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The Spiral Magnetic Structure of β-Chromium(III) Orthophosphate (β-$CrPO_4$)

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Magnetic susceptibility measurements have shown that β-$CrPO_4$ orders antiferromagnetically at 37 K, and the magnetic structure at 5 K has been determined from a fixed-wavelength powder neutron diffraction experiment. The magnetic structure consists of a cycloidal spiral of moments which propagates along [100] with a periodicity of $3.07 \pm 0.03a_0$. The magnetic properties are compared to those of the isomorphic compounds $CrVO_4$ and $MnSO_4$. © 1985 Academic Press, Inc.

Introduction

In common with several other trivalent metal orthophosphates (*1*) and divalent metal sulfates and chromates (*2, 3*), β-chromium orthophosphate adopts the orthorhombic chromium vanadate structure (*2*), which consists of infinite chains of *trans*-edge sharing CrO_6 octahedra parallel to [001] with VO_4 tetrahedra linking the chains (Fig. 1). These compounds have interesting magnetic properties because the short cation–cation distances along the chains give rise to strong direct-exchange interactions and even metal–metal bonding in some cases (*1, 4*). Several magnetic structures have been determined at 4.2 K. Frazer and Brown (*2*) found that both $FeSO_4$ and $NiSO_4$ exhibit ferromagnetic intrachain coupling and antiferromagnetic interchain coupling, whereas $CrVO_4$ has antiferromagnetically ordered chains which are coupled together ferromagnetically. α-$CoSO_4$ was found to have a noncollinear variant of the former structure. Will *et al.* (*5*) showed that $MnSO_4$ has an incommensurate, cycloidal cone spiral of moments in the (001) plane of the orthorhombic structure with the propagation vector directed along *a* and spiral components in the *ab* plane; the moments are antiferromagnetically coupled along the chains. From theoretical considerations, Sólyom (*6*) has predicted that this magnetic structure should arise after cooling through three separate phase transitions and should be elliptical with an oscillating *z* component. His predictions have been borne out by specific heat measurements (*7*) and neutron diffraction studies as a function of temperature (*8*); the latter indicated that the axis of the cone on which the moments lie is tilted 7° from *c* in the *ac* plane.

Previous work on β-$CrPO_4$ (*1*) has shown

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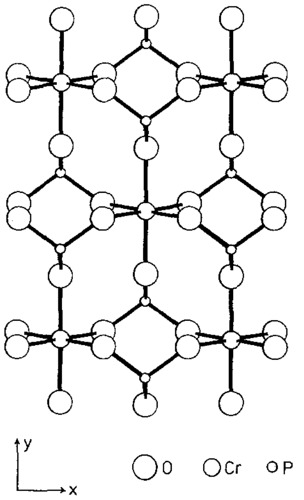

FIG. 1. The structure of β-$CrPO_4$ projected on (001).

that the magnetic susceptibility follows the Curie–Weiss law above 78 K, with an effective magnetic moment of 3.9 μ_B and a Weiss temperature of −80 K. These values show that the system contains localized-electron $3d^3:{}^4A_{1g}$ Cr^{3+} ions, which might be expected to order antiferromagnetically at low temperatures. We have determined both the ordering temperature and the nature of the magnetic structure found at 5 K, and have compared the magnetic properties of β-$CrPO_4$ with those of other $CrVO_4$ isomorphs.

Experimental

Approximately 10 g of green, polycrystalline β-$CrPO_4$ was prepared by boiling to dryness a solution containing equimolar quantities of BDH "GPR" $Cr(NO_3)_3 \cdot 9H_2O$ and "Analar" $(NH_4)H_2PO_4$, and heating the residue to 1000°C in air.

The X-ray powder pattern agreed with that reported previously (*9*) and no other lines were observed. Analytical electron microscopy using the thin-crystal method (*10*) showed that the material was homogeneous. The magnetic susceptibility of a polycrystalline sample (~15 mg) was measured between 4.2 and 70 K using an Oxford Instruments Faraday Balance with an applied field of 9.95 kG and a field gradient of 122 Oe cm^{-1}. The powder diffraction data were collected at 5 K on D1a at the ILL, Grenoble, using neutrons with a mean wavelength of 1.909 Å.

Results and Discussion

The variation of molar susceptibility with temperature (Fig. 2) suggests that β-$CrPO_4$ is antiferromagnetically ordered at low temperatures. The broadness of the susceptibility maximum at 37 K indicates that there is an initial one-dimensional, short-range ordering along the chains parallel to *c*; our data give no clear indication of the temperature at which long-range, three-dimensional ordering occurs. This could be determined by specific heat measurements or variable temperature neutron diffraction experiments, as was done in the case of $MnSO_4$ (*7, 8*). However, the Néel Temperature of β-$CrPO_4$ is clearly lower than that of ~50 K reported for the isomorphous $CrVO_4$ (*2*), reflecting the relative Cr–Cr distances along the chains in the two compounds (equal to half the lattice constant c_0) which are 3.067 Å in β-$CrPO_4$ and 2.989 Å in $CrVO_4$ at 298 K. Both of these are greater than the critical distance for metal–metal

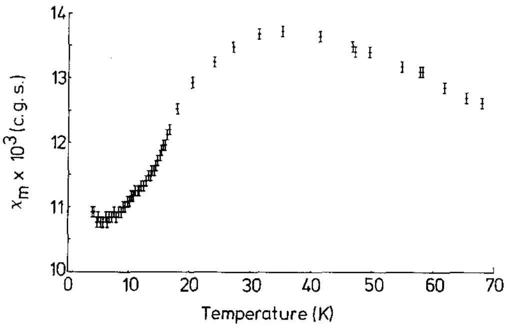

FIG. 2. The molar magnetic susceptibility of β-$CrPO_4$ as a function of temperature.

bonding (2.84 Å) proposed by Goodenough (*11*).

The neutron data were analyzed using a program based on the Rietveld method (*12*). Initially, the low angle data were excluded and the atomic structure was refined in space group *Cmcm* starting from the coordinates of $CrVO_4$ (*2*), using a single, isotropic temperature factor and scattering lengths from Bacon (*13*). The difference profile was then plotted for the entire data range, revealing peaks at low angles that could be indexed neither on the original unit cell nor on a simple enlarged cell. These were found to be satellites of the type observed for the incommensurate magnetic structure of $MnSO_4$, with d spacings given by the formula

$$1/(d_{\pm})^2 = [(h/a) \pm \tau]^2 + k^2/b^2 + l^2/c^2$$

where τ is the magnitude of the reciprocal lattice propagation vector, which lies along [100]. A mean value of 0.0631 ± 0.0006 Å^{-1} was computed for τ, corresponding to a periodicity of $3.07 \pm 0.03a_0$, and the magnetic structure was conveniently refined using a unit cell with the dimensions $3a_0 \times b_0 \times c_0$. The free ion form factor of Freeman and Watson (*14*) was used to calculate the magnetic scattering. A section of the proposed magnetic model is shown in Fig. 3. The moments are collinear and antiferromagnetically coupled along the chains, and lie in the (001) plane as a consequence of dipole–dipole interactions. The ordering between chains gives rise to a cycloidal spiral of moments that propagates along [100]. Refinement of the usual structural parameters and the components of the magnetic moment on the Cr^{3+} ions led to a weighted profile R factor of 13.2%, and a value of $2.55 \pm 0.10\mu_B$ for the component of the magnetic moment in the ab plane. No peaks characteristic of an out-of-plane component were seen. The magnetic moment of $2.55 \pm 0.10\mu_B$ per cation is in reasonable agreement with those reported previously (*15*) for Cr^{3+} in an oxide environment. Refined values of structural and atomic parameters are given in Table I, together with selected bond distances and angles. The final observed, calculated and difference profiles are shown in Fig. 4.

TABLE I

STRUCTURAL DATA FOR β-$CrPO_4$ AT 5 K

Cell parameters (Å)

$a_0 = 5.1710(4)$ $b_0 = 7.7573(2)$ $c_0 = 6.1183(2)$

Overall isotropic temperature factor = 0.22(2) Å^2

Atomic coordinates in *Cmcm* (No. 63)

Atom	Symmetry position	x	y	z
Cr	4a	0	0	0
P	4c	0	0.3503(3)	$\frac{1}{4}$
O_I	8f	0	0.2459(2)	0.0429(3)
O_{II}	8g	0.2462(4)	0.4706(2)	$\frac{1}{4}$

Selected bond distances and angles

Distance (Å)	Angle (deg)	
$Cr–O_I$ (×2) 1.925(2)	$O_I–Cr–O_{II}$	89.5
$Cr–O_{II}$ (×4) 2.028(2)	$O_I–Cr–O'_{II}$	90.5
$P–O_I$ (×2) 1.504(3)	$O_{II}–Cr–O'_{II}$	99.4
$P–O_{II}$ (×2) 1.579(3)	$O_{II}–Cr–O''_{II}$	80.6
	$Cr–O_{II}–Cr'$	97.9
	$O_I–P–O'_I$	114.9
	$O_{II}–P–O'_{II}$	107.5
	$O_I–P–O_{II}$	108.6

Note. Estimated standard deviations in parenthesis.

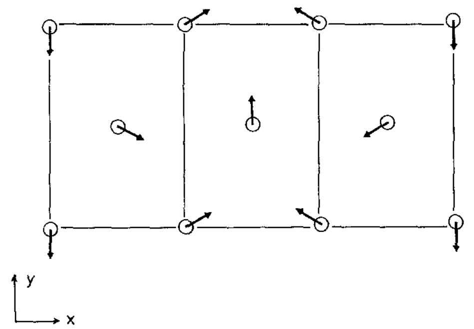

FIG. 3. Magnetic ordering in the (001) plane of β-$CrPO_4$ at 5 K.

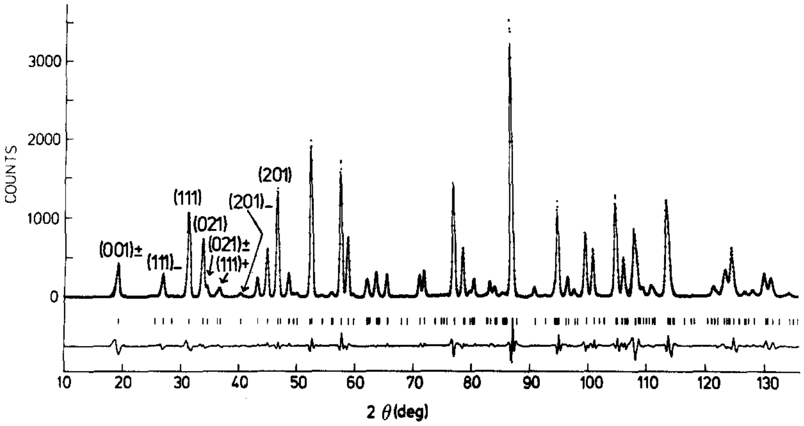

FIG. 4. Observed (points), calculated (full line), and difference profiles for the powder neutron diffraction pattern of β-$CrPO_4$ at 5 K. Reflection positions are marked and low angle nuclear peaks and their magnetic satellites $(hkl)_\pm$ are labeled.

This is only the second time that a spiral magnetic structure has been observed in an inorganic oxosalt with orthorhombic or lower symmetry, the first example being in the isomorphous $MnSO_4$ where the periodicity was found to be $\sim 6a_0$ rather than $\sim 3a_0$ as in β-$CrPO_4$. The two magnetic structures differ further in that $MnSO_4$ has a non-zero spin component parallel to c. In general, noncollinear magnetic structures arise when ordering interactions of comparable strengths are in competition. In this structure the competing superexchange interactions are mediated by the Cr–O–Cr linkages along individual chains and by Cr–O–P–O–Cr linkages between chains. The superexchange interactions in both $MnSO_4$ and β-$CrPO_4$ will be inherently antiferromagnetic and, not surprisingly, the M–O–M interaction within the chains is dominant in both materials. The interchain coupling via the tetrahedral ion is a weaker effect and the magnetic ordering scheme in each material is presumably dictated by the slightly differing geometries of the linkages and the different metal $3d$ configurations. Polarized neutron experiments would help to clarify the interaction scheme but suitable single crystals have not yet been prepared.

Finally, it is interesting to review previous work on $CrVO_4$ in the light of our results. From a low resolution experiment using a mean neutron wavelength of 1.05 Å, Frazer and Brown (*2*) proposed that $CrVO_4$ has a commensurate magnetic structure, with spin vector orientation angles of $\xi_x = 27 \pm 15°$, $\xi_y = 64 \pm 10°$, and $\xi_z = 81 \pm 15°$ and a magnetic moment of $2.1 \pm 0.2\mu_B$. They concluded that, within their error limits, a model with spins parallel to a was plausible. Our results for β-$CrPO_4$, in conjunction with the anomalously low reported magnetic moment of $CrVO_4$, suggest that the magnetic structure of this compound may be more complex than hitherto reported, and we are currently reinvestigating this material.

Acknowledgments

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