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Magnetic Behavior of Tetrahedral Cr^{4+} Compounds: Sr_2CrO_4, Ba_2CrO_4, and Ba_3CrO_5

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The preparation of the compounds Sr_2CrO_4, Ba_2CrO_4, and Ba_3CrO_5 is described. The characterization of these three Cr^{4+} compounds by X-ray and magnetic susceptibility experiments has been conducted. The magnetic moments for Sr_2CrO_4, Ba_2CrO_4, and Ba_3CrO_5 were determined to be in good agreement with the calculated value expected for a tetrahedral Cr^{4+} ion. Weak antiferromagnetic ordering for all three compounds is indicated from the small paramagnetic Weiss constants determined from the susceptibility data in the temperature region 80–300 K. Distortions of the tetrahedra from ideality, as determined from the structural features, further cause a reduction in the magnetic moments from the theoretical values.

Introduction

Many texts and review articles report that the Cr^{4+} ion is a rare and unusual oxidation state and that few of its physical properties have been reported. It is now known that the normal coordination for this ion is tetrahedral and that most of the compounds prepared with oxygen as the ligand and under normal conditions of pressure and temperature are ternary compounds in which an alkali and alkaline earth cation is used to stabilize the unusual oxidation state.

The ternary oxides of Cr^{4+} include Sr_2CrO_4, Ba_2CrO_4, and Ba_3CrO_5. The syntheses of these three compounds have been published in the literature (*1*) but few of their properties have been given. Structural studies have been carried out on Sr_2CrO_4 and Ba_2CrO_4 (*2, 3*). Isostructural features between Ba_3CrO_5 and Cs_3CoCl_5 have been presented (*4*).

Recently the preparation and properties of two alkali metal Cr^{4+} oxides have been reported (*5*). These compounds, Na_4CrO_4 and K_4CrO_4, both exhibit Curie–Weiss behavior with slightly reduced magnetic moments: 2.80 μ_B vs a theoretical spin-only moment of 2.83 μ_B. These two compounds contain Cr^{4+} ions in tetrahedral sites and are structurally related to the Na_4SiO_4 structure possessing triclinic symmetry.

High pressure methods have been used to convert the coordination of Cr^{4+} from tetrahedral to octahedral: Sr_2CrO_4 with the K_2NiF_4 structure has been prepared in this manner (*6*).

Our interest in the Cr^{4+} ion has been to determine the physical properties of this unusual oxidation state for chromium and

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the correlation of properties with structure. In the present report, the magnetic properties of tetrahedral Cr^{4+} in the alkaline earth ternary oxides Ba_2CrO_4, Sr_2CrO_4, and Ba_3CrO_5 are reported.

Preparation

The syntheses of the three compounds have been reported previously but since great difficulty was observed in isolating pure samples for magnetic characterizations, a summary of some of the key features in the preparation of each member of this series will be given.

Reactants for the synthesis of the ternary compounds include $BaCrO_4$, Fisher Scientific Company, C.P. 99.5%; $SrCrO_4$, Ventron 98%; $Ba(OH)_2 \cdot 8H_2O$, Mallinckrodt Chemical Works, 98% min.; $Sr(OH)_2 \cdot 8H_2O$, Ventron; $BaCO_3$, Fisher Scientific Company, precipitated, certified reagent; $SrCO_3$, B&A reagent; and fine-grained Cr_2O_3 prepared by the thermal decomposition of chromium oxalate, $Cr_2(C_2O_4)_3$, J. T. Baker, C.P. anal. at 500°C.

Sr_2CrO_4

The synthesis of Sr_2CrO_4 was attempted by reacting $SrCrO_4$, Cr_2O_3, and $Sr(OH)_2 \cdot 8H_2O$ in a 1 : 1 : 5 molar ratio under a nitrogen- or oxygen-free argon atmosphere at 900°C for several hours. In these preparations, however, the product obtained was either impure Sr_2CrO_4 or $Sr_5(CrO_4)_3(OH)$. The reaction mixture was heated with a slight excess of $Sr(OH)_2$ in a vacuum system to generate a pure product after repeated firings at 900–950°C. A single-phase product was obtained after six separate heatings for 1 to 4 hr under these conditions. X-Ray-pure Sr_2CrO_4 was obtained after a total heating period of 13.5 hr at 900–950°C *in vacuo*. The color of the product was blue-black.

Ba_2CrO_4

The synthesis of Ba_2CrO_4 was carried out by reacting $BaCrO_4$, Cr_2O_3, and $Ba(OH)_2 \cdot 8H_2O$ in a 1 : 1 : 5 molar ratio with a 10% weight excess of $Ba(OH)_2$. The solid-state reaction of this mixture in air, in N_2, or in O_2-free Ar generally yielded only the highly stable $Ba_3(CrO_4)_2$ or $Ba_5(CrO_4)_3(OH)$. When the reaction was carried out *in vacuo* at 1000°C for a total of 10.5 hr (three separate heatings) pure, dark green Ba_2CrO_4 was isolated.

Ba_3CrO_5

The preparation of Ba_3CrO_5 was accomplished by reacting $BaCrO_4$, Cr_2O_3, and $Ba(OH)_2 \cdot 8H_2O$ in a molar ratio of 1 : 1 : 12 at 960–1200°C *in vacuo* for a total heating time of 61 hr and 9 separate heating steps, with grinding of the products between each heating. The proportion of Ba_3CrO_5 increased during each heating cycle. The final product, a light blue solid, contained BaO from the excess $Ba(OH)_2$, and also some $BaCO_3$. The excess $Ba(OH)_2$ was used to prevent the formation of highly stable Ba_2CrO_4 and $Ba_3(CrO_4)_2$. Products were kept in a desiccator to prevent decomposition by air or moisture. Since both of these impurities are diamagnetic and difficult to separate from Ba_3CrO_5, no purification was attempted but consideration of their presence was made during the interpretation of the magnetic data. A chemical analysis of the product was carried out by determining the amount of BaO and $BaCO_3$ present in the sample. The final chemical analysis indicated the composition: 1.0 Ba_3CrO_5 : 0.49 $BaCO_3$: 0.81 BaO. This analyzed material was used in the magnetic experiment.

Instrumentation

X-Ray Instrument

The X-ray unit used in this study was a GE powder diffractometer XRD-5, utilizing

Cu$K\alpha$ radiation. The powder data were also obtained in a Debye–Scherrer camera with Cu$K\alpha$ radiation. Unit cell parameters were calculated using a least-squares refinement program.

Magnetic Balance

The magnetic studies were performed on a Faraday system utilizing a Cahn microbalance in the temperature range 80–300 K. The observed susceptibilities were corrected for diamagnetism according to the values given in Selwood (*7*).

Results

The preparations of the ternary alkaline earth Cr^{4+} oxides were conducted as described above. The purity and identity of these products were established from the X-ray crystallographic data. The unit cell parameters for each compound are given in Table I and are compared to those published in the literature.

The structures of Sr_2CrO_4 and Ba_2CrO_4 have been previously determined (*1*). Both compounds crystallize with the $Pn2_1a$ space group but differ in unit cell content and the coordination of the alkaline-earth cations. Their fundamental structure type is that of β-K_2SO_4, which contains discrete anionic tetrahedral groups. The CrO_4^{4-} tetrahedra, however, are highly distorted and this greatly reduces their overall symmetry.

TABLE I

CRYSTALLOGRAPHIC DATA

		Unit cell parameter (Å)			
Compound	Symmetry	*a*	*b*	*c*	Ref.
Sr_2CrO_4	Orthorhombic	14.08(1)	5.860(4)	10.215(5)	This work
		14.18(1)	5.79 (3)	10.10 (2)	(*2*)
Ba_2CrO_4	Orthorhombic	7.600(5)	5.967(8)	10.496(7)	This work
		7.621(2)	5.918(1)	10.484(3)	This work
		7.67	5.89	10.39	(*3*)
Ba_3CrO_5	Tetragonal	7.330(6)	—	11.59(3)	This work
		7.32 (1)	—	11.67(1)	(*4*)

TABLE II

System		Distance (Å)				Mean distance (Å)
Sr_2CrO_4	Cr(1)–O	1.66	1.83	1.83	1.86	1.80
	Cr(2)–O	1.67	1.87	1.90	1.95	1.85
Ba_2CrO_4	Cr–O	1.75	1.79	1.86	1.86	1.82

The Cr–O distances (in Å) for each system are given in Table II. These data indicate the distortions of the respective CrO_4^{4-} tetrahedra. The mean bond distances are consistent with the predicted bond distance for $^{IV}Cr^{4+}$ and $^{III}O^{2-}$ of 1.80 Å (*8*). The bond angles around Cr in Sr_2CrO_4 vary by ±3% for Cr(1) and ±12% for Cr(2) from the ideal tetrahedral value. The corresponding deviation from ideality in Ba_2CrO_4 is approximately ±10%. The individual CrO_4^{4-} tetrahedra are separated by fairly large distances within each unit cell; the nearest Cr–Cr distances are 4.12 Å in Sr_2CrO_4 and 4.81 Å in Ba_2CrO_4.

Further supporting evidence for the tetrahedral CrO_4^{4-} distortion was obtained from infrared studies. Both $BaCrO_4$ and $SrCrO_4$, containing discrete CrO_4^{2-} groups with little or no distortion, possess sharp and well-defined absorptions in the region 1000 to 400 cm^{-1}. The IR spectra for Ba_2CrO_4 and Sr_2CrO_4, however, show complex and multiple absorptions in the same region indicating major tetrahedral distortion of CrO_4^{4-} groups. The coordination numbers for the two Sr atoms in Sr_2CrO_4 are VI and VIII, whereas those for the Ba atoms in Ba_2CrO_4 are VIII and IX. These differences in alkaline earth coordinations (and ionic sizes) cause the compounds to have different structures and they are therefore not isostructural. Slight differences also exist between Ba_2CrO_4 and Ba_2TiO_4 or Ba_2CoO_4.

Interpretation of the Magnetic Data

The inverse susceptibility versus temperature curve for Sr_2CrO_4 is shown in Fig. 1.

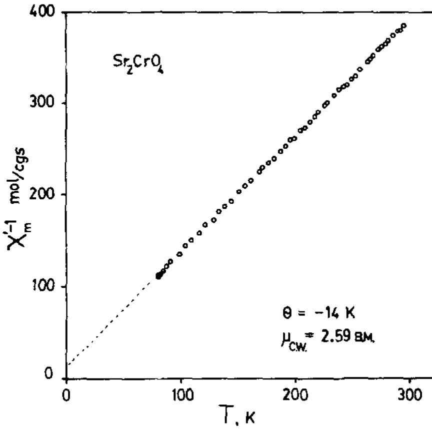

FIG. 1. Plot of the inverse magnetic susceptibility vs absolute temperature for Sr_2CrO_4.

The data can be fit to the Curie–Weiss law, and indicate a Curie–Weiss moment of 2.59 μ_B with $\theta = -14$ K. The behavior of Ba_2CrO_4 is nearly identical to that of Sr_2CrO_4, as seen in Fig. 2, and similarly indicates a Curie–Weiss moment of 2.63 μ_B with $\theta = -17$ K. Precise measurements of the susceptibility of Ba_3CrO_5 were not possible due to the difficulties encountered in its preparation, and particularly due to the hygroscopic nature of BaO present in the sample. Its inverse susceptibility versus temperature is very similar to that of Sr_2CrO_4 and Ba_2CrO_4, and indicate an approximate Curie–Weiss moment of 2.5–2.6 μ_B with θ about −10 K.

Cr^{4+} is a d^2 ion with a ground term $^3A_2$ (e_g^2) in tetrahedral coordination. As a first approximation, therefore, complete quenching of any orbital contribution is expected. Slight deviations from spin-only moments can arise, however, from the effect of spin-orbit coupling, which in the case of a ground A term may be considered to mix in terms of differing orbital degeneracy: for tetrahedral Cr^{4+}, the A_2 ground term has a T_2 term above with the same spin multiplicity. The magnitude of this first-order Zeeman effect determines the deviation from spin-only behavior, and depends on the relative energies of the spin–orbit coupling constant λ and the ligand field splitting (10*Dq*). The magnetic moment is expected to be temperature-independent, and may deviate (*9*) from the spin-only moment μ(s.o.) according to

$$\mu(\text{eff}) = \mu(\text{s.o.})(1 - 4\lambda/10Dq).$$

The ligand field splitting for Cr^{4+} in octahedral coordination by oxygen is of the order of 20,000 cm^{-1} (*9, 10*), while that of Cr^{5+} in tetrahedral coordination by oxygen is approximately 10,000 cm^{-1} (*11*). From these values, a ligand field splitting of 8000 cm^{-1} was estimated for tetrahedral Cr^{4+} coordinated by oxygen. Using a reduced spin–orbit coupling constant of 110 cm^{-1}, 70% of the free-ion value (*12*), the calculated moment is 2.7 μ_B, as compared to the spin-only value of 2.83 μ_B. The magnetic moments obtained for Sr_2CrO_4, Ba_2CrO_4, and Ba_3CrO_5, are slightly lower than the calculated moment. These results are consistent with appreciable distortion of the CrO_4 tetrahedra: the lower values of the cubic ligand field in tetrahedral coordination make the effects of low-symmetry ligand field components more obvious than, for example, octahedrally coordinated analogs, since their energies represent larger frac-

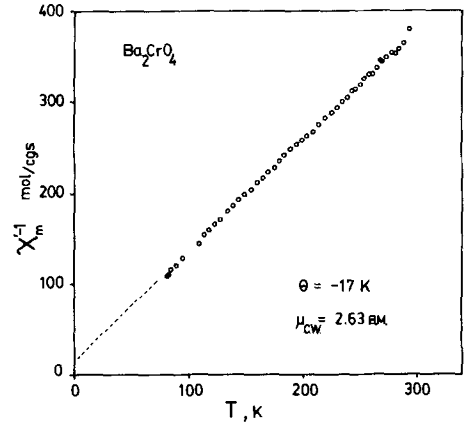

FIG. 2. Plot of the inverse magnetic susceptibility vs absolute temperature for Ba_2CrO_4.

tions of the field splittings. The small negative θ values obtained for all three compounds may indicate weak antiferromagnetic ordering at low temperatures not accessible in the present study.

Acknowledgments

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