JOURNAL OF SOLID STATE CHEMISTRY 5, 39–41 (1972)

A Study on the $PbCrO_3$ Perovskite

B. L. CHAMBERLAND AND C. W. MOELLER

Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268

Received October 4, 1971

The perovskite compound $PbCrO_3$ has been prepared from CrO_2 and PbO at high pressure. The product was formed as small black cubes suitable for electrical resistivity measurements. Magnetic susceptibility data were obtained in the region 77 to 550°K. The oxide phase was found to be a semiconductor with antiferromagnetic behavior below a transition temperature of about 160°K.

Introduction

The preparation of $PbCrO_3$ by various methods at high pressure has been reported previously by DeVries and Roth (*1*, *2*) The results of their preparations indicated that it is an equilibrium phase at high pressure (55–75 kbar) above 800°C. In many of their products, however, slight amounts of an impurity phase were present which interfered with the high temperature magnetic properties (*2*).

Neutron diffraction data (*1*) suggested antiferromagnetic behavior below 240°K with a magnetic moment of 1.9 μB per chromium atom, which is approximately the spin value of Cr^{4+} (d^2 state). The susceptibility data particularly at high temperature, i.e., above the Néel point, showed much scatter and the paramagnetic moment could not be accurately determined from these data. The electrical transport properties have not been reported.

This investigation was carried out in an attempt to isolate a pure $PbCrO_3$ compound and to reinvestigate the magnetic properties of this phase. An effort was also made to prepare single crystals of the material suitable for the measurement of electrical transport properties.

Experimental Section

High purity PbO obtained from Electronic Space Products, Inc. and CrO_2 prepared from a hydrothermal reaction (*3*) were used directly as reactants. Equimolar amounts of the oxides were intimately mixed in an agate mortar and pestle and heated to 800–900°C at 60–65 kbar pressure in a tetrahedral anvil press. The reaction products formed after 2–4 hr were quenched to room temperature prior to the release of pressure. Black cubes of $PbCrO_3$ were isolated in the platinum reaction vessel.

The crystallographic data were obtained on several products with a Hägg–Guinier camera using Cu$K\alpha_1$ radiation and an internal KCl standard ($a = 6.2931$ Å). The magnetic studies were performed on a Faraday balance utilizing a Cahn microbalance. A standard four-probe technique was used to determine the electrical resistivities on a small bar cut from a crystalline chunk of $PbCrO_3$ product. The activation energy was calculated from the slope of a plot of $1/T$ vs. log ρ. The anomaly observed in the electrical transport properties was reproducible.

Results

The crystallographic results were consistent with a perovskite-type product with lattice parameter $a = 4.0050 \pm 4$ Å (vol. = 64.24 Å^3). All the reflections were consistent with the perovskite structure and space group *Pm3m*. The powder diffraction lines, however, were quite broad even with the strictly monochromatic Cu$K\alpha_1$ radiation used with the Guinier camera.

The $PbCrO_3$ obtained in this investigation was found to be crystallographically pure and possessed no magnetic field dependence in the

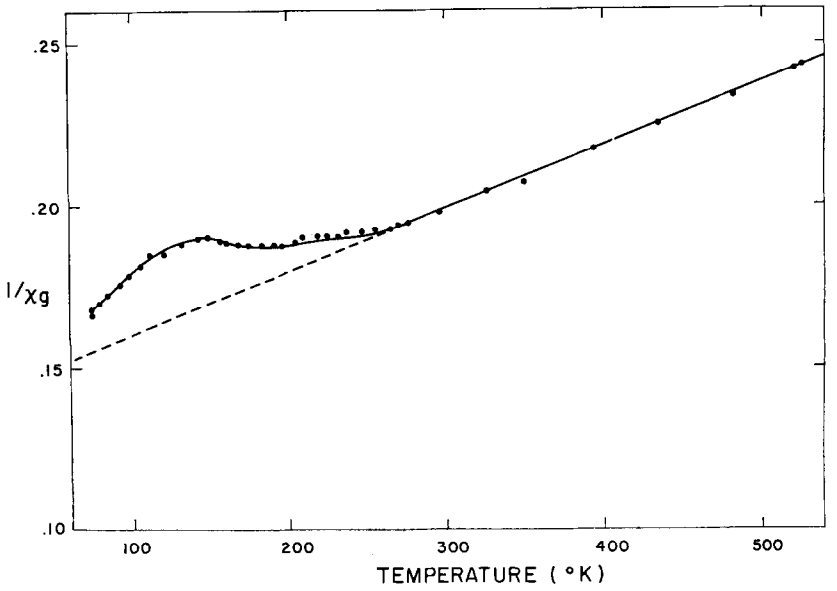

FIG. 1. Reciprocal gram susceptibility vs. temperature (°K) for $PbCrO_3$.

region 77 to 550°K. The magnetic data at high temperature suggest Curie–Weiss behavior with a θ of −817°K if spin-only behavior is assumed for Cr(IV). (Fig. 1). Magnetometer studies (*4*) did not indicate any well defined magnetic transitions in the temperature region 4 to 100°K but some slight field dependence was noted at liquid He temperature.

The electrical resistivity data suggest semiconductor behavior with a room temperature resistivity of 2.6×10^3 Ω cm. The observed activation energy from the resistivity plot was 0.27 eV (Fig. 2).

The electrical transport anomaly at 100°K might suggest some transition in this region. This is the same approximate temperature at which the magnetic susceptibility sharply increases.

The product decomposes rapidly in acids and is unstable above 550°K as noted in our high temperature magnetic studies. A similar decomposition temperature has been reported by DeVries and Roth (*2*).

Discussion

The perovskite-type $PbCrO_3$ product obtained in this study appears to be identical to that prepared by DeVries and Roth (*1*, *2*). The lattice parameter for this phase is essentially the same but no impurities were observed in the powder diffraction patterns of the products used in this study. The magnetic susceptibility data also indicate a pure phase.

The $PbCrO_3$ perovskite appears to be a semiconducting antiferromagnetic with $T_N = 160$°K. At room temperature and above the magnetic moment derived from the Curie–Weiss equation

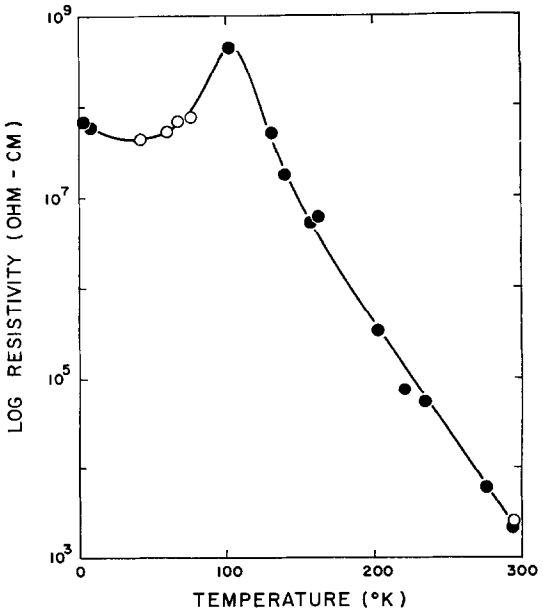

FIG. 2. Logarithm of resistivity vs. temperature for $PbCrO_3$. ● represent data taken on lowering temperature, while o represent data obtained on warming sample to room temperature.

TABLE I

CALCULATED AND OBSERVED MAGNETIC MOMENTS FOR $PbCrO_3$

T(°K)	μ_{calc}	μ_{obs}	T(°K)	μ_{calc}	μ_{obs}
175	2.32	2.37	275	2.58	2.60
183	2.34	2.40	296	2.62	2.63
190	2.37	2.42	326	2.66	2.66
197	2.39	2.43	350	2.69	2.70
209	2.42	2.45	394	2.74	2.74
219	2.45	2.48	431	2.78	2.79
232	2.48	2.51	435	2.78	2.78
244	2.51	2.51	482	2.82	2.82
257	2.54	2.56	520	2.84	2.85
265	2.56	2.59	524	2.85	2.85
270	2.57	2.59	572	2.87	2.89

is high (3.80 μB) and the Weiss constant is also large (−817°K). To account for the magnetic data, the minimum in the reciprocal susceptibility vs. temperature plot was taken as the Néel point (160°K). It was assumed that spin–orbit coupling in the paramagnetic region above 175°K could be used to calculate the effective magnetic moment. It is found that orbital contributions are of significant magnitude for the d^2 configuration in the octahedral crystal field of the perovskite structure. With a reduced spin–orbit coupling constant (80% of the free ion value, 162.5 cm^{-1}) and a moderate ligand field, $A = 1.0$, the theoretical magnetic moments for Cr(IV) were calculated (*5*).

The experimental magnetic moments were determined by using the observed magnetic susceptibility values corrected for atomic diamagnetism according to the values given in Selwood (*6*), and a Weiss constant which gave the best agreement with the theoretical moments, $\theta = -235°$. The two sets of magnetic moments for the temperature range 175 to 572°K are compared in Table I.

The calculated and observed intensities from neutron diffraction and X-ray crystallography studies (*1*, *2*) were used as good evidence to support the composition of $PbCrO_3$. The lattice parameters of our products and those of the previous authors are in good agreement and it is believed that the $PbCrO_3$ phase is stoichiometric and contains tetravalent chromium. The neutron diffraction data (*1*) also strongly suggest antiferromagnetic interactions (*G*-type structure where $a_{mag} = 2a_{nucl.}$) at low temperature with two unpaired electrons corresponding to a d^2 state of Cr(IV). Our low temperature magnetic susceptibility data support this conclusion. The temperature dependence of magnetic scattering from the (111) plane of $PbCrO_3$, however, does not fit a well defined Brillouin function with rapid decreasing intensity as expected. The tail in the intensity data reported by DeVries and Roth (*1*) is used to give the higher Néel point of 240°K. In our study we have used the point where a high deviation from the calculated and observed magnetic moment occur as the Néel temperature and this has an uncertainty of about 40° which would place the maximum Néel temperature at 200°K.

The results of the calculations suggest that the Weiss constant to Néel temperature ratio is −1.47 which is more consistent with ratios observed in other similar oxide systems. A similar treatment of the magnetic data obtained on the perovskite $CaCrO_3$ (*7*) was used to explain the high magnetic moment and large Weiss constant calculated according to the spin-only theory.

Below 140°K some canted spin arrangement or ferromagnetic impurity might give rise to the increasing susceptibility values, the low-temperature magnetic field dependence, and the electrical transport anomaly.

Acknowledgments

The authors are indebted to Peter Furmonavicius for his assistance in obtaining the magnetic data and Mr. J. L. Gillson for the resistivity data. The financial support from the University of Connecticut Research Foundation and the Research Corporation are gratefully acknowledged.

References

1. W. L. ROTH AND R. C. DEVRIES, *J. Appl. Phys.* **38**, 951 (1967).
2. R. C. DEVRIES AND W. L. ROTH, *J. Amer. Ceram. Soc.* **51**, 72 (1968).
3. T. J. SWOBODA, P. ARTHUR, JR., N. L. COX, J. N. INGRAHAM, A. L. OPPEGARD, AND M. S. SADLER, *J. Appl. Phys.* **32**, 3745 (1961).
4. J. M. LONGO carried out these experiments at Lincoln Laboratories, MIT.
5. B. N. FIGGIS, "Introduction to Ligand Fields," p. 271. Eq. 10.25, where $x = \lambda/kT$. Interscience, New York (1966).
6. P. W. SELWOOD, "Magnetochemistry," 2nd ed. Interscience, New York (1956).
7. J. F. WEIHER, B. L. CHAMBERLAND, AND J. L. GILLSON, *J. Solid State Chem.* **3**, 529 (1971).