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BAND ANTIFERROMAGNETISM AND THE NEW PEROVSKITE $CaCrO_3$

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ABSTRACT

The perovskite $CaCrO_3$ has been prepared by the solid-state reaction of CaO and CrO_2 at 65 kbar and 700°C. It has the O-orthorhombic structure with a = 5.287Å, b = 5.316Å, and c = 7.486Å. Below $T_N = 90^oK$, it exhibits a parasitic ferromagnetism with $\sigma_o = 0.295$ emu/gm at 4.2°K. Up to 6 kbar, the pressure dependence of T_N gives $dT_N/dP = -0.23^oK/kbar$. Four-probe resistivity measurements on a polycrystalline bar give resistivities of 10^6 and 10^4 ohm-cm at 77 and 300°K. Comparison with the properties of other ABO_3 perovskites having B = Mo^{4+}, Cr^{4+}, V^{3+} indicates that $CaCrO_3$ represents spontaneous collective-electron magnetism.

Introduction

Transition-metal oxides ABO_3 having the perovskite structure provide an isostructural set of compounds that are important for studying the change from localized to collective d electrons [1]. The perovskites $A^{2+}MoO_3$, $A^{2+}CrO_3$, $A^{3+}VO_3$ are significant because they each contain two d electrons per molecule while their properties vary from metallic with Pauli paramagnetism to semiconducting with spontaneous magnetism and crystallographic distortions characteristic of localized electrons. This means that, without varying the number of outer d electrons, we can study the transition from collective d electrons having no spontaneous magnetism to localized d electrons.

This paper reports the preparation and some properties of the new perovskite $CaCrO_3$, which belongs to this series, and compares these properties with those of the other members and with a phenomenological description of the localized-electron to collective-electron transition.

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Experimental

The existence of Cr^{4+} in solid state compounds is not common and, in most cases, is synthesized only at high pressures. In known Cr^{4+}-containing compounds that do not require high-pressure synthesis, the ratio of alkaline-earth cation to Cr^{4+} ion is greater than one (i.e. Sr_2CrO_4, Ba_2CrO_4, and Ba_3CrO_5). Two cubic perovskites containing Cr^{4+} cations have previously been prepared under high pressure: antiferromagnetic, semiconducting $PbCrO_3$ [2] and metallic, Pauli paramagnetic $SrCrO_3$ [3].

We have prepared $CaCrO_3$ by the solid state reaction of CaO and CrO_2 at 65 kbar and 700°C for 15 mins. The CaO was prepared by decomposition of $CaCO_3$ while the CrO_2 was prepared by the decomposition of CrO_3 at 400°C and 20 kbars. It was found necessary to dry the reactants at 100°C and quickly transfer them after weighing to a nitrogen-filled glove bag. To ensure complete reaction, the reactants were ground together in the glove bag (agate mortar and pestle) and loaded tightly into a cylindrical gold liner (4 mm dia x 10 mm) with gold end plugs. For reactions above 1000°C, platinum liners and end plugs were used. The samples were subjected to the desired pressure before the temperature was raised. After completion of the run, the sample was quenched by shutting off the power to the furnace. When the sample reached room temperature (about 1 min), the pressure was released and the sample examined with a Norelco X-ray powder diffractometer using CuKα radiation. The temperature of reaction was determined from a watts vs temperature plot that had previously been established with a thermocouple inserted into the cell.

The product of stoichiometric reaction always included varying amounts of Cr_2O_3, which could not be removed by washing. However, a small excess of CaO (5-10%) almost completely eliminated the Cr_2O_3 impurity, and the CaO impurity could be washed out with dilute acid. The Cr_2O_3 impurity most likely arises from local pressure variations or chemical inhomogeneities, both of which may cause CrO_2 to lose oxygen before it reacts with the CaO present. This same impurity problem has been reported by DeVries and Roth [4] in the preparation of $PbCrO_3$. When CaO was reacted with CrO_3 instead of CrO_2, the yellow Cr^{6+} compound $CaCrO_4$ was always formed. This compound was extremely stable and did not lose oxygen to form a perovskite phase up to 1200°C and 65 kbar. This is in contrast with $PbCrO_4$, which at 1300°C and 60 kbar gave mostly $PbCrO_3$ [4].