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Abstract

Neutron diffraction investigation of crystal structures and magnetic ordering of cobalt iodine boracite (Co311B7O13I) is reported. The canted antiferromagnetic structure has been detd. at 31 and 9 K, and revealed a magnetic ordering in two steps, without any change in the symmetry of the antiferromagnetic arrangement.

Reference

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MAGNETIC PHASE TRANSITION IN COBALT IODINE BORACITE

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Neutron diffraction investigation of crystal structures and magnetic ordering of cobalt iodine boracite ($Co_3{}^{11}B_7O_{13}I$) is reported. The canted antiferromagnetic structure has been determined at 31 K and 9 K, and revealed a magnetic ordering in two steps, without any change in the symmetry of the antiferromagnetic arrangement.

KEY WORDS: Co-I-boracite, magnetic phase transition, weak ferromagnetism.

1 INTRODUCTION

Cobalt iodine boracite (Co-I-boracite) belongs to a large family of compounds with the general formula $M_3B_7O_{13}X$ (M = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and X = OH, F, Cl, Br, I). These compounds crystallize at high temperature in a cubic phase $F\bar{4}3cl'$ (Yto *et al.*, 1951), and show at lower temperature a great variety of phase transitions (Dowty *et al.*, 1973; Schmid *et al.*, 1978). Among them, Co-I-boracite undergoes a first order ferroelectric/ferroelastic phase transition at about 200 K from the high symmetry phase $F\bar{4}3cl'$ (Saifuddinov, 1980) to a low symmetry phase $Pca2_11'$ (Schmid *et al.*, 1978). Evidence for ferroelectricity on a single crystal of Co-I-boracite was first observed by Ascher *et al.* (1964), by dielectric measurements and optical observations of domain walls motion under an applied electric field. The spontaneous

polarization, estimated just below the transition temperature by means of hysteresis curve, is 1.5 $\mu c/cm^2$ (Smutny, 1970). At 37.5 K, a second order weak ferromagnetic transition has been reported by Quezel and Schmid (1968) from magnetic susceptibility versus temperature measurements. Although a previous low resolution neutron diffraction study by Plakhtii *et al.* (1976) has been performed on a polycrystalline sample, the type of magnetic ordering was not reliably determined. The symmetry of the ferromagnetic phase below 37.5 K, determined by optical domain study of the ferromagnetic/ferroelectric/ferroelastic phase of Co-I-boracite, is consistent with the magnetic point group m'm2' (Clin *et al.*, 1985), leading to the following sequence of phases:

$$F\bar{4}3c1' \xrightarrow[k=1/2\ \ 1/2\ \ 0]{200\ K} Pca2_11' \xrightarrow[k=0\ \ 0\ \ 0]{37.5\ K} m'm2'$$

On the other hand, anomalous temperature dependences have been found around 28 K by Baturov *et al.* (1981) on spontaneous magnetization, and spontaneous birefringence (Clin *et al.*, 1985). This has incited us to attempt neutron diffraction investigation of the magnetic structure of Co-I-boracite above and below 28 K.

2 EXPERIMENTAL AND RESULTS

The samples of Co-I-boracite were grown by chemical vapour transport with ^{11}B (Schmid, 1965). Neutron diffraction measurements were originally undertaken on a single crystal of about 1 mm^3, using the two axis spectrometer ($\lambda = 1.05$ Å) performed in the temperature range from 9 K to 50 K, at the Saphir reactor, Würenlingen. The temperature dependence of peak intensities of the 103_{orth} and 101_{orth} magnetic reflections is shown in Figure 1. However, due to the small dimension of the crystal, for a full structural analysis over and extended $\sin\theta/\lambda$ region, we completed our measurements with a set of four powder patterns collected with the D.M.C. (double axis multi counter system) using of wavelength of $\lambda = 1.713$ Å. The step increment of the diffraction angle 2θ was 0.1°. Figure 2 displays the neutron patterns in the paramagnetic state for the cubic and orthorhombic phases at respectively 293 K and 51 K, due to the fact that $k = (0, 0, 0)$, the magnetic contribution and the magnetic behavior are better visualized at 31 K and 9 K in the difference diagrams obtained by subtracting the 51 K data of the orthorhombic paramagnetic phase as shown in Figure 3. The data were corrected for absorption and evaluated by line profile analysis (Rietveld, 1969).

2a Crystal structure

The paraelectric/paramagnetic phase of Co-I-boracite is cubic, and the unit cell (a = 12.122 Å) contains eight formula units $Co_3B_7O_{13}I$, Co atoms of which are located on equivalent positions of the space group $F\bar{4}3c1'$. After refinement of the data, the R factors are $R_n = 6.92\%$, $R_{wp} = 6.92\%$ and $R_{exp} = 5.05\%$. The nuclear structure of the ferroelectric phase has been determined at 51 K, the unit cell,

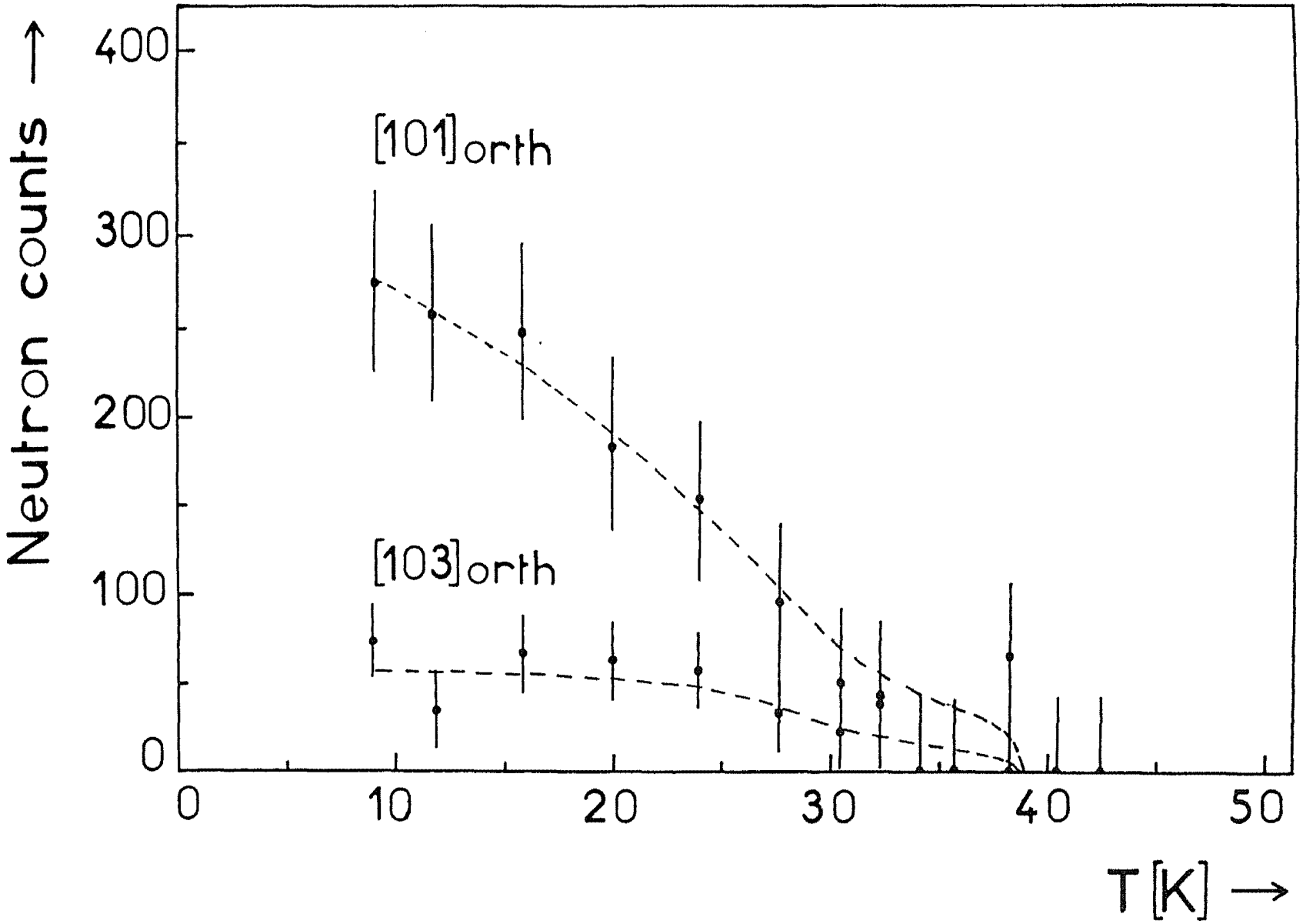
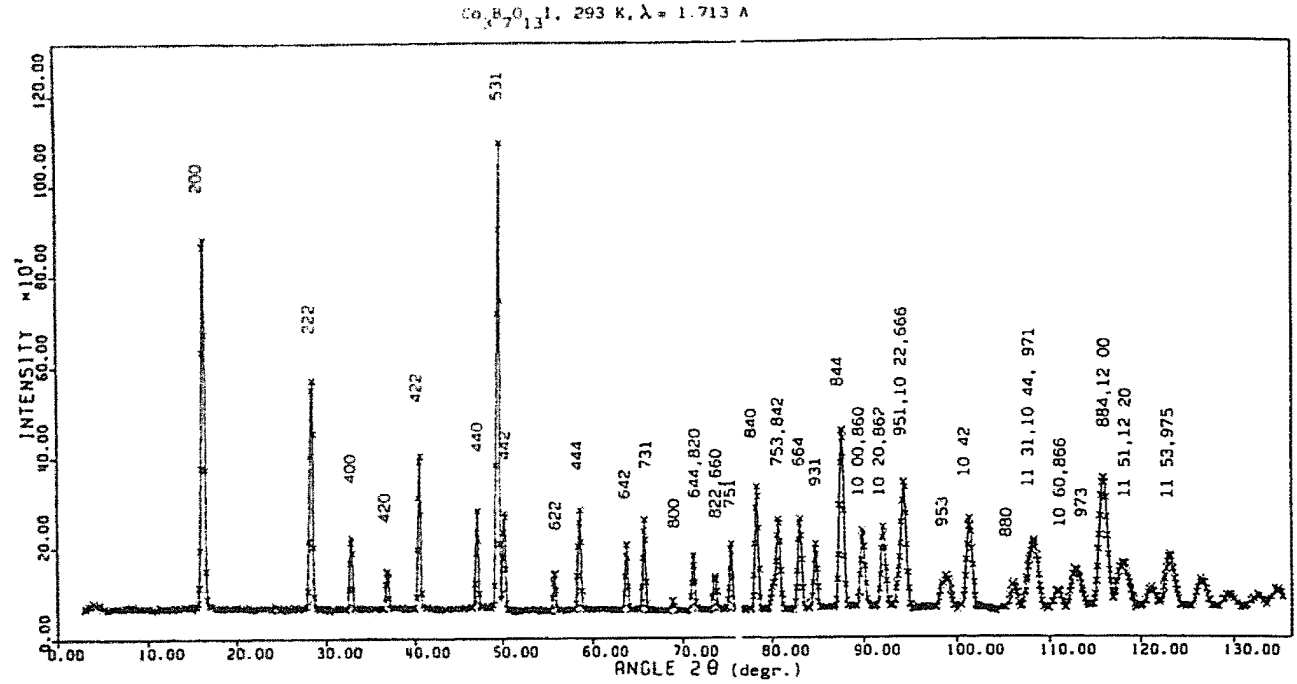


Figure 1 Temperature dependence of peak intensities of magnetic reflections $(103)_{orth}$ and $(101)_{orth}$ of $Co_3B_7O_{13}I$. The lines are a guide to eyes.



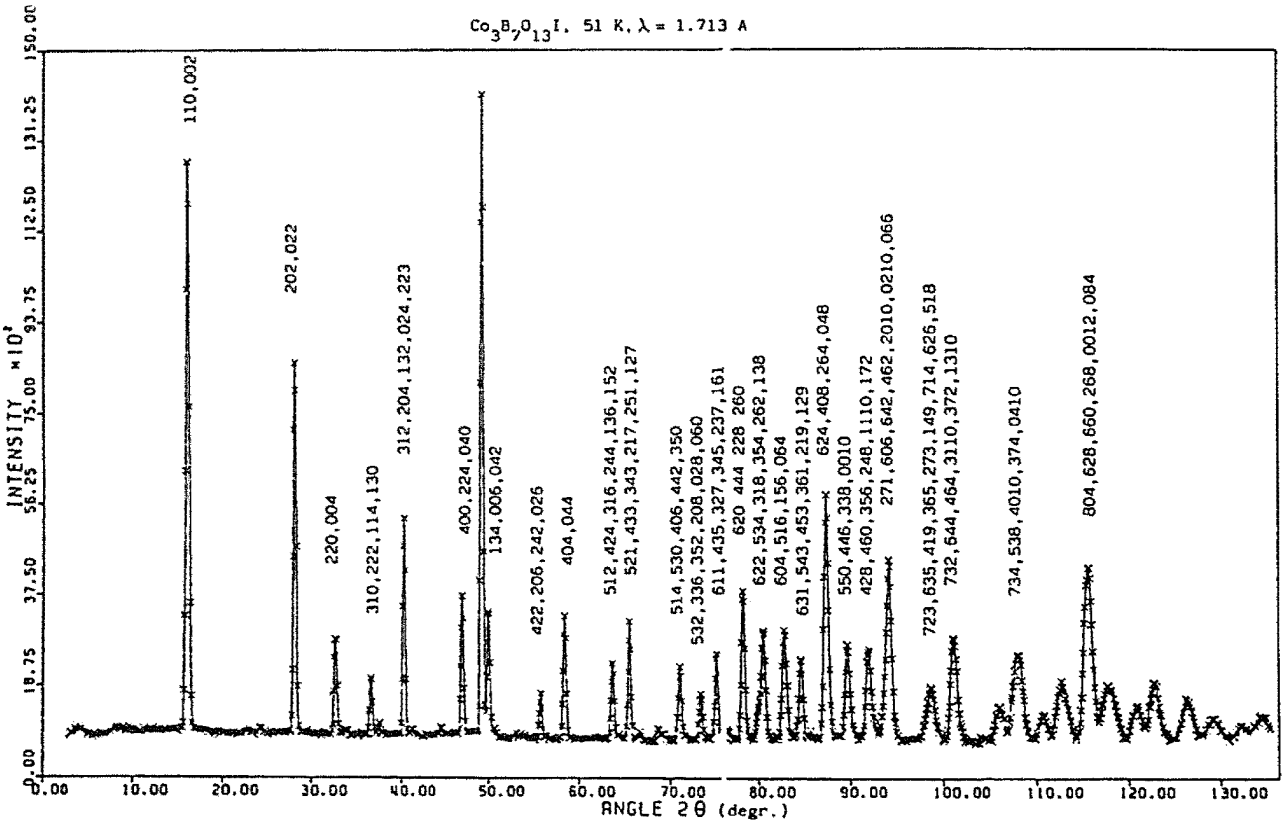
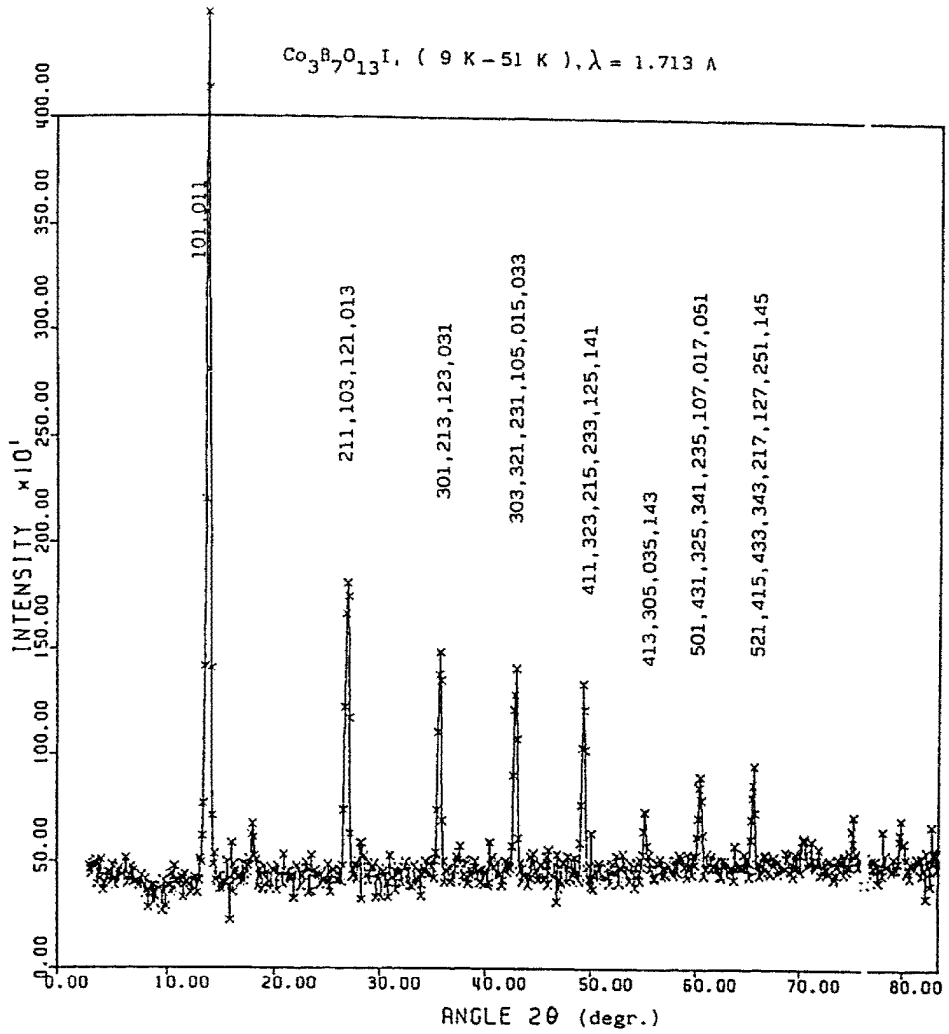


Figure 2 Neutron diffraction patterns of $Clo_3B_7O_{13}I$ in the paramagnetic cubic phase at 293 K (Figure 2(a)) and at 51 K in the ferroelectric orthorhombic phase (Figure 2(b)).



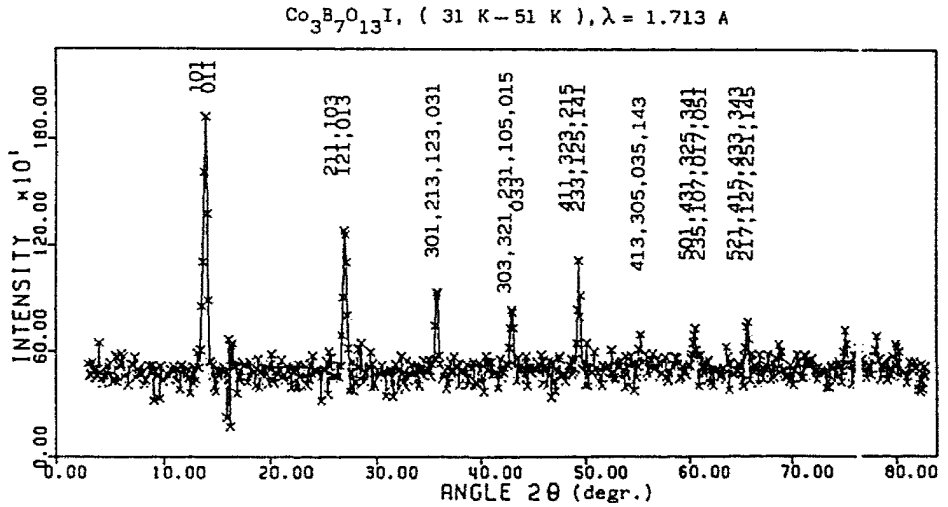


Figure 3 Neutron diffraction patterns of the magnetic reflections of $Co_3B_7O_{13}I$ obtained by subtracting the data found in the orthorhombic paramagnetic state at 51 K. Figure 3 (a) and (b), magnetic reflections at 9 K and 31 K respectively.

orthorhombic (a = 8.601 Å, b = 8.569 Å and c = 12.120 Å), contains four formula units, and cobalt atoms are splitted in three sublattices denoted by Co_1, Co_2 and Co_3 (see Figure 4). The space group is $Pca2_11'$ and the R factors are $R_n = 6.43\%$, $R_{wp} = 10.46\%$ and $R_{exp} = 5.29\%$, the crystallographic data are listed in Table 1.

2b Magnetic structure

At 31 K in the magnetic phase, the nuclear and magnetic cells are the same ($k = 0$). After refinement of the data, Co_1 and Co_2 cobalt sublattices have been found magnetically ordered with a canted antiferromagnetic arrangement L_1^x and L_2^z respectively (see below). The refined magnetic values for Co_1 and Co_2 are 3.43 μB and 1.23μB respectively, and the magnetic space group is $Pc'a2_1'$.

At 9 K, the third cobalt sublattice Co_3 is magnetically ordered under the same antiferromagnetic arrangement L_2^z which appears just below the weak ferromagnetic transition at 37.5 K for Co_2. The magnetic moment values for the three cobalt sublattices are: $Co_1 = 4.19$ μB, $Co_2 = 3.28$ μB and $Co_3 = 1.8$ μB.

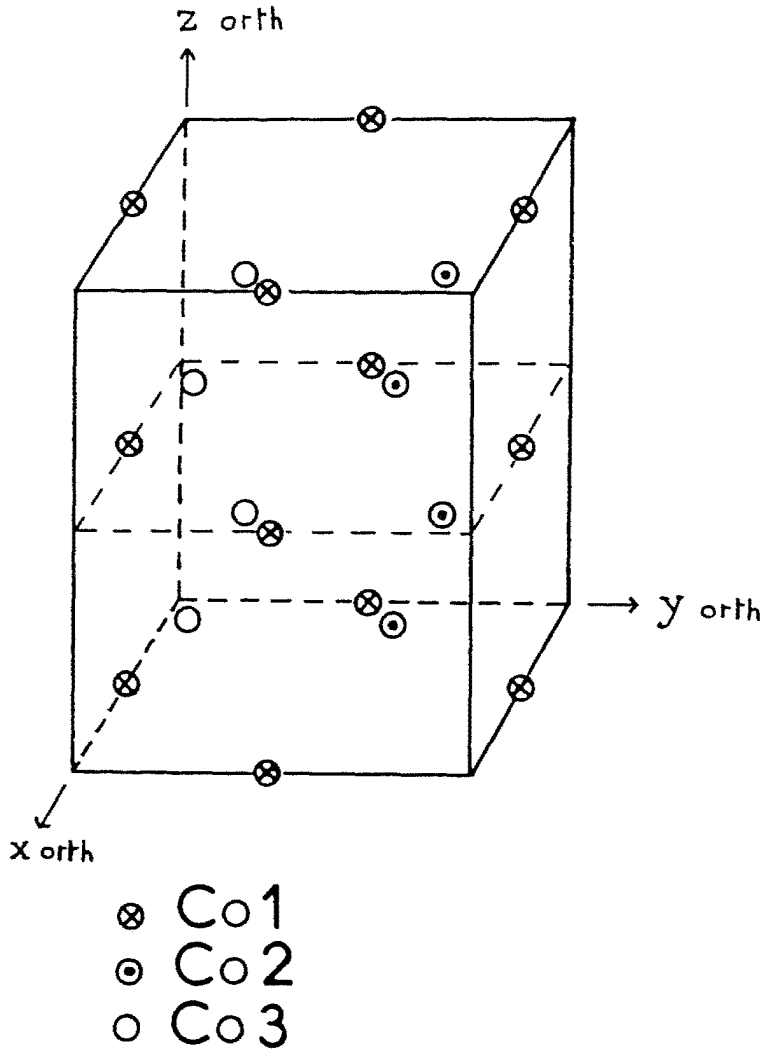


Figure 4 Position of the 12 cobalt ions in the orthorhombic unit cell $Pca2_11'$. Co_1, Co_2 and Co_3 represent the three cobalt sublattices.

Table 1 Refined parameters obtained for the chemical structure in the orthorhombic $Pca2_11'$ ferroelectric phase of $Co_3B_7O_{13}I$ at 51 K.

Atom	*X*	*SX*	*Y*	*SY*	*Z*	*SZ*
CO1	0.0000	0.0000	0.5000	0.0000	0.5000	0.0000
CO2	0.2557	0.0092	0.7180	0.0100	0.2651	0.0105
CO3	0.2390	0.0093	0.2639	0.0109	0.2605	0.0112
B1	0.2463	0.0033	0.7459	0.0055	0.5162	0.0068
B2	0.0043	0.0032	1.0084	0.0046	0.2642	0.0064
B3	0.2506	0.0034	0.2442	0.0052	0.5123	0.0065
B4	0.0097	0.0030	0.1585	0.0039	0.4425	0.0065
B5	−0.0007	0.0034	0.8329	0.0038	0.4466	0.0062
B6	0.1532	0.0029	0.9946	0.0053	0.5927	0.0059
B7	0.3056	0.0018	0.4924	0.0047	0.6168	0.0058
O1	0.0149	0.0026	0.0120	0.0043	0.5120	0.0059
O2	0.0858	0.0039	0.7300	0.0047	0.5055	0.0065
O3	0.1554	0.0043	0.2034	0.0050	0.4223	0.0064
O4	0.0817	0.0049	0.8825	0.0048	0.3348	0.0071
O5	−0.0881	0.0037	0.2680	0.0047	0.5002	0.0065
O6	−0.1525	0.0050	0.8037	0.0050	0.4288	0.0065
O7	−0.0757	0.0047	0.1079	0.0049	0.3355	0.0069
O8	0.1249	0.0037	0.0668	0.0039	0.2047	0.0068
O9	0.2944	0.0045	0.6599	0.0045	0.6255	0.0060
O10	0.2827	0.0041	0.9253	0.0048	0.5432	0.0064
O11	0.0995	0.0034	0.9246	0.0045	0.7047	0.0063
O12	0.2021	0.0043	0.1657	0.0044	0.6267	0.0065
O13	0.2074	0.0038	0.4346	0.0064	0.5447	0.0064
I1	0.0059	0.0037	0.5012	0.0069	0.2706	0.0057

R-Factors
Rn = 6.43, Rwp = 10.46%
R exp = 5.29%
2
$x = 4.35$

Axes [A]
8.6012 (10)
8.5695 (9)
12.1208 (18)
V = 893.40 (8) [A]

3 DISCUSSION

The mean spins of the sublattices Co_1, Co_2 and Co_3 are respectively symbolized by $S_1^1, S_1^2, S_1^3, S_1^4$; $S_2^1, S_2^2, S_2^3, S_2^4$; and $S_3^1, S_3^2, S_3^3, S_3^4$, their coordinates are given in Table 2.

Following the approach developed by Dzyaloshinskii (1957), we can define the four vectors:

$$M = (S_1^1 + S_2^1 + S_3^1) + (S_1^2 + S_2^2 + S_3^2) + (S_1^3 + S_2^3 + S_3^3) + (S_1^4 + S_2^4 + S_3^4);$$
$$L_1 = (S_1^1 + S_2^1 + S_3^1) + (S_1^2 + S_2^2 + S_3^2) - (S_1^3 + S_2^3 + S_3^3) - (S_1^4 + S_2^4 + S_3^4);$$
$$L_2 = (S_1^1 + S_2^1 + S_3^1) - (S_1^2 + S_2^2 + S_3^2) + (S_1^3 + S_2^3 + S_3^3) - (S_1^4 + S_2^4 + S_3^4);$$
$$L_3 = (S_1^1 + S_2^1 + S_3^1) - (S_1^2 + S_2^2 + S_3^2) - (S_1^3 + S_2^3 + S_3^3) + (S_1^4 + S_2^4 + S_3^4).$$

These vectors form a basis for the irreducible corepresentations of the group $Pca2_11'$ at the center of the Brillouin zone. The components L_1^x, L_2^z and M^y transform as the one dimensional irreducible corepresentation which induces a low symmetry

Table 2 Coordinates of the cobalt ions associated with the 12 average spins S_i^j ($i = 1$–3, $j = 1$–4) in the three sublattices denoted Co_1, Co_2 and Co_3 in the orthorhombic $Pca2_11'$ cell.

CO_1	CO_2	CO_3
S_1^1 $(0\ \frac{1}{2}\ \frac{1}{2})$	S_2^1 $(\frac{1}{4}\ \frac{3}{4}\ \frac{1}{4})$	S_3^1 $(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})$
S_1^2 $(\frac{1}{2}\ 0\ 0)$	S_2^2 $(\frac{1}{4}\ \frac{3}{4}\ \frac{3}{4})$	S_3^2 $(\frac{1}{4}\ \frac{1}{4}\ \frac{3}{4})$
S_1^3 $(0\ \frac{1}{2}\ 0)$	S_2^3 $(\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4})$	S_3^3 $(\frac{3}{4}\ \frac{1}{4}\ \frac{3}{4})$
S_1^4 $(\frac{1}{2}\ 0\ \frac{1}{2})$	S_2^4 $(\frac{3}{4}\ \frac{3}{4}\ \frac{1}{4})$	S_3^4 $(\frac{3}{4}\ \frac{1}{4}\ \frac{1}{4})$

group $Pc'a2_1'$. The Landau phenomenological expansion associated with the $Pca2_11'$ $\rightarrow$ $Pc'a2_1'$ transition can be written:

$$F = \sum_{i=1,3} \left(\frac{a_i}{2} L_i^2 + \frac{b_i}{4} L_i^4 \right) + \frac{1}{2\chi} M^2 + \frac{\alpha_i}{2} (L_i^v)^2 + \delta_i L_j^v L_k^w + M^u(\delta_i' L_i^v + \delta_k' L_k^w)$$

$i, j, k = 1, 2, 3$; $u, v, w = x, y, z$.

At T_c, the cancellation of one of the coefficients a_i brings the appearance of an antiferromagnetic spin arrangement of purely exchange origin, described by the vector L_i. Our experimental data suggest an antiferromagnetic ordering along the x and z directions. At 31 K, the Co_1 and Co_2 cobalt sublattices are magnetically ordered leading to:

$$L_1^x = S_1^{1x} + S_1^{2x} - S_1^{3x} - S_1^{4x}$$
$$L_2^z = S_2^{1z} - S_2^{2z} + S_2^{3z} - S_2^{4z}$$

At 9 K, the three cobalt sublattices are magnetically ordered, one obtains:

$$L_1^x = S_1^{1x} + S_1^{2x} - S_1^{3x} - S_1^{4x}$$
$$L_2^z = (S_2^{1z} + S_3^{1z}) - (S_2^{2z} + S_3^{2z}) + (S_2^{3z} + S_3^{3z}) - (S_2^{4z} + S_3^{4z})$$

The weak magnetic moment M^y which results from a canting of the spins, is described by the coupling term $M^y(\delta_1' L_1^x + \delta_2' L_2^z)$.

In summary, we have determined for the first time the magnetic structure of an orthorhombic boracite, as well as the precise value of the magnetic moment of the transition metal ions.

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