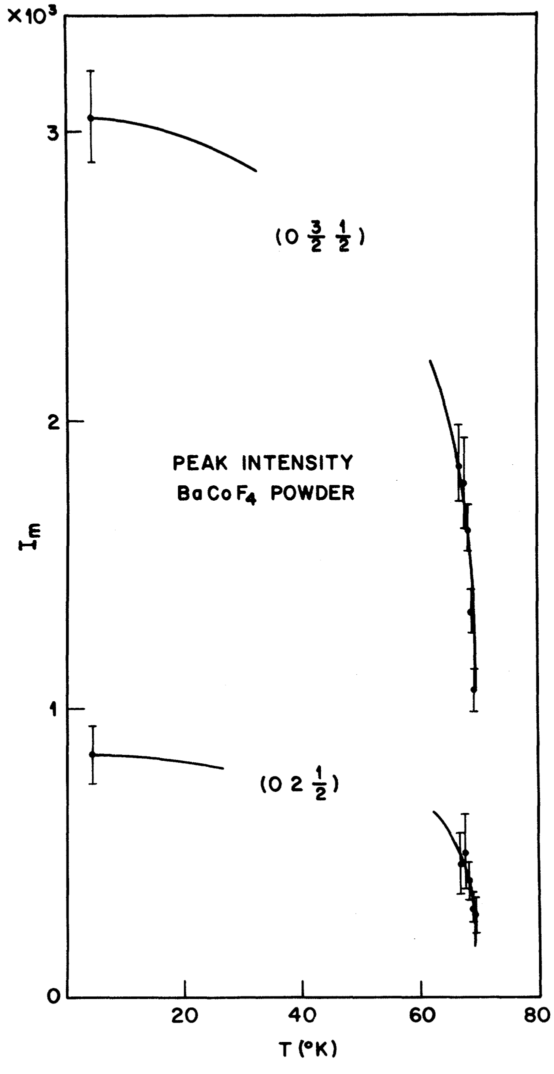

FIG. 6. Variation of observed powder magnetic intensities (I_m) from $BaCoF_4$ as a function of temperature.

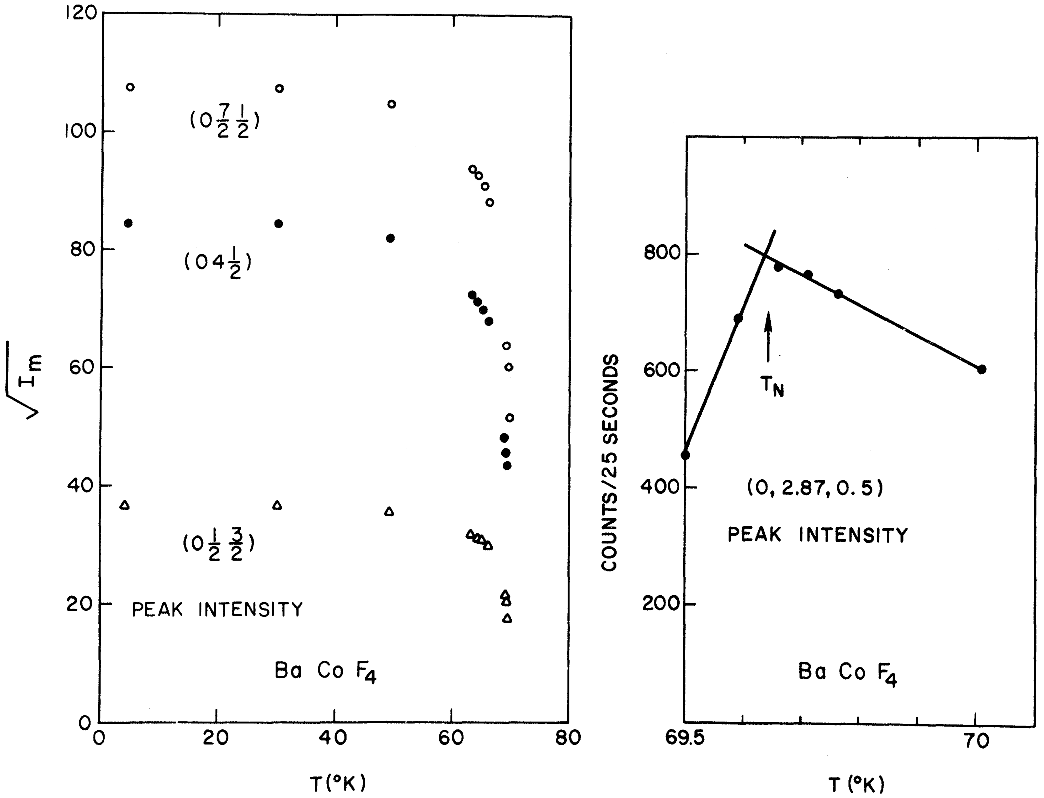

FIG. 7. (a) Variation of the square root of the observed single-crystal magnetic intensities (I_m) from $BaCoF_4$ as a function of temperature. (b) Intensity variation in $BaCoF_4$ at a point slightly off the Bragg peak (0, 2.87, 0.5) as a function of temperature in the immediate vicinity of the phase transition.

C. Temperature Dependence of Magnetic Intensities

The temperature dependence of the magnetic Bragg reflections was measured in order to determine the temperatures at which three-dimensional ordering occurs in each domain. The variations of the magnetic intensities of the $(0\frac{3}{2}\frac{1}{2})$ and $(02\frac{1}{2})$ peaks from the powder data are shown in Fig. 6. The variation of the square root of the magnetic intensities (uncorrected for absorption) for the $(0\frac{1}{2}\frac{3}{2})$, $(04\frac{1}{2})$, and $(0\frac{7}{2}\frac{1}{2})$ peaks from the single-crystal measurements is plotted in Fig. 7(a).

The main result of the measurements in both powder and single-crystal samples is that both phases are found to order three dimensionally at the same temperature $T_N = (69.6 \pm 0.1)^\circ$ K. The temperature variation of the critical scattering at a point slightly off the Bragg peak is also shown in Fig. 7(b). From this figure it may be seen that the magnetic intensity at the point (0, 2.87, 0.5) reaches a maximum at T_N and decreases very rapidly with decreasing temperature below T_N. Simultaneously, the magnetic Bragg intensities increase very rapidly with decreasing temperature [see Fig. 7(a)]. Roughly the same temperature dependence is observed for the three reflections normalized to unity at 4.2 °K, the maximum deviation being 8%. This indicates that the sublattice magnetization is independent of the third dimension at all temperatures and depends solely on the two-dimensional magnetic structure, just as in Rb_2MnF_4.[6] No attempt was made to derive an accurate value for the critical exponent β owing to the limited amount of data.

IV. DISCUSSION

The behavior of the magnetic susceptibility, which shows broad maxima and different curves for χ_a, χ_b, and χ_c, reveals that the magnetic ordering is highly anisotropic (Ising-like), and is characteristic of an anisotropic two-dimensional antiferromagnet. In this context it is interesting to note that due to the high anisotropy in $BaCoF_4$ the substitution of 0.5 at.% Co^{2+} in $BaMnF_4$ is sufficient to change the direction of the moments from the b axis to the a axis at $T < T_N$.[9]

The existence of two magnetic phases in $BaCoF_4$ closely parallels the behavior of Rb_2MnF_4.[6] The two magnetic phases differ only in the stacking of the layers 14 Å apart. In each case there is antiferromagnetic ordering within the (010) sheets with probably quite strong exchange interactions. Interactions between nearest-neighbor (nn) sheets average out to zero, while interactions between next-nearest-neighbor (nnn) sheets are very weak because of the large separation. In both phases the moments are directed along the a axis rather than the b axis as observed in the isostructural compounts $BaNiF_4$ and $BaFeF_4$, and both order three dimensionally at the same temperature. The different ratios of $A:B$ observed in powder and single-crystal samples suggest that local microscopic phenomena determine which structure appears in a given region of the samples.

Owing to the fact that exchange J_b between nnn layers is much smaller than the intralayer exchange J_{ac} it is possible to offer another explanation of the simultaneous existence of the two magnetic phases in the same sample.[10] For $J_b < 0$, an antiparallel alignment of the moments 14 Å apart (phase A) is favored, while for $J_b > 0$ a parallel alignment of the moments results (phase B). A small distortion of the crystallographic structure of phase A to monoclinic symmetry in a given region of the sample could lead to a difference in J_b and therefore two magnetic phases.

It is interesting to note that the crystals of $BaMF_4$ (M = Mg, Co, Ni, and Zn) have been found to be ferroelectric, and those with M = Mn and Fe have been demonstrated to be pyroelectric.[11] If a crystal is to show a linear magnetoelectric effect it must have no center of symmetry and must also be time asymmetric.[12] The noncentrosymmetric space group $C_{2v}^{12} - A2_1am$ allows the presence of a magnetoelectric effect if the magnetic unit cell is identical to the chemical cell. Our results, however, indicate that a linear magnetoelectric effect should not be present in $BaCoF_4$ owing to the enlargement of the unit cell in both phases, which introduces time reversal as a symmetry element into the magnetic point group.[12] This conclusion is in disagreement with the observation of a linear magnetoelectric effect in $BaCoF_4$ by Al'shin *et al.*[13]

V. CONCLUSION

The compound $BaCoF_4$ behaves as a two-dimensional antiferromagnet, with the spins aligned along the a axis. The material is highly anisotropic (Ising-like), and exhibits two magnetic phases, both of which order in three dimensions at the same temperature.

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