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Citation: Journal of Applied Physics **40**, 1124 (1969); doi: 10.1063/1.1657557
View online: http://dx.doi.org/10.1063/1.1657557
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/40/3?ver=pdfcov
Published by the AIP Publishing

Magnetic Structures

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Neutron Diffraction Investigation of the Spiral Magnetic Structure in Cr_2BeO_4

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Cr_2BeO_4 is orthorhombic with the olivine (Mg_2SiO_4) type of crystal structure. Previous magnetic susceptibility, neutron diffraction and AFMR measurements have revealed that the compound undergoes an antiferromagnetic transition at about 28°K, probably to a noncollinear spin arrangement. More accurate neutron powder data have now been obtained at 4.5°K with 1.1 and 2.5 Å neutrons which reveal that the magnetic structure is a cycloidal spiral having a propagation vector directed along the c axis (*Pbnm* orientation). The spiral periodicity is about 65 Å, which is roughly 12 times the unit cell length in this direction. The observed intensities are accounted for reasonably well by a simple model in which there is modulation of a basic antiferromagnetic arrangement consisting of a G mode on the Cr(I) inversion sites coupled with a G mode on the Cr(II) mirror sites. The moments lie in the ac plane, and there is an additional phase factor of 90° between the moments of the Cr ions on the two kinds of site.

Cr_2BeO_4 is orthorhombic and isostructural with olivine (Mg_2SiO_4), with Cr^{3+} in octahedral and Be^{2+} in tetrahedral sites of an approximately hcp lattice of oxygen ions. Magnetic susceptibility measurements have revealed an antiferromagnetic transition at about 28°K,[1] and a preliminary neutron powder diffraction investigation yielded a complex magnetic pattern from which the possibility of a spiral configuration was suggested.[2] The existence of a noncollinear structure has also been inferred from recent AFMR measurements.[3] The present paper describes briefly the results of a more detailed neutron powder study which proves that the magnetic structure of Cr_2BeO_4 is indeed a spiral, with properties that can be qualitatively understood from a very simple consideration of the exchange energy.

The sample used in this study was the one previously used,[1,2] prepared by heating the coprecipitated hydroxides at 1300°C. The lattice parameters agreed very closely with those of Weir and Van Valkenburg[4] (a= 4.555 Å, b=9.792 Å, c=5.663 Å, Pbnm orientation). Neutron powder data were obtained at 150° and 4.5°K initially with neutrons of wavelength 1.12_5 Å, and a number of magnetic peaks were observed at the lower temperature. Although it proved possible to deduce the basic features of the spiral arrangement from these, it was difficult to make a quantitative intensity comparison owing to the fact that most of the magnetic peaks were quite weak and overlapping the nuclear ones. High-resolution data were therefore obtained with neutrons of wavelength 2.51 Å from which unwanted higher-order wavelengths had been removed by a filter of pyrolytic graphite.

TABLE I. Least-squares parameter values in Cr_2BeO_4.

	Site	x	y	z
Cr(I)	4(a)	0	0	0
Cr(II)	4(c)	−0.005	0.268	0.25
Be	4(c)	0.431	0.094	0.25
O(I)	4(c)	0.777	0.093	0.25
O(II)	4(c)	0.231	0.439	0.25
O(III)	8(d)	0.257	0.162	0.022

The nuclear data from the two runs above the transition temperature were combined and a least-squares refinement of the eleven structural parameters was carried out. The final values were quite similar to those of isostructural Al_2BeO_4[5] and are listed in Table I.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] R. P. Santoro and R. E. Newnham, J. Am. Ceram. Soc. **47**, 491 (1964).

[2] R. P. Santoro and R. E. Newnham, Acta Cryst. **22**, 344 (1967).

[3] P. R. Elliston and G. J. Troup, Proc. Phys. Soc. (London) **92**, 1040 (1967).

[4] C. E. Weir and A. Van Valkenburg, J. Res. Natl. Bur. Std. **64A**, 103 (1960).

[5] E. F. Farrell, J. H. Fang, and R. E. Newnham, Am. Mineralogist **48**, 804 (1963).

The Cr^{+3} spins in this structure are situated on two types of site with the following coordinates:

Cr(I): $S_1(000), S_2(00\frac{1}{2}), S_3(\frac{1}{2}\frac{1}{2}0), S_4(\frac{1}{2}\frac{1}{2}\frac{1}{2})$.

Cr(II): $S_5(xy\frac{1}{4}), S_6(\bar{x}\bar{y}\frac{3}{4}), S_7(\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{4}),$

$S_8(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4})$.

The magnetic structure finally deduced is shown schematically in Fig. 1. It consists of a modulated arrangement of G type antiferromagnetic modes (in the notation of Bertaut[6]) on both Cr^{3+} lattices, i.e., $S_1(+)$, $S_2(-)$, $S_3(-)$, $S_4(+)$ and $S_5(+)$, $S_6(-)$, $S_7(+)$, $S_8(-)$. The spiral wave vector is directed along the c axis with a periodicity of 65 A. The moments lie in the ac plane, in agreement with the AFMR observations,[3] and there is an additional phase factor of 90° between nearest-neighbor Cr(I) and Cr(II) ions. Observed and calculated intensities for this model are compared in Table II. These values were obtained with moments of 1.55 μ_B and 2.75 μ_B for Cr(I) and Cr(II), respectively, with the theoretical Watson and Freeman spherical form factor.[7] It is not clear why the moment of Cr(I) is so abnormally low; covalency effects are hardly likely to account for a reduction of this magnitude, and it appears as if there must be considerable disorder on these sites.

It is possible to account qualitatively for the basic features of the spiral configuration by a very simple model. The exchange scheme may be approximated by two interactions, J_1 between all configurations of nearest neighbors approximately 2.8 Å apart such as S_1 and S_5, and J_2 between next nearest neighbors approximately 3.6 Å apart such as S_1 and S_8. For negative J_1 and positive J_2, the isotropic exchange energy of the spiral is less than that of the unmodulated collinear arrangement for a wide range of values of ϕ, and is minimized when ϕ is 90°. The predicted periodicity of $3c$ in this case is only about one quarter of that actually observed, but quantitative agreement in this respect is not to be expected with such a crude model.

A detailed account of this work will be given in a future publication.

We wish to thank Dr. P. R. Elliston and Dr. G. J. Troup for sending us a preprint of their AFMR work prior to publication.

TABLE II. Comparison of calculated and observed magnetic intensities for Cr_2BeO_4 at 4.5°K for the spiral model described in text.

	I_{calc}	I_{obs}
010(−)	243.2	486.8
010(+)	243.2	
011(−)	37.9	37.7
011(+)	11.8	12.1
110(−)	0.0	<5
110(+)	0.0	
101(−)	5.1	<5
101(+)	54.7	47.9
111(−)	0.0	
120(−)	1.5	<5
120(+)	1.5	
030(−)	17.4	28.8
030(+)	17.4	
111(+)	0.0	
121(−)	93.0	75.1
031(−)	1.4	<5
012(−)	13.9	20.8
121(+)	5.7	
031(+)	16.4	10.9
012(+)	10.7	11.2

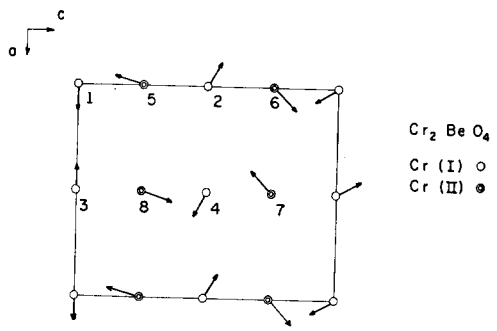

FIG. 1. Schematic representation of the spiral-spin arrangement in Cr_2BeO_4 projected on (010). Cr^{3+} ions only are shown, numbered as described in text.

[6] E. F. Bertaut. *Magnetism*, G. T. Rado and H. Suhl, Eds. (Academic Press Inc., New York, 1963), Vol. 3, p. 149. Note that S_3 and S_4 have been interchanged in the present paper.

[7] R. E. Watson and A. J. Freeman, Acta Cryst. **14**, 27 (1961).