

Short Communications

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Spin orientation and extinction in ferrimagnetic $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ by neutron diffraction. By J. A. GOEDKOOP, J. HVOSLEF and M. ŽIVADINOVIĆ,* Joint Establishment for Nuclear Energy Research, Kjeller, Norway

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Braun (1957) has recently reported X-ray studies of a new group of ferrimagnetic oxides of hexagonal or rhombohedral symmetry. They may be divided into two groups depending on whether the direction of spontaneous magnetization is parallel or perpendicular to the hexagonal (or trigonal) axis. The present investigation concerns a compound of the latter type, $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, also designated Zn-Y by Braun.

Using Anderson's treatment of super-exchange, Gorter (1957) has proposed a distribution of the spins of the iron ions in these compounds. Fig. 1 shows part of the unit

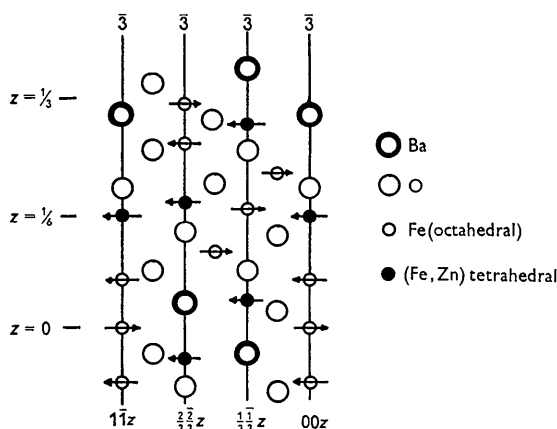


Fig. 1. Section of a (110)-plane of $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ with the spin directions of the iron ions drawn in.

cell with the proposed spin directions drawn in. The object of the investigation was to verify this spin distribution by measuring the $000l$ neutron-diffraction intensities. The main interest of the work, however, turned out to be the very strong extinction which occurred.

$\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ crystallizes in the space group $R\bar{3}m$ with 3 formula units in the cell, which has dimensions $a = 5.87_6$ Å, $c = 43.55_8$ Å. The crystal used was grown from the melt by Mr A. L. Stuijts at Philips Research Laboratories; it was in the shape of a rectangular slab, dimensions $2.1 \times 3.5 \times 7.5$ mm³, with the c -axis normal to the slab.

Using a neutron wavelength of 1.026 Å the first 18 non-zero reflections $000l$ ($l = 3, 6, \dots, 54$) were measured in one traverse of the counter. A second run was made after the crystal had several times been subjected

to a treatment consisting of heating to 450 °C. followed by quenching in water.

Comparison between the observed integrated intensities and those calculated for Braun's atomic positions and Gorter's spin distribution gave fair agreement for the weaker reflections, but the strong reflections were observed too low. No improvement was obtained by changing the spin distribution, and it was therefore assumed that the latter was correct but that the observed intensities were suffering from extinction.

It has recently been shown by Hamilton (1958) that intensities consisting of both nuclear and magnetic contributions are more severely influenced by extinction than either purely nuclear or purely magnetic reflections. Without this effect the primary extinction factor E_p^0 for a reflection of structure factor F is given by (James, 1954):

$$E_p^0 = \frac{\tanh k|F|}{k|F|} \quad (1)$$

where

$$k = \lambda t / V_c \sin \theta \quad (2)$$

with λ the wavelength, V_c the unit-cell volume, t the thickness of the mosaic block and θ the Bragg angle. For a reflection consisting of a nuclear part $F_{\text{nucl.}}$ and a magnetic part $F_{\text{magn.}}$ one has:

$$F^2 = F_{\text{nucl.}}^2 + q^2 F_{\text{magn.}}^2 \quad (3)$$

where $\sin^{-1} q$ is the angle between the spin direction and the scattering vector. Thus:

$$E_p^0 = \frac{\tanh k(F_{\text{nucl.}}^2 + q^2 F_{\text{magn.}}^2)^{1/2}}{k(F_{\text{nucl.}}^2 + q^2 F_{\text{magn.}}^2)^{1/2}} \quad (4)$$

Hamilton now shows that actually the primary-extinction factor for a mixed reflection is (his equation (35))

$$E_p = \frac{|F_{\text{nucl.}} + qF_{\text{magn.}}| \tanh(k|F_{\text{nucl.}} + qF_{\text{magn.}}|) + |F_{\text{nucl.}} - qF_{\text{magn.}}| \tanh(k|F_{\text{nucl.}} - qF_{\text{magn.}}|)}{2k(F_{\text{nucl.}}^2 + q^2 F_{\text{magn.}}^2)} \quad (5)$$

which is smaller than E_p^0 . He uses this effect to estimate the primary extinction for a crystal with a random magnetization, which requires an averaging of (5) over different q values. In our case the situation is simpler since $q = 1$ for all domains; hence (5) may be applied directly.

The procedure is then as follows: From (4) and (5), with $q = 1$, graphs are constructed of E_p/E_p^0 as a function of $|F_{\text{nucl.}}/F_{\text{magn.}}|$ for different values of E_p^0 . The observed intensities are then plotted against their cal-

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Table 1. *A survey of observed and calculated intensities and their corrections*

E_p^0 is the primary extinction correction for a purely nuclear or magnetic reflection, E_p the corresponding value for a mixed reflection. $E(1)_s$ and $E(2)_s$ denote the secondary-extinction correction before and after quenching, respectively. $I(1)_{\text{obs.}}$ and $I(2)_{\text{obs.}}$ are the corresponding observed intensities. No changes were found in the E_p 's after quenching.

000 <i>l</i>	$F_{\text{nuc.}}^2$	$F_{\text{magn.}}^2$	$I_{\text{calc.}}$	E_p^0	E_p	$E(1)_s$	$E_p E(1)_s I_{\text{calc.}}$	$I(1)_{\text{obs.}}$	$E(2)_s$	$E_p E(2)_s I_{\text{calc.}}$	$I(2)_{\text{obs.}}$
3	72.4	165.6	338	0.23	0.19	0.69	44	58	0.78	50	85
6	28.9	2.9	21	0.85	0.82	0.90	15	22	0.94	16	25
9	55.7	981.6	487	0.34	0.32	0.40	62	85	0.55	86	98
12	19.9	2.4	8	0.97	0.96	0.96	7	13	0.97	7	12
15	105.5	171.1	77	0.76	0.62	0.76	36	31	0.83	40	31
18	209.7	286.3	113	0.72	0.57	0.68	44	40	0.78	50	44
21	1.1	15.1	3	0.99	0.99	0.98	3	2	0.99	3	—
24	21.0	0.6	4	0.99	0.99	0.98	4	1	0.99	4	—
27	340.8	40.4	56	1.00	0.99	0.72	40	36	0.81	45	39
30	22.1	0.4	3	1.00	0.99	0.98	3	10	0.99	3	7
33	24.2	16.9	5	1.00	0.99	0.97	5	7	0.98	5	6
36	2146.5	45.2	230	0.78	0.77	0.36	64	67	0.51	90	93
39	243.4	0.3	24	0.96	0.96	0.87	20	20	0.91	21	21
42	197.7	0.3	17	0.98	0.98	0.91	15	26	0.94	16	30
45	1499.2	0.1	118	0.87	0.87	0.55	56	51	0.67	69	64
48	10.2	0	1	1.00	1.00	0.96	1	1	1.00	1	0
51	343.0	0	23	1.00	1.00	0.87	20	20	0.92	21	20
54	282.9	0	18	1.00	1.00	0.90	16	14	0.93	17	13

culated values and a curve drawn through those of either predominantly nuclear or magnetic origin. The others are found to be somewhat below this curve, and the ratio of the calculated intensities estimated from the curve to the actual calculated intensities is equal to E_p/E_p^0 . By using the aforementioned graphs, the values of E_p^0 and the E_p for these reflections are found. From these, and using (1) and (2), a mean mosaic block thickness of $t = 0.00125$ cm was found both before and after heat treatment.

The secondary extinction coefficients E_s were now calculated, using the expression given by Hamilton (1957 and 1958a):

$$E_s = \exp(-c_s I_{\text{calc.}} E_p) \quad (6)$$

where $c_s = 8\lambda^3 A^{1/2} / \eta V^2 (2\pi)^{3/2}$; A is the cross-sectional area of the crystal and η is the standard angular deviation of the mosaic blocks. Using the equation $I_{\text{obs.}} = E_s E_p I_{\text{calc.}}$ for some of the weaker reflections, c_s and hence η could be estimated. This yielded $\eta = 16''$ for the first run and $\eta = 24''$ for the second. These values may be compared with those found by Hamilton (1958a) for a laboratory-grown crystal of magnetite: $t = 0.0014$ cm. and $\eta = 15.4''$.

The final results are shown in Table 1. The intensities before extinction correction are defined as:

$$I_{\text{calc.}} = \frac{10^{23}}{\sin 2\theta} (F_{\text{nuc.}}^2 + F_{\text{magn.}}^2) \exp(-1.31 (\sin \theta / \lambda)^2)$$

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The thermal expansion of solid chlorine. By L. L. HAWES and G. H. CHEESMAN, *The University of Tasmania, Hobart, Tasmania*

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The lattice parameters of solid chlorine have been determined at 77.4 °K. and at 158.2 °K. by the use of powder diffraction photographs. Values are given for the co-

the temperature factor being taken from Braun's X-ray work. The table shows how severe both primary and secondary extinction are for a crystal of this type, and it is seen that the applied heat treatment does little to improve the situation. Taking the large corrections into account, the agreement between observed and calculated intensities is seen to be quite reasonable, indicating that the spin alignment is correct. Some of the remaining discrepancy might of course also be due to errors in the light-atom positions which would influence the neutron data more strongly than the X-ray data. No improvement resulted by assuming an ordered arrangement of the Zn-atoms (Fig. 1). In view of the considerable difference in scattering power between Fe and Zn this provides further support for Braun's conclusion that the Zn and the Fe atom are randomly distributed over two positions.

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efficients of linear and volume expansion as well as expressions relating lattice parameters and density to temperature.