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Abstract. A previous study of single crystals of monoclinic barium holmium fluoride, BaHo₂F₈, has shown that, as a result of crystal field splittings, the ground state of the Ho³⁺ ion, 4f¹⁰, ⁵I₈, is a non-Kramers doublet, with a single g value of 14.24, parallel to the crystallographic a axis. A transition to an antiferromagnetically ordered state occurs at about $T_N = 1.76$ K but the precise nature of the magnetically ordered state cannot be determined from these measurements alone. This paper describes the results of a neutron diffraction investigation from 4.2 K down to 0.3 K. An initial measurement on a powdered sample at 0.31 K was sufficient to determine which of three group theoretically allowed magnetic arrangements is present; the structure determined is antiferromagnetic with a $(1\,0\,\frac{1}{2})$ magnetic propagation vector.

1. Introduction

Barium holmium fluoride, BaHo₂F₈, is one of a small group of isomorphous compounds of the heavier ions of the lanthanide series, ranging from dysprosium to lutecium, together with yttrium. Crystal field splitting of the electronic energy levels of the trivalent holmium ion, 4f¹⁰, ⁵I₈, produces excited levels ranging from 60 K almost to 600 K (Christensen H P unpublished, quoted by Nielsen (1985)). The ground state is a non-Kramers doublet, for which the electron spin magnetic resonance (ESR) spectrum of ¹⁶⁵Ho (0.1%) in BaY₂F₈ was observed by Kurkin and co-workers (1979) at liquid helium temperatures. Their measurements, at frequencies from 19 to 71 GHz, showed that the ground doublet has an initial electronic splitting of 0.24 cm⁻¹ = 7.3 GHz, and a single g value of $g = 14.24(3)$. The extensive hyperfine structure of the single stable isotope ¹⁶⁵Ho, $I = \frac{7}{2}$, has been studied by Nielsen (1985) using nuclear magnetic resonance (NMR) at a frequency of 152 MHz. The spectra were fitted accurately using a hyperfine constant $A/h = 9.31$ GHz calculated from the standard relation $A/A_J = g/g_J$, with $A_J = 0.812$ GHz, $g_J = 1.25$. These NMR measurements confirm the parameters found by ESR in the dilute compound.

Later measurements at Oxford (Abraham *et al* 1991) on the compound BaHo₂F₈ have determined (i) the heat capacity from 0.43 K to 22 K, (ii) the Zeeman splittings of lines in the optical absorption spectrum; (iii) the magnetic susceptibility from 0.5 to 4.2 K, and (iv) the magnetic moment at 0.5 K in fields up to 1.5 T. It was shown that antiferromagnetic order sets in at $T_N = 1.76$ K; below this temperature, the heat capacity falls to a minimum at about 1 K, followed by an increase arising from the hyperfine splitting in the ordered

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state. Between 0.43 and 0.6 K the heat capacity is fitted using eight hyperfine levels, equally spaced by $A/k = 0.2234$ K; the corresponding values for the nuclear polarization rise from 33% at 1.4 K to 50% at 0.6 K and 75% at 0.3 K. Some 40% of the electronic magnetic entropy is contained in the heat capacity above the ordering temperature; this is interpreted as evidence for the presence of considerable short-range order.

The magnetization measurements reported by Abraham *et al* (1991) indicate that in the antiferromagnetic state the moments are aligned parallel and antiparallel to the crystallographic a axis. However, these measurements, taken in isolation, are insufficient to determine uniquely the true magnetic configuration of Ho^{3+} moments. In the space group $C2/m$ (C_{2h}^3) appropriate to $BaHo_2F_8$, group theoretical arguments based on the tables of Bradley and Cracknell (1972) determine the possible orientations of the four magnetic ions in the unit cell. Provided that the symmetry of the space group is unaffected by the magnetic phase transition, the magnetic moments of the holmium ions are constrained either to be oriented along the y axis, or to lie in the x–z (a–c) plane. Only one of the four magnetic space groups with (000) as the propagation vector has such properties, but there are two further possibilities. These are again antiferromagnetic, with moments in the x–z plane, and arise if the C lattice translation is associated with a propagation vector along either (100) or (010). In all, there are three alternative ordering arrangements with identical chemical and magnetic cells in each case. Thus the detailed nature of the magnetically ordered state cannot be predicted from symmetry arguments alone and requires the more precise analysis afforded by neutron diffraction.

2. The crystals

For the neutron diffraction experiments at the Risø National Laboratory described in this paper, both a powdered sample and a single crystal of the compound $BaHo_2F_8$ were prepared. The crystals were grown using the Czochralski pulling technique under a partial atmosphere of HF. The starting materials, BaF_2 (BDH Ltd, Optran grade) and HoF_3 (Johnson Matthey Chemicals Ltd, electronic grade), were separately heat treated under HF before being melted together. This produced crystals yellow in colour and optically transparent.

The crystal structure of the isomorphous compound $BaTm_2F_8$ has been determined by Izotova and Aleksandrov (1970); it is monoclinic, space group $C2/m$ (C_{2h}^3). The lattice constants of $BaTm_2F_8$, as determined by x-rays at room temperature, are $a, b, c = 6.935$, 10.457, 4.243 Å, $\beta = 99.7°$. The atomic positions are

$$(000) + \qquad (\tfrac{1}{2}\tfrac{1}{2}0)+$$

Atom	Site	Symmetry		
Ba	(2a)	$2/m$	$(0, 0, 0)$	
Tm	(4h)	2	$\pm(0, y, \tfrac{1}{2})$	$y = 0.176$
F1	(8j)	1	$\pm(x, y, z); (x, \bar{y}, z)$	$x = 0.187, y = 0.140, z = 0.560$
F2	(4m)	m	$\pm(x, 0, z)$	$x = 0.393, z = 0.227$
F3	(4g)	2	$\pm(0, y, 0)$	$y = 0.239$

The positions of the rare earth atoms for two unit cells are illustrated in figure 1; they all lie in the plane at $z = 0.5$. The rare earth ion is surrounded by eight fluorine ions in a slightly distorted cube, with overall symmetry 2 (C2). Barium ions are situated at $(0, 0, 0)$ and $(\tfrac{1}{2}, \tfrac{1}{2}, 0)$.
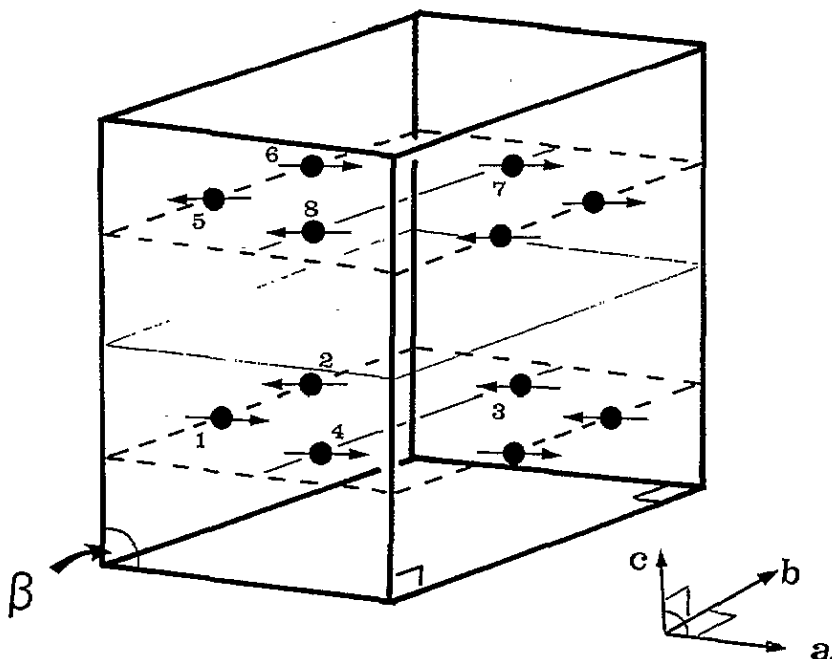
Figure 1. The positions of the rare earth atoms for two unit cells of $BaHo_2F_8$ and the antiferromagnetic configuration below $T_N = 1.665$ K: the Ho^{3+} moment makes an angle of $\pm 95.9(9)°$ to [001].

3. Neutron determination of the ordered antiferromagnetic state

In the experiments at Risø, neutrons of wavelength 2.4237 Å were used for a range of measurements at temperatures from 4.2 K down to 0.3 K, produced by a cryostat fitted with an Oxford Instruments Heliox insert. This made it possible to achieve reproducible measurements at intervals of 1 mK, which is of special importance for measurements close to the Néel point. A preliminary powdered sample profile, obtained at 4 K, well above the Néel temperature, was modelled using the Rietveld method, which confirmed that the crystal structure was isomorphous with that of $BaTm_2F_8$ and established its cell dimensions, the parameters describing the evolution of the line shape as a function of 2Θ and any offset to the zero of the 2Θ scale. The former are found to be $a = 6.948(2)$, $b = 10.447(2)$, $c = 4.2341(2)$ Å, $\beta = 99.6(1.6)°$; these may be compared to the values obtained from x-ray diffraction data for the Tm compound reported above. The neutron data did not extend beyond $\sin \Theta / \lambda = 0.28$ Å^{-1}, so the atomic positional parameters could not be refined with any degree of precision and were consequently fixed at the values obtained from the x-ray study for the Tm isomorph, see above.

A second profile was obtained at $T = 0.31$ K $\ll T_N$ on the same powdered sample. This contained extra reflections of magnetic origin, the $0, 1, \frac{1}{2}$ and $0, 1, \frac{3}{2}$ being particularly strong. Rather than refine the low-temperature data directly, which has the effect of reducing the sensitivity of the overall R factor to the goodness of fit to the magnetic intensities, it was decided to work with the difference profile ($I_{cold} - I_{hot}$). This was fitted in the range $10° < 2\theta < 70°$ to a model with magnetic propagation vector $(1, 0, \frac{1}{2})$ and symmetry $C2'/m$, which confines the holmium moments to lie in the a–c plane. In this refinement,

the line shape parameters and the overall scale factor were fixed to the values obtained from the 4 K nuclear intensity refinement. Figure 2 shows the 'difference fit' obtained for a model with holmium moment $\mu = 6.92(2)\mu_B$, making an angle of $95.5(9)°$ to [001]. Collectively these data indicate that in the ordered antiferromagnetic state the magnetic unit cell is twice the chemical cell along the c axis and an arrangement of Ho^{3+} moments $(+--+)$ is reversed $((-++-))$ in alternate planes at distance $\pm c$. This ordered structure, shown in figure 1, is strongly favoured by magnetic dipolar interactions (see section 4), and the exchange interactions would therefore appear to be relatively weaker. It is clear that BaHo$_2$F$_8$ and its erbium isomorph (work to be published) form magnetic structures with propagation vectors $(1, 0, \frac{1}{2})$. In the latter material the strongest low-angle magnetic reflection is again $0, 1, \frac{1}{2}$ and all the observed additional reflections of magnetic origin can be indexed without debasing the monoclinic symmetry.
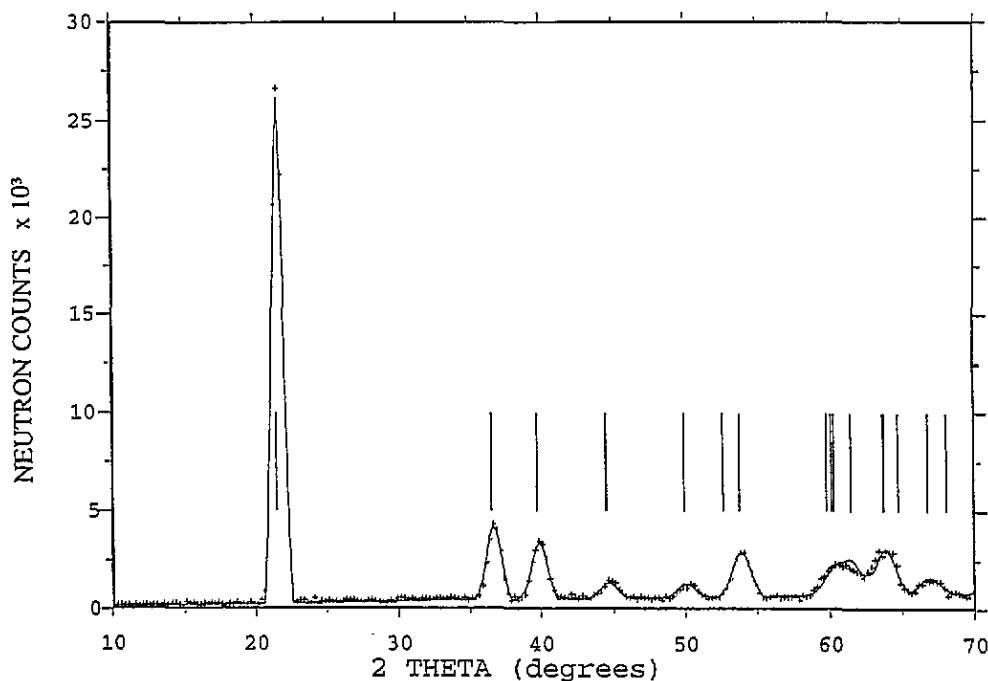

Figure 2. The refinement of the neutron diffraction data with Ho^{3+} moment $\mu = 6.29(2)\mu_B$ at an angle of $\pm 95.5(9)°$ to [001]; the most intense line corresponds to the $0, 1, \frac{1}{2}$ magnetic reflection.

4. Discussion

For the computation of dipolar interactions, the lanthanide ions are labelled 1–8 (see figure 1) and occupy crystallographic positions as follows:

$$\text{ion } 1,5 \text{ at } (0, y, \pm \tfrac{1}{2})$$

$$\text{ion } 2,6 \text{ at } (0, y, \pm \tfrac{1}{2})$$

ion 3,7 at $(\frac{1}{2}, \frac{1}{2} + y, \pm\frac{1}{2})$

ion 4,8 at $(\frac{1}{2}, \frac{1}{2} - y, \pm\frac{1}{2})$ with $y = 0.324$.

Each set of four ions is coplanar, with distance c between the two planes. The shortest interionic distances are $1, 2 = 3.70$ Å and $1, 4 = 2, 3 = 3.82$ Å.

As stated in our earlier paper (Abraham *et al* 1991), provided the symmetry of the space group is unaffected by the magnetic phase transition, there are three possible antiferromagnetic configurations with moments confined to the *a–c* plane: $\langle + - -+\rangle$, $\langle + - +-\rangle$, $\langle + + --\rangle$, and the magnetic unit cell may be double the chemical unit cell. The uncertainty has been removed by this neutron diffraction experiment, which clearly shows that the magnetic unit cell is twice that of the chemical cell along the *c* axis and the magnetic arrangement is $\langle +--+\rangle\langle -++-\rangle$. Thus the calculation of the dipolar interaction field reduces to

$$\langle + - -+\rangle\langle - + +-\rangle \qquad +781$$
$$\langle + - +-\rangle\langle - + -+\rangle \qquad -159$$
$$\langle + + --\rangle\langle - - ++\rangle \qquad -381$$
$$\langle + + ++\rangle\langle - - --\rangle \qquad +683$$

where for completeness we include the other group theoretically allowed possibilities and a modified 'ferromagnetic' configuration. The units are in 10^{-4} tesla for one Bohr magneton at each site.

Of these arrangements $\langle + - -+\rangle\langle - + +-\rangle$ has the highest dipolar field, but that of the last possibility—'ferromagnetic' sheets with adjacent, antiparallel ferromagnetic sheets—is only marginally less. The neutron experiment confirms that the ground configuration is $\langle + - -+\rangle\langle - + +-\rangle$, and it follows that dipolar interactions must predominate, and account for substantially all the experimental results. A comparison may be made with the fully ferromagnetic configuration $\langle + + ++\rangle\langle + + ++\rangle$; for this arrangement the dipole sum is $+111$, which differs from that of $+781$ for the most favourable configuration by 670×10^{-4} T μ_B^{-1}. Since the ordered moment is $6.29\mu_B$, the field required to 'close up' all the moments is 0.42 T. This is in substantial agreement with the field of about 0.5 T required to reach the full magnetic moment, as shown in figure 5 of Abraham *et al*.

A calculation of the total dipolar field in the antiferromagnetic state gives $6.29\mu_B \cdot 0.0781$ T $\mu_B^{-1} = +0.491$ T for our experimental configuration, which, expressed as a temperature, is $\frac{1}{2}MB/k = 1.12$ K, comparable with T_N.

5. Conclusion

The structural analysis of the ordered magnetic state in BaHo₂F₈ is therefore complete. The result of the neutron diffraction experiment is a clear advance over the situation obtained from purely bulk magnetic, optical and thermal data (Abraham *et al* 1991): only neutron diffraction measurements are able to deduce the true nature of the ordered magnetic state. The fit indicates that the directions of the magnetic moments are canted some 4° away from the *a* axis, but confined to the *a–c* plane. This is consistent with the previous measurements.

Further measurements are planned that will enable us to make more precise measurements of the ordered magnetic state. This will include a determination of the

sublattice magnetization M as a function of temperature and in particular the value of the critical exponent β in the formula $M = f(t)^\beta$, from a plot of $\ln M$ versus $\ln t$. (Here the reduced temperature $t = (T_N - T)/T_N$.) However there are difficulties associated with this type of study. Below T_N, where the 0, 1, $\frac{1}{2}$ reflection has an instrumentally limited Gaussian line shape, the sublattice magnetization may be derived from the temperature dependence of the line intensity. A prerequisite for such an analysis is that the Bragg scattering term may be successfully deconvoluted from the integrated line intensity. Whilst in principle this is theoretically possible it remains to be seen whether other terms such as magnetic excitation scattering and magnetic critical scattering can be independently evaluated by experiment.

We are also able to contrast the behaviour of $BaHo_2F_8$ with the erbium compound. Erbium is the element next to holmium in the lanthanide series, with the spectroscopic state $4f^{11}$, $^4I_{15/2}$. In BaY_2F_8, ESR (Kurkin *et al* 1979) showed that the crystal field leaves as the ground state a very anisotropic Kramers doublet with $g = 14.37$ along the a axis. In the compound $BaEr_2F_8$, magnetic and optical spectroscopic measurements (unpublished) show that it orders antiferromagnetically at $T_N = 1.73$ K, with a moment of $7.15\mu_B$ close to the a axis. Both this moment and the value of T_N are very close to those for $BaHo_2F_8$, and preliminary neutron measurements (unpublished) suggest that the ordered state has the same structure. This is further evidence for the interactions being predominantly dipolar in both compounds, since it is improbable that the exchange interaction would be the same for both.

Holmium compounds are unusual in that a number of them attain magnetically ordered states at temperatures of the order of 1 K through predominantly magnetic dipole interaction. They are listed in table 1, in order of increasing transition temperatures, with the volumes containing one holmium ion, together with $BaEr_2F_8$. They are all very anisotropic, and the number of nearest neighbours to each holmium ion is four. The ordered state of $LiHoF_4$ is ferromagnetic; the others are all antiferromagnetic, but with significant differences. The electronic ground states of $HoVO_4$ and HoF_3 are singlets, the first excited levels being at 30 K and 9.5 K respectively. The former is a strongly enhanced nuclear system, with ordered moments in the plane normal to the tetragonal axis (Bleaney 1980). For the other compounds, the electronic ground state is a non-Kramers doublet; for $HoPO_4$ and $LiHoF_4$ the moments are confined to the tetragonal axis, while those for $BaHo_2F_8$ are close to the a axis; the magnetic structure for $BaEr_2F_8$ is the subject of current work.

Table 1.

Compound	Volume (nm^3)	T_N (K)	Ordered moment (μ_B)	Reference
HoVO$_4$	0.0798	0.0048	0.46	Bleaney 1980
HoF$_3$	0.0482	0.53	5.7(2)[a]	Brown *et al* 1990
HoPO$_4$	0.0716	1.39	~8.0	Cooke *et al* 1973
LiHoF$_4$	0.0720	1.53	7.0	Cooke *et al* 1975
BaHo$_2$F$_8$	0.0770	1.665	6.29	Abraham *et al* 1991
BaEr$_2$F$_8$	~0.0770	1.673	5.9(2)	Bleaney *et al* [b]

[a] This includes a substantial contribution from the 'pseudomagnetic' moment.
[b] In preparation.

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