

Neutron-diffraction study of $\text{Co}_3\text{B}_2\text{O}_6$

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With 4 figures

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Auszug

Kobaltborat $\text{Co}_3\text{B}_2\text{O}_6$ ist isotyp mit dem rhombischen Kotoit und antiferromagnetisch unterhalb 37°K . Neutroneninterferenzen wurden sowohl oberhalb als auch unterhalb des magnetischen Umwandlungspunkts an einer mit dem B^{11} -Isotop angereicherten Probe registriert, wodurch der große Einfangquerschnitt des B^{10} vermieden wurde. Aus den Kernintensitäten folgte für B^{11} eine kohärente Streuamplitude von $+0,65 \times 10^{-12}$. Die magnetischen Reflexionen wurden für eine $(a \times 2b \times 2c)$ -Überstrukturzelle indiziert. Auf einem Vier-spin-Modell basierende Berechnungen ergaben eine annehmbare Übereinstimmung mit den beobachteten Intensitäten. Die magnetischen Momente von Kobalt sind in ferromagnetischen Ketten längs a geordnet, die Spinrichtungen senkrecht zu c aufweisen.

Abstract

Cobalt borate, $\text{Co}_3\text{B}_2\text{O}_6$, is isotypic with the orthorhombic mineral kotoite and is antiferromagnetic below 37°K . Neutron-diffraction patterns were recorded above and below the magnetic transition using a sample enriched in isotope B^{11} , thereby avoiding the large capture cross-section of B^{10} . A coherent scattering amplitude of $+0.65 \times 10^{-12}$ cm was obtained for B^{11} from the nuclear intensities. The magnetic reflections in the low-temperature pattern were indexed on an $a \times 2b \times 2c$ supercell, and calculations based upon a four-spin model gave reasonable agreement with the observed intensities. Cobalt moments are arranged in ferromagnetic chains along a having spin directions perpendicular to c .

Cobalt borate is isotypic with the mineral kotoite, $\text{Mg}_3\text{B}_2\text{O}_6$, as are nickel¹ and manganese² borate. Independent x-ray analyses of the

¹ W. GÖTZ, Raumgruppenbestimmung des Nickelborates $\text{Ni}_3\text{B}_2\text{O}_6$. Naturwissenschaften **50** (1963) 567.

² G. STALLINGS and M. J. REDMAN, private communication.

kotoite structure were carried out by SADANAGA³ and by BERGER⁴. The atomic coordinates and lattice parameters reported by BERGER are given in Table 1. The kotoite structure can be described as a distorted, hexagonal close-packed oxygen arrangement, with boron in triangular coordination and magnesium or divalent transition-metal ions in octahedral positions.

Table 1. *Summary of crystallographic data for $\text{Co}_3\text{B}_2\text{O}_6$*
(after BERGER⁴)

Space group: $Pn\bar{m}n$ $Z = 2$
Lattice parameters: $a = 5.462$, $b = 8.436$, $c = 4.529$ Å
Atomic positions:

Atom	Equipoint	x	y	z
Co_1	$2a$	0	0	0
Co_2	$4f$	0	.321	$\frac{1}{2}$
B	$4g$.25	0	.56
O_1	$4g$.316	0	.258
O_2	$8h$.218	.139	.705

Few, if any, boron compounds have been investigated by neutron diffraction because of the huge capture cross-section of isotope B^{10} . An obvious solution to the problem is isotope B^{11} , which has a negligible absorption coefficient and is relatively inexpensive. Boric acid and elemental boron enriched to 98% B^{11} can be purchased from the Isotopes Development Center, Oak Ridge National Laboratory, Oak Ridge, Tenn. Polycrystalline $\text{Co}_3\text{B}_2\text{O}_6$ was prepared by heating a stoichiometric mixture of CoO and vitreous B_2O_3 at 900°C .

The magnetic susceptibility of sintered cobalt borate was measured from liquid helium to room temperature. The experiments were performed on a vibrating-sample magnetometer⁵ using a field of 12 kG; no field dependence of the susceptibility was observed. When plotted as a function of temperature (Fig. 1), the data shows a maximum at $37 \pm 2^\circ\text{K}$, indicating a paramagnetic-antiferromagnetic phase transition. Susceptibility measurements in the paramagnetic region show typical Curie-Weiss law behavior.

³ R. SADANAGA, The crystal structure of kotoite $\text{Mg}_3\text{B}_2\text{O}_6$. *X-rays* **5** (1948) 2-7.

⁴ S. V. BERGER, The crystal structures of the isomorphous orthoborates of cobalt and magnesium. *Acta Chemica Scand.* **3** (1949) 660-675.

⁵ S. FONER, Versatile and sensitive vibrating-sample magnetometer. *Rev. Sci. Instr.* **30** (1959) 548-557.

High- and low-temperature neutron-diffraction powder patterns taken at the M.I.T. reactor are shown in Fig. 2. The data were collected at angular intervals of $3'$ in 2θ using a cylindrical aluminum specimen holder of 2 cm diameter and 6 cm height. Tables 2 and 3 list the observed nuclear and magnetic intensities.

The coherent scattering length of B^{11} was determined from the nuclear intensities. Structure factors were computed using the coordinates in Table 1, and scattering amplitudes of $+0.28$ for cobalt,

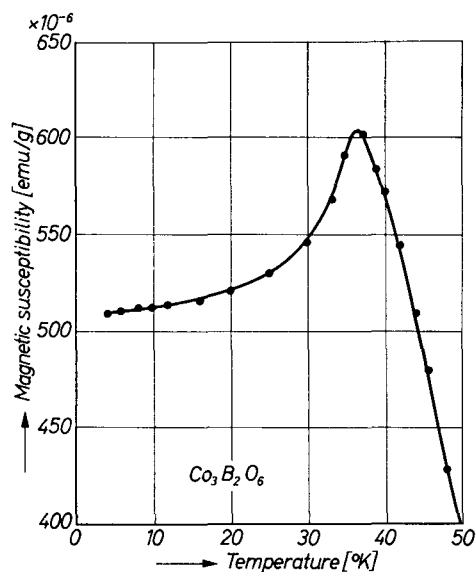


Fig. 1. Low-temperature magnetic susceptibility measurements on polycrystalline cobalt kotoite showing the paramagnetic-antiferromagnetic transition near 37°K

$+0.577$ for oxygen, and values ranging from -0.4 to $+1.0$ for boron. Multiplicity and Lorentz factors were included in the calculation, and absorption and thermal vibration corrections proved negligible. The calculated intensities were scaled to the observed values and an R factor was evaluated from the discrepancies for individual reflections. As shown graphically in Fig. 3, a well-defined minimum in R was obtained for $b_B = +0.65$. Such a value is typical for potential scattering⁶ and does not differ significantly from those of neighboring nuclei such as Li^6 , Be^9 , C^{12} , and O^{16} . Since the boron scattering length is

⁶ G. E. BACON, Neutron diffraction. Oxford (1955), Chapter II.

comparable to those of cobalt and oxygen, the excellent agreement between the calculated and observed nuclear intensities (Table 2) also serves to substantiate the boron coordinates in kotoite.

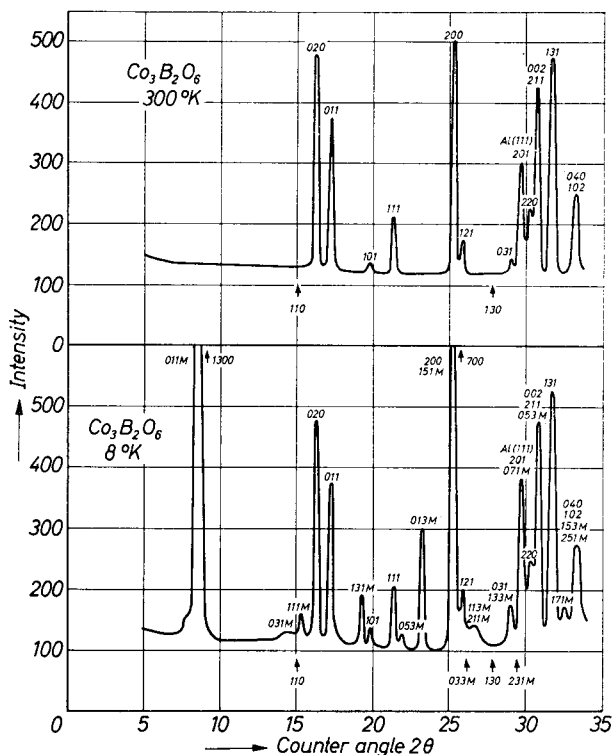


Fig. 2. Neutron-diffraction powder patterns of $\text{Co}_3\text{B}_2\text{O}_6$ taken at room temperature and at 8°K. The neutron wavelength is 1.20 Å. M denotes the magnetic reflections indexed on the orthorhombic supercell

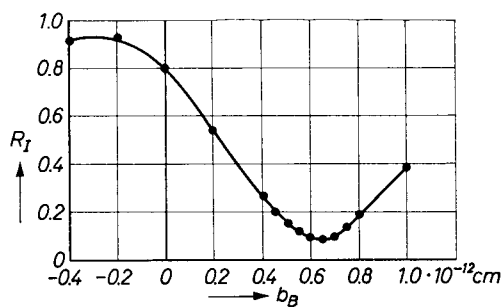


Fig. 3. The R factor for $\text{Co}_3\text{B}_2\text{O}_6$ nuclear reflections plotted as a function of b_B , the coherent scattering amplitude of B^{11} . $R_I = \frac{\sum_{hkl} |I_{\text{obs}} - I_{\text{calc}}|}{\sum_{hkl} I_{\text{obs}}}$

Table 2. Comparison of observed nuclear intensities with values computed using a coherent scattering length of 0.65×10^{-12} cm for B¹¹

<i>hkl</i>	d_{calc}	I_{calc}	I_{obs}	d_{obs}
110	4.58	0	< 2	—
020	4.22	28	28	4.23
011	3.99	18	17	4.00
101	3.49	2	2	3.50
111	3.22	6	7	3.23
200	2.73	34	41	2.74
121	2.69	6	5	2.68
130	2.50	0	< 2	—
031	2.39	5	3	2.39
201	2.34	4	22*	2.35
220	2.29	14	13	2.30
002	2.26	4)	41	2.26
211	2.25	38)		
131	2.19	49	48	2.20
040	2.11	0	< 2	—
102	2.09	13	14	2.09

* Al(111) superposed.

Table 3. Magnetic intensities calculated from the spin structure shown in Fig. 4
The reflections are indexed on an $a \times 2b \times 2c$ supercell

<i>hkl</i>	d_{calc}	I_{calc}	I_{obs}	d_{obs}
011	7.98	158	161	7.97
031	4.77	3	2	4.80
111	4.51	4	4	4.52
131	3.59	7	7	3.61
051	3.16	1	2	3.16
013	2.97	17	16	2.98
151	2.73	17	21	2.74
033	2.66	1	< 2	—
113	2.61	1)	7	2.61
211	2.60	11)		
133	2.39	3	4	2.39
231	2.37	1	< 2	—
071	2.33	0	< 2	—
053	2.25	1	< 2	—
171	2.13	5	6	2.14
153	2.08	9)	9	2.09
251	2.07	1)		

The magnetic reflections in the low-temperature neutron-diffraction pattern could not be indexed on the chemical unit cell. Doubling the b and c dimensions gave a set of interplanar spacings in accord

with experiment (Table 3), and a magnetic unit cell containing 24 cobalt atoms. When indexed on the $a \times 2b \times 2c$ supercell, only odd values of k and l occur, suggesting that spins related by translational vectors along b and c are antiparallel. This implies that cobalt moments related by $b+c$ are parallel giving an A -face-centered magnetic unit cell. The relative spin directions within a single chemical unit cell and their orientation with respect to the crystallographic axes remained to be determined.

The kotoite and olivine structures are closely related and a trial magnetic structure for $\text{Co}_3\text{B}_2\text{O}_6$ was deduced from those^{7,8} of Co_2SiO_4 and Ni_2SiO_4 . Divalent cobalt ions occupy half the octahedral interstices of a hexagonal close-packed oxygen structure in both $\text{Co}_3\text{B}_2\text{O}_6$ and

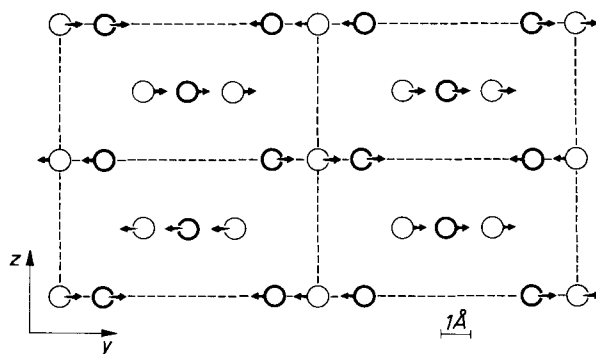


Fig. 4. Possible spin arrangement in antiferromagnetic $\text{Co}_3\text{B}_2\text{O}_6$ projected on (100). Cobalt atoms at $x = 0$ are drawn as light circles and those at $x = \frac{1}{2}$ are dark. Boron and oxygen positions are not shown. The magnetic unit cell and four chemical subcells are outlined

Co_2SiO_4 . The transitional-metal ions share edges along the a axis of kotoite and along b in olivine. In cobalt and nickel orthosilicate the ions within each chain are ferromagnetically coupled. Assuming a similar configuration for cobalt borate, the cobalt spins at $0, 0, 0$; $\frac{1}{2}, \frac{1}{2} - y, 0$ and $\frac{1}{2}, y - \frac{1}{2}, 0$ are parallel to a unit vector \mathbf{S} . Those at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $0, y, \frac{1}{2}$ and $0, 1 - y, \frac{1}{2}$ are parallel to a second direction \mathbf{S}' . Reasonable agreement with the observed intensities was achieved by choosing mutually perpendicular directions in (001) for \mathbf{S} and \mathbf{S}' . The

⁷ S. NOMURA, R. SANTORO, J. FANG and R. NEWNHAM, Antiferromagnetism in cobalt orthosilicate *J. Physic. Chem. Solids* **25** (1964) 901–905.

⁸ R. NEWNHAM, R. SANTORO, J. FANG and S. NOMURA, Antiferromagnetism in nickel orthosilicate. *Acta Crystallogr.* **19** (1965) 147–148.

proposed magnetic structure is illustrated in Fig.4. Because of its complexity, the spin array cannot be fully substantiated by neutron-diffraction powder data.

Regardless of the details, the magnetic structure of $\text{Co}_3\text{B}_2\text{O}_6$ is more complicated than might be expected. If only direct and superchange forces were important, an antiferromagnetic structure is predicted in which the Co moments at height $z = 0$ are parallel to one another and antiparallel to those at $z = \frac{1}{2}$. The chemical and magnetic unit cells coincide for this model and no supercell reflections should occur. Long-range Co—O—O—Co interactions, similar to those observed in the antiferromagnetic ilmenites⁹, appear to be operative in cobalt borate.

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⁹ G. SHIRANE, S. J. PICKART and Y. ISHIKAWA, *J. Physic. Soc. Japan* **14** (1959) 1352—1360.