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Crystal and Magnetic Structure of $PbCrO_3$

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$PbCrO_3$ has been synthesized in the high-pressure "belt" apparatus from PbO and CrO_2 at 1150°C and a pressure in excess of 50 kbar. Single-crystal and powder x-ray diffraction at room temperature show the compound has the cubic perovskite structure with $a_0=4.00$ Å. No deformation of the cubic structure was discerned in neutron diffraction patterns at 77° and 4.2°K. At low temperature the magnetic moments of the chromium atoms are ordered in the antiferromagnetic *G*-type structure in which the spins on each Cr are antiparallel to those of the six nearest neighbors. Assuming the magnetic form factor of chromium can be approximated by that of Cr^{3+}, the magnetic intensities give a moment of 1.9 μ_B per chromium atom, approximately the spin value for Cr^{4+} ($3d^2$). The temperature dependence of the (111) magnetic peak was measured and the results fitted to a Brillouin function with $T_N \approx 240$°K. The magnetic susceptibility does not show a maximum at the Néel point but does obey a Curie–Weiss law above T_N, consistent with the neutron-diffraction results.

WE have recently synthesized $PbCrO_3$ by superpressure methods, and here report some magnetic properties of the Cr^{4+} ion.

SYNTHESIS

Polycrystalline $PbCrO_3$ was synthesized from PbO and CrO_2 in the high-pressure "belt" apparatus at 1150°C and pressures in excess of 50 kbar. A few 100-μ crystals were grown by maintaining a temperature gradient across a large pressure cell. The crystals were black and of cubic habit.

CRYSTAL STRUCTURE

X-ray photographs exhibited asterism showing the crystals were badly strained. Two individual crystals were examined; one was twinned, and the second was a single crystal with cubic lattice parameter of 4.00 Å. Visual estimates from precession photographs agreed with intensities calculated for the perovskite arrangement.

The polycrystalline material contained 5%–10% impurities: Pb_2CrO_5 and Pb_3O_4 were probably present; PbO, $PbCrO_4$, CrO_2, and Cr_2O_3 were absent; a few x-ray lines remained unidentified.

MAGNETIC STRUCTURE

Neutron-diffraction patterns were obtained with the G.E. spectrometer located at Brookhaven National Laboratory. Impurity interferences and the small Cr moment resulted in relatively poor-quality intensity data. However, the magnetic structure is simple and some definite conclusions about the ordered state are possible.

The intensities of perovskite and impurity peaks did not change on cooling, but new peaks appeared which could be indexed by a magnetic cell with $a_{\text{mag}}=2a_{\text{nucl}}$. The spins order in the antiferromagnetic *G* structure[1,2] in which the moment on each chromium is antiparallel to those on the six nearest chromium neighbors. Intensities were computed with an over-all temperature factor $2B=2.04$ Å^2, nuclear scattering amplitudes Pb=0.96, Cr=0.35, O=0.58×10^{-12} cm, the Cr^{+3} form factor,[3] and $gS=1.9$ for the chromium moment. The spin direction could not be determined because $\langle q^2\rangle_{\text{Av}}=\frac{2}{3}$ for all directions. The observed chromium form factor is compared in Fig. 1 with experimental and calculated values for Mn^{2+},[4] Ni^{2+},[5] and Cr^{3+}.[3] The temperature variation of the (111) magnetic peak (Fig. 2) can be approximated with a Brillouin function based on $J=1$ and $T_N=240$°K.

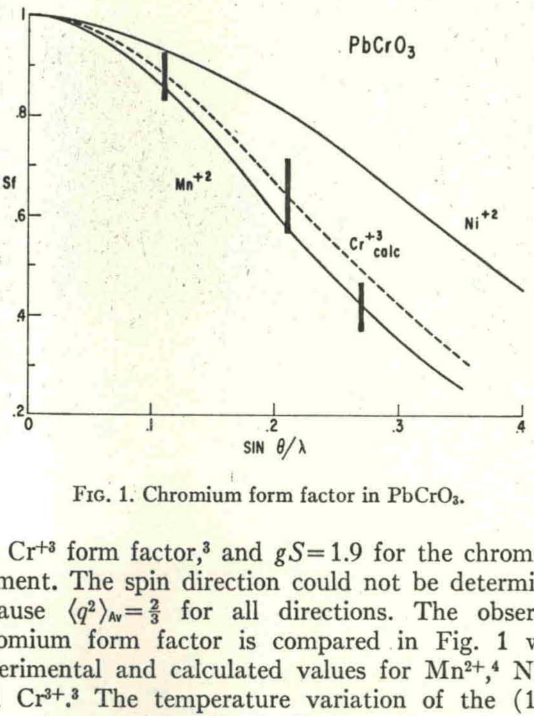

FIG. 1. Chromium form factor in $PbCrO_3$.

MAGNETIC SUSCEPTIBILITY

The susceptibility, $\chi=M/H$, was calculated from the magnetization measured at 25 kOe. *M* was linear with field above room temperature, but nonlinearity and a small remanence were observed at low temperature. χ increased with decreasing temperature from

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[1] J. Goodenough, *Magnetism and the Chemical Bond* (Interscience Publishers, New York, 1963).

[2] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

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

[4] J. M. Hastings, N. Elliott, and L. M. Corliss, Phys. Rev. **115**, 13 (1959).

[5] H. Alperin, J. Phys. Soc. Japan **17**, BIII, 12 (1962).

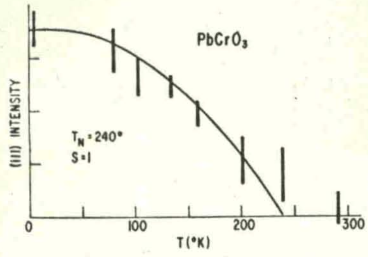

FIG. 2. Temperature dependence of magnetic scattering from $PbCrO_3$.

570° to 4.2°K, but did not show a maximum indicative of transition to an ordered antiferromagnetic state (Fig. 3). High-field measurements between 40 and 80 kOe show a differential susceptibility smaller than that measured at 25 kOe. The $1/\chi$-vs-T curve is nearly linear, and within experimental error can be fitted to a Curie–Weiss law $\chi = C/(T-\theta)$ with $C = 326\times10^{-5}$ and $\theta = -240$°K, corresponding to a pure spin moment and $-\theta = T_N$. The effective paramagnetic moment is $p = 2.83$; however, there is considerable uncertainty in the high-temperature data and the region above 350°K could be fitted by smaller values of p and $|\theta|$.

DISCUSSION

Our results are consistent with the interpretation that Cr^{4+} ions with moment $gS = 2$ order antiferromagnetically below 240°K. The bonding is predominantly ionic and the Pb–O distance is 2.88 Å, slightly greater than 2.78 Å calculated from ionic radii. The antiferromagnetic G structure, which now has been observed for d^2, d^3, and d^5 cations ($PbCrO_3$, $LaCrO_3$, $CaMnO_3$, and $LaFeO_3$), is due to indirect antiferromagnetic exchange interactions which take place by overlap of the cation d orbitals with the intervening anion p orbitals.

It is possible that Cr^{4+} may dissociate into ions with different valence and develop ferromagnetism by virtual double exchange.[6] Although no evidence for this was found in the neutron-diffraction patterns, a small ferromagnetic component easily could have escaped detection. Such interactions would account for the remanence below T_N, as well as the possibility that $|\theta| < T_N$. The decreased susceptibility in higher fields suggests the saturation of this component and probably better represents the antiferromagnetic contribution to the susceptibility.

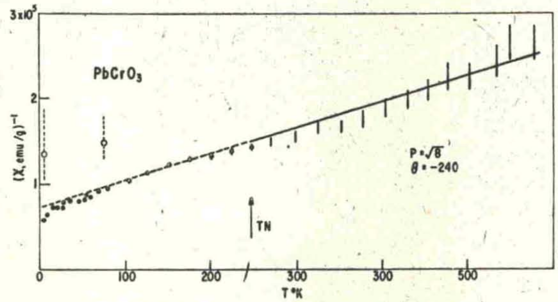

FIG. 3. Magnetic susceptibility of $PbCrO_3$. ●: 25 kOe; ○: differential susceptibility measured between 40 and 80 kOe.

There is a problem understanding the spin-only moment for octahedral Cr^{4+}. Crystal field theory predicts the ground term should be $^3T_1$ which has threefold orbital degeneracy and therefore an orbital moment. Neutron diffraction measures the product of the moment and form factor. Consequently, a reduction of chromium moment below the spin value requires the f curve be displaced upwards, implying a more compressed spin density. The high-temperature susceptibility could be consistent with a lower chromium moment. Alternatively, the orbital moment might be quenched by distortion of the crystal fields about the chromium, either by crystal defects or Jahn–Teller interactions. This interpretation is supported by the discrepancies in Table I which may be due to small deformations of the oxygen octahedron sufficient to lift the orbital degeneracy.

TABLE I. Nuclear and magnetic intensities of $PbCrO_3$ at 4.2°K.

			Intensity	
hkl	Type	2θ	Calc	Obs
111	mag	12°33′	179	176
100	nucl	14°32′	1	21
110	nucl	20°35′	342	375
113	mag	24°15′	73	73
111	nucl	25°20′	1528	1537
200	nucl	29°20′	1421	1357
331	mag	32°03′	23	17
210	nucl	33°03′	1	76
211	nucl	36°08′	207	76
220	nucl	41°55′	1293	1114
221,300	nucl	44°38′	0	18
310	nucl	47°10′	113	0
311	nucl	49°38′	1050	1043
222	nucl	52°00′	526	634

ACKNOWLEDGMENTS

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[6] C. Zener, Phys. Rev. **82**, 403 (1951).