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Magnetic Properties of the Mixed-Valence Compounds $CaMn_3O_6$ and $CaMn_4O_8$*

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The preparation of two new mixed-valence compounds, $CaMn_3O_6$ and $CaMn_4O_8$, are described and their magntic and EPR behavior investigated. The Mn moments in both compounds have nearly spin-only values. $CaMn_3O_6$ and $CaMn_4O_8$ order ferrimagnetically near 3 and 89 K, respectively. The broad, Lorentzian EPR lines indicate a significant exchange interaction between Mn^{3+} and Mn^{4+} ions. The magnetic and EPR results suggest a strong ferromagnetic interaction between Mn^{3+} and Mn^{4+} ions and a comparable antiferromagnetic Mn^{3+}–Mn^{3+} and/or Mn^{4+}–Mn^{4+} interaction.

Introduction

Mixed-metal oxides represent a large class of inorganic solids which have many important properties not found in the more limited binary oxides. In mixed-metal oxides it is possible to stabilize high or mixed oxidation states of transitional elements, to have extensive ranges of either anion or cation nonstoichiometry, and to generate new structural arrangements not possible in the simpler binary oxides.

Mixed-metal oxides containing Mn are particularly interesting due to their abundance, and the ability of Mn to adopt a variety of oxidation states. Such oxides also exhibit interesting magnetic behavior. A detailed neutron diffraction study of the magnetic properties of the perovskite-type mixed-metal manganites $Ca_x^{2+}La_{1-x}^{3+}Mn_x^{4+}Mn_{1-x}^{3+}O_3$ has revealed that these compounds exhibit ferromagnetic and antiferromagnetic properties depending on the fraction of Mn^{4+} present (*1*). The results of this study are in excellent agreement with Goodenough's predictions based on the theory of semicovalent exchange (*2*).

Of particular interest to us is the Ca–Mn–O system, which has a complex phase diagram (*3–6*) due both to the range of valence states of Mn and to the ability of the very electropositive Ca to stabilize high valence states of Mn and to the ability of the very electropositive Ca to stabilize

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high valence states of transitional ions. In this paper we describe the preparation of the new mixed-valence compounds $CaMn^{3+}_{2}Mn^{4+}O_6$ and $CaMn^{3+}_{2}Mn^{4+}_{2}O_8$ (*6*) and investigate their magnetic and electron paramagnetic resonance (EPR) behavior.

Experimental

Sample Preparation and Characterization

Samples of $CaMn_3O_6$ and $CaMn_4O_8$ were prepared from solid-solution calcite precursors (*6, 7*). The precursors were synthesized by first preparing an aqueous solution containing the appropriate molar amounts of calcium and manganese cations. This aqueous solution was obtained by dissolving $CaCO_3$ and $MnCO_3$ in dilute nitric acid. The $CaCO_3$ used was reagent grade. The $MnCO_3$ used was freshly precipitated from a manganese nitrate solution with a large excess of ammonium carbonate, dried at 100°C in a vacuum oven and stored in sealed containers until used. Commercially available reagent grade $MnCO_3$ was unacceptable because it always contained significant amounts of oxidized manganese products, as evidenced by its brown color. The aqueous solution of calcium and manganese cations was then added, with stirring, to a large excess of approximately 2 *M* ammonium carbonate. The resulting precipitate was a single-phase, solid-solution carbonate with the calcite structure whose composition could be expressed as $Ca_{1-x}Mn_xCO_3$. Precipitates were dried at 100°C in a vacuum oven and stored in an inert atmosphere to prevent any premature oxidation of divalent manganese.

The solid-solution precursors were reacted to mixed-metal oxides by firing them in recrystallized alumina boats in an atmosphere of flowing oxygen. The syntheses of pure $CaMn_3O_6$, and pure $CaMn_4O_8$ were achieved by firing the appropriate solid-solution, carbonate precursors for 1 hr at 800°C with one interruption for regrinding.

The reacted mixed-metal oxides were examined by powder X-ray diffraction using a Phillips diffracted-beam monochromator. A thorough analysis of the X-ray patterns of $CaMn_3O_6$ and $CaMn_4O_8$ is not complete, but it does appear that these two phases are related structurally. The tabulated X-ray diffraction data for both compounds are presented in Ref. (*6*).

Both $CaMn_3O_6$ and $CaMn_4O_8$ were examined by electron microscopy using a JOEL 100B electron microscope. The electron diffraction patterns of different crystallites of the same compound were well defined and identical, indicating that both compounds were well crystallized and monophasic. The electron diffraction pattern of $CaMn_3O_6$ could be indexed on a monoclinic cell having dimensions $a \simeq 10$ Å, $b \simeq 12$ Å, $c \simeq 8$ Å, and $\beta \simeq 120°$, whereas that for $CaMn_4O_8$ was consistent with a cell having either monoclinic or orthorhombic symmetry.

The calcium and manganese contents of both compounds were analyzed by X-ray fluorescence (XRF) using metal oxides as standards, and the oxygen contents were calculated by difference. The results of the XRF analysis (±1 wt%) are: 14 wt% Ca, 55 wt% Mn, and 31 wt% O (theoretical wt% Ca, Mn, and O = 13.3, 54.8, and 31.9 wt%, respectively). A similar XRF analysis for $CaMn_4O_8$ resulted in 11 wt% Ca, 58 wt% Mn, and 31 wt% O (theoretical wt% Ca, Mn, and O = 10.3, 56.7, and 33.0 wt%, respectively). These results are consistent with cation stoichiometries (experimentally determined by an alternate method) for $CaMn_3O_6$ and $CaMn_4O_8$ reported elsewhere (*6*).

The oxygen content of both phases was determined with a Fischer thermogravimetric analyzer containing a Cahn electrobalance. Samples were reduced in hydrogen and weight loss was attributed to reduction of manganese with oxidation states higher than 2+. Thermogravimetric analyses of the two compounds under investigation resulted in formulas of $CaMn_3O_{6.0\pm0.1}$ and $CaMn_4O_{8.1\pm0.1}$ assuming Ca : Mn ratios of 1 : 3 and 1 : 4, respectively.

All of the compositional analyses reported here support ideal formulas of $CaMn_3O_6$ and $CaMn_4O_8$; but other similar stoichiometries cannot be conclusively ruled out without a careful structural study.

The electrical resistivites of $CaMn_3O_6$ and $CaMn_4O_8$ were measured on pressed powder samples by the four-probe method, at room temperature. The resistivity cell consisted of a cylindrical die. The current flow was supplied through the end plungers of the die, while the voltage measurement was made between annular electrodes formed by two metal foils situated between the end plungers. The resistivites of both compounds were found to be ~10^4 Ω-cm.

Magnetic Susceptibility Measurements

The magnetic susceptibility was measured in the range 4.2–300 K using Faraday apparatus described elsewhere (*8*). The maximum field was 13 kG and $H(dH/dz) = 27\ (\mathrm{kG})^2/\mathrm{cm}$. The setup was calibrated with Pt and $HgCo(SCN)_4$. The susceptibility was measured at five field strengths ranging from 2.5 to 13 kG at each temperature. The susceptibilities have not been corrected for ionic diamagnetism and are believed to be accurate within 2%.

EPR Measurements

EPR spectra were recorded at 296 K using a Varian E-12 spectrometer. The *g* factors were determined using pitch in KCl as an internal standard.

Results

The magnetic susceptibility was independent of field at all temperatures in $CaMn_3O_6$ and above 90 K in $CaMn_4O_8$. Below 90 K in $CaMn_4O_8$ the susceptibility increases with decreasing temperature in a manner typical of ferromagnetism or ferrimagnetism. The temperature dependences of the reciprocal susceptibility per mole of $CaMn_3O_6$ and $CaMn_4O_8$ are shown in Fig. 1, and the resulting curves are typical of ferrimagnetic behavior. The susceptibility obeys the Curie–Weiss law above about 30 and 140 K in $CaMn_3O_6$ and $CaMn_4O_8$, respectively, and increases abruptly in both compounds below these temperatures. The Curie temperature T_c was determined from the temperature intercept on the reciprocal susceptibility vs temperature curve and is about 3 K in $CaMn_3O_6$ and about 89 K in $CaMn_4O_8$. The magnetic parameters are summarized in Table I.

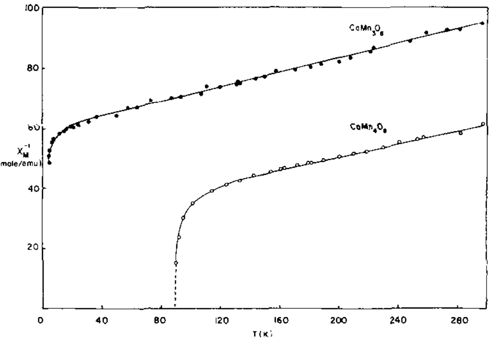

FIG. 1. Temperature dependences of the reciprocal susceptibility per mole of $CaMn_3O_6$ (solid circles) and $CaMn_4O_8$ (open circles).

The EPR spectrum of $CaMn_4O_8$ at 296

TABLE I

MAGNETIC PARAMETERS

Compound	$\mu_{SO}{}^a$ (μ_B)	μ^a (μ_B)	θ (K)	T_c (K)
$CaMn_3O_6$	4.56	4.78	−513	3
$CaMn_4O_8$	4.39	4.33	−273	89

[a] μ_{SO} and μ are the calculated spin-only and experimental magnetic moments, respectively, expressed in Bohr magnetons. Here $\mu_{SO} = [a\mu(Mn^{3+}) + b\mu(Mn^{4+})]/(a + b)$, where *a* and *b* are the number of moles of Mn^{3+} and Mn^{4+}, respectively, per mole of oxide.

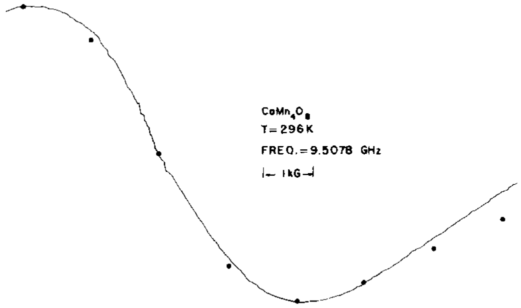

FIG. 2. EPR spectrum of CaMn$_4$O$_8$ at 196 K. The dots are values computed from a Lorentzian lineshape function.

K is shown in Fig. 2. The broad resonance is due to the compound, and the multiline spectrum centered at $g = 2$ results from Mn^{2+}. In the compound, the lineshape is Lorentzian in the central region, the peak-to-peak linewidth $\Delta H_{\mathrm{p-p}}$ is 5200 ± 50 G, and the g factor is 1.94 ± 0.01. From the relative intensities of the Mn^{2+} and CaMn$_4$O$_8$ resonances we have estimated that Mn^{2+} is present at a level of about 100 ppm. The Mn^{2+} spectrum (Fig. 3), which consists of 6 strong allowed hyperfine lines and 10 weaker forbidden transitions occurring as doublets between the main hyperfine lines, is characteristic of magnetically isolated Mn^{2+} in an axially distorted environment. The zero-field-splitting parameter (D) can be evaluated from either the intensity ratio of two allowed transitions (usually for transitions having $m_\mathrm{I} = \frac{1}{2}$ and $\frac{5}{2}$) (*9*) or of forbidden and allowed transitions (usually those having $m_\mathrm{I} = \frac{1}{2}$) (*10*). In both cases we find $D = 123 \pm 5$ G. Similar results are found for CaMn$_3$O$_6$, except that the Mn^{2+} level is about an order of magnitude higher than that in CaMn$_4$O$_8$. The EPR parameters are summarized in Table II.

TABLE II

EPR PARAMETERS

Compound	$\Delta H_{\mathrm{p-p}}$ (G)	g	Mn^{2+} (ppm)	D (G)
CaMn$_3$O$_6$	4875 ± 50	1.94 ± 0.01	1000	113 ± 10
CaMn$_4$O$_8$	5200 ± 50	1.94 ± 0.01	100	123 ± 5

Interpretation

The proximity of the g factor to the spin-only value indicates that the orbital contribution to the Mn moment is small, and this conclusion is reinforced by the good agreement between the calculated spin-only and experimental magnetic moments. Nearly spin-only Mn^{3+} and Mn^{4+} moments are not uncommon. Such moments have been observed in other compounds containing Mn^{3+} or Mn^{4+} octahedrally coordinated by six oxygens (*11*, *12*), and a theoretical explanation of these moments has been given by Van Vleck (*13*) and Siegert (*14*).

The Lorentzian lineshape in the central region is characteristic of exchange-coupled localized moments (*15*). In general, interaction between identical moments leads to exchange narrowing and between different moments results in exchange broadening (*16*). Hence the broad resonances observed in both compounds well above T_c suggest that exchange interactions between Mn^{3+} and Mn^{4+} ions are strong, and the observed ferrimagnetic behavior implies that the exchange coupling is probably ferromagnetic between Mn^{3+} and Mn^{4+} ions. This finding is consistent with the

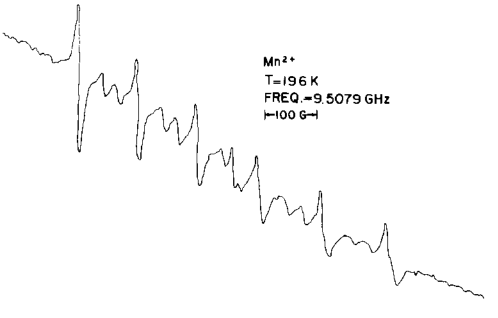

FIG. 3. Resolution of the weak Mn^{2+} EPR spectrum of CaMn$_4$O$_8$ in Fig. 2.

results of the neutron diffraction study of $Ca_x^{2+}La_{1-x}^{3+}Mn_x^{4+}Mn_{1-x}^{3+}O_3$ (*1*), in which it was concluded that the exchange coupling is in general (a) ferromagnetic between Mn^{3+} and Mn^{4+} ions, (b) antiferromagnetic between Mn^{4+} ions, and (c) either ferromagnetic or antiferromagnetic between Mn^{3+} ions, with the type determined by the intercation separation (the coupling will be antiferromagnetic when the Mn^{3+} separation is less than about 2.8 Å). Since the ionic arrangements in $CaMn_3O_6$ and $CaMn_4O_8$ are unknown, detailed predictions concerning the exchange coupling cannot be made. However, it is useful to compare the observed magnetic behavior to that in the $Ca_xLa_{1-x}MnO_3$ system (*1*). In the latter the Curie temperatures attained their maximum values (~250 K) in the range 30 to 50% Mn^{4+}. The sharp decline in T_c above 50% Mn^{4+} is due in part to the formation of antiferromagnetic Mn^{4+}–O–Mn^{4+} and Mn^{3+}–O–Mn^{3+} bonds, and the less pronounced decrease in T_c below 30% Mn^{4+} is due in part to the development of antiferromagnetic Mn^{4+}–O–Mn^{4+} and ferromagnetic Mn^{3+}–O–Mn^{3+} bonds. Hence the dramatic decrease in T_c in going from $CaMn_4O_8$ (50% Mn^{4+}) to $CaMn_3O_6$ (33% Mn^{4+}) suggests a strong ferromagnetic coupling between Mn^{3+} and Mn^{4+} ions and a comparable antiferromagnetic Mn^{3+}–Mn^{3+} and/or Mn^{4+}–Mn^{4+} interaction.

The *D* values given in Table II, which are equal within experimental error and in the range commonly found in solids, may have structural significance if Mn^{2+} is indeed incorporated into the $CaMn_3O_6$ and $CaMn_4O_8$ structures. In such a case the high resolution of the Mn^{2+} spectrum implies that Mn^{2+}–Mn^{3+} and Mn^{2+}–Mn^{4+} exchange interactions are negligible.

We are currently using neutron diffraction to investigate the crystal and magnetic structures of these new compounds.

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