

Electrical and magnetic properties of $(\text{Ca}_{1-x}\text{A}_x)_2\text{MnO}_4$ ($\text{A}=\text{La}$ and Na)

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Electrical and magnetic properties of $(\text{Ca}_{1-x}\text{A}_x)_2\text{MnO}_4$ ($\text{A}=\text{La}$ and Na) have been studied. When a certain amount of La is doped to the Ca site, i.e., electrons are doped, antiferromagnetically ordered magnetic moments are canted and show spontaneous magnetization below 115 K. Electrical conduction is dominated by thermally activated electrons above 115 K, and by hopping electrons below 115 K. The Na doped or hole doped samples $(\text{Ca},\text{Na})_2\text{MnO}_4$ also exhibit spontaneous magnetization below 115 K. The electrical conduction mechanism in $(\text{Ca},\text{Na})_2\text{MnO}_4$ is the same as that in $(\text{Ca},\text{La})_2\text{MnO}_4$. However, when a low magnetic field (<30 Oe) is applied to a $(\text{Ca},\text{Na})_2\text{MnO}_4$ sample, the magnetic susceptibility becomes negative below 40 K. [S0163-1829(96)04521-3]

I. INTRODUCTION

Since it was found that Ca_2MnO_4 has a K_2NiF_4 -type structure,¹ physical properties have been studied for both nondoped Ca_2MnO_4 (Refs. 2–5) and electron-doped Ca_2MnO_4 [with Y (Ref. 6) or Sn (Ref. 7) substituted for the Ca site or F for the O site⁸]. The main interest in the study of Ca_2MnO_4 has been to understand the magnetic interaction between Mn-O layers in $\text{Ca}_n\text{Mn}_{n-1}\text{O}_y$ ($n=2, 3$, and ∞).^{2–5} It has been known that Ca_2MnO_4 is antiferromagnetic below 114 K (Ref. 2) and an insulator having a band gap of 1.4 eV.⁵ Since substituents Y^{3+} , Sn^{4+} , and F^- works to decrease the valence of Mn ions, all of these have been considered to act as electron donors. From these studies, it is clear that the antiferromagnetically ordered spins are canted and thus $(\text{Ca}_{1-x}\text{A}_x)_2\text{MnO}_4$ ($\text{A}=\text{La}$ and Na) shows weak ferromagnetism.

Although the mechanism of high- T_c superconductivity has not been fully understood, some important conditions for the occurrence of superconductivity have been revealed. Most of high temperature superconductors satisfy the following conditions: (1) the parent phases of high- T_c superconductors have the $3d_{x^2-y^2}$ level partially filled, (2) the parent phases are antiferromagnetic insulators, and (3) when certain amounts of the proper elements are used as dopants, superconductivity appears. For the case of Ca_2MnO_4 , the second condition is satisfied. Because the valence of Mn^{4+} is ($3d_3$) in this compound, a single Mn^{4+} ion has a magnetic moment of $3\mu_B$. Although this compound does not satisfy all of the conditions (1)–(3), mentioned above, it is important to compare high temperature superconductors with other materials which have similar electronic and/or magnetic states. In the present study, the electrical and magnetic properties of $(\text{Ca}_{1-x}\text{A}_x)_2\text{MnO}_4$ are studied using both electron doped ($\text{A}=\text{La}$) and hole doped ($\text{A}=\text{Na}$) samples.

II. EXPERIMENT

$(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ samples having the nominal compositions $x=0, 0.01, 0.02, 0.025, 0.0375, 0.05, 0.075, 0.1, 0.125, 0.15$, and 0.175 and $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ samples with $x=0,$

$0.025, 0.05, 0.075, 0.1,$ and 0.125 were prepared using a solid state reaction method. Appropriate amounts of CaCO_3 , MnO_2 , and La_2O_3 or Na_2CO_3 powders were mixed and calcined at 950°C for 10 h in air. Calcined powders were pulverized and pressed into parallel-piped bars and then sintered at 1300°C for 20 h with an intermediate grinding. For the case of $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$, the sintering process was performed in a closed system to minimize the evaporation of Na.

The phases formed in these samples were analyzed using x-ray-diffraction techniques. A conventional four probe technique was used for resistivity measurements in the temperature range of $4.2\text{--}300$ K. The magnetic properties were measured by a superconducting quantum interference device magnetometer (Quantum Design: Model MPMS) in magnetic fields between -2.5 and 2.5 T at temperatures between 4.2 and 400 K.

III. RESULTS AND DISCUSSION

A. $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$

It was revealed by x-ray diffraction that $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ samples with $x=0\text{--}0.125$ were single phase. The lattice parameters of these compounds were measured versus x as shown in Fig. 1. The length of the a axis increases with increasing x , while that of the c axis decreases. Using the data of the temperature dependence of the magnetic susceptibility for Ca_2MnO_4 given in Ref. 8, the effective magnetic moment, M_{eff} , for Mn^{4+} in Ca_2MnO_4 can be calculated to be $3.93 \mu_B/\text{Mn}$. This value is close to the theoretical value for M_{eff} , i.e., $3.84 \mu_B$ for Mn^{4+} which has three electrons in the $3d$ band. Since Mn^{4+} has the electronic distribution of $3d_3$, no Jahn-Teller effect should occur in this system. When La^{3+} is introduced in the system, symmetry of the $3d\epsilon$ (or t_{2g}) level is broken and the Jahn-Teller effect should appear. However, as shown in Fig. 1, as the La content increases, the a axis elongates and the c axis shortens. This distortion is opposite to that expected from the Jahn-Teller effect. The lattice parameter shift may be explained as follows. The inverse susceptibility of Ca_2MnO_4 is linearly proportional to temperature only above 500 K. In other

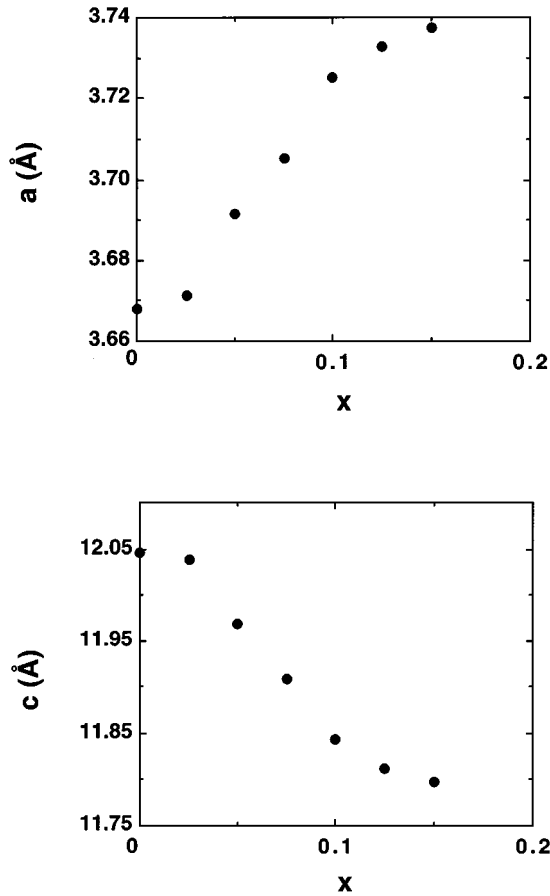


FIG. 1. Tetragonal unit-cell parameters, a and c , vs the La content, x , for $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$.

words, at temperatures between 115 and 500 K, the magnetic properties of Ca_2MnO_4 do not follow the Currie-Weiss law. This deviation seems to indicate that magnetic ordering is about to occur below 500 K accompanied by lattice distortion. Thus it is probable that the doped electrons which are introduced by substituting La for Ca, alter the magnetic states of Ca_2MnO_4 , and the magnetic ordering shortens the c axis and elongates the a axis.

The temperature dependence of the electrical resistivity of $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ is shown in Fig. 2 in terms of La content x . All the samples are semiconductive, i.e., the electrical resistivity decreases as temperature is raised, and the resistivity at 300 K decreases monotonically with increasing x . The mechanism of electrical conduction may be explained with reference to the data for the temperature dependence of electrical resistivity for each x . In general, electrical resistivity, r , can be written as a function of temperature, T , as follows:⁹

$$r = r_0 \exp[E/(kT^n)], \quad (1)$$

where r is resistivity, r_0 a constant, E an activation energy, k Boltzmann's constant, and n a factor which depends on the electrical conduction mechanism. Here, $n=1$ for thermally activated conduction and $n=1/4$ variable-range hopping conduction.⁹ In Fig. 2, resistivity is plotted against inverse temperature and linearity was observed between 150 and 300 K for all the samples. This means that the resistivity follows Eq. (1) with $n=1$, which indicates that thermally activated

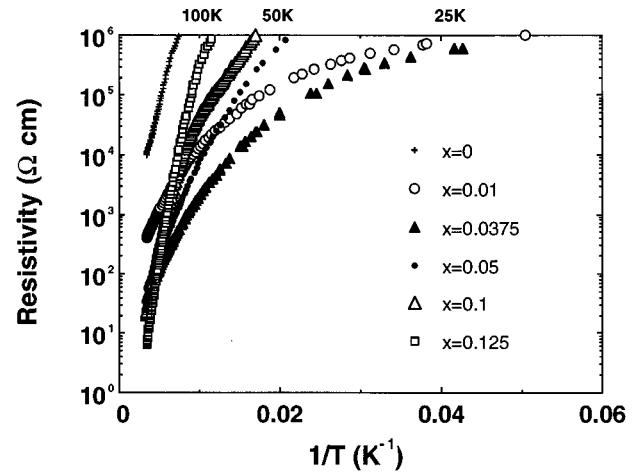


FIG. 2. Temperature dependence of the electrical resistivity for $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$.

electrons dominate the electrical conduction in this temperature range. On the other hand, below 115 K, the $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ samples with $x=0.01-0.0375$ do not follow the relationship expressed by Eq. (1) with $n=1$. It is clear that the electrical conduction mechanism changes from a thermal activation type, to a hopping one as temperature decreases. Using Eq. (1) with $n=1$, the activation energies for all the samples were calculated and plotted against the La content, x , in the temperature range between 150 and 300 K (Fig. 3). Initially, the activation energy which is 0.1 eV for Ca_2MnO_4 reduces to 0.05 eV as La is added up to $x=0.01-0.0375$ in $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$. The activation energy then increases to 0.16 eV with a further increment in the La content. This band gap shift may be attributed to the presence of an impurity level. As is shown in Fig. 1, since the lattice parameter is also shifting with the La content, the band gap will be determined also by the change in the shape of the density of state.

The curve of susceptibility versus temperature for Ca_2MnO_4 ($x=0$ curve in Fig. 8) indicates that Ca_2MnO_4 is antiferromagnetic below the temperature (T_N) of ~ 115 K, which is in good agreement with that of 114 K reported by

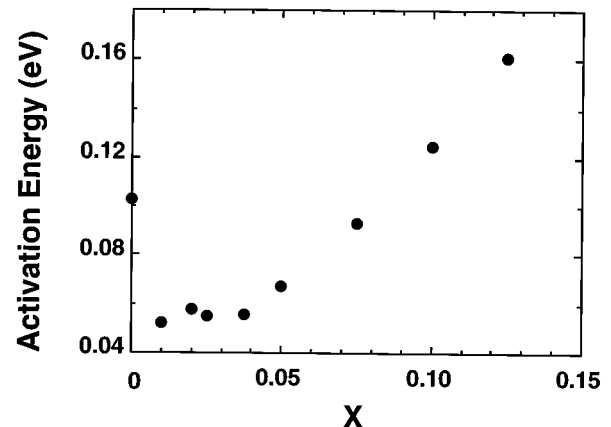


FIG. 3. Activation energy for electrical conduction calculated using the data for the temperature range between 150 and 300 K for $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$.

MacChesney *et al.*² The magnetization was measured as a function of magnetic field (M - H curves) in the range between -2.5 and 2.5 T at temperatures above and below T_N . The magnetization is linearly proportional to the applied magnetic field in the temperature range between 4 and 300 K. Since Ca_2MnO_4 does not show spontaneous magnetization, it should be confirmed that Ca_2MnO_4 is antiferromagnetic. For the samples containing La, the temperature dependence of susceptibility clearly shows spontaneous magnetization below 270 K. However, this spontaneous magnetization from a secondary phase must also be considered in this Ca-La-Mn-O system. It should be noted that $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is known to be ferromagnetic^{10,11} with the Curie temperature at 270 K and the spontaneous magnetization of $3.7 \mu_B/\text{Mn}$ at 90 K. Assuming that $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ exists in the $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ samples as an impurity phase, the mole fraction of the impurity phase can be calculated from the M - H curves using the following equation:

$$M_s = NM, \quad (2)$$

where M_s is the saturated magnetic moment, N the number of magnetic ions per unit weight, and M the average magnetic moment per magnetic ion. First of all, the ferromagnetic component is separated from the hysteresis curve. Then the saturated magnetization is obtained from the ferromagnetic component. If the ferromagnetic component is attributed to the impurity phase, the mole fraction of the impurity phase can be calculated using Eq. (2). For example, the calculated value of mole fraction of the impurity phase, $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, is 0.54% for the $(\text{Ca}_{0.975}\text{La}_{0.125})_2\text{MnO}_4$ sample. This is not discrepant to the fact that no secondary phases are detected by x-ray diffraction because impurity phases of less than 1 mol % may not be detected by conventional x-ray diffraction. Assuming that the ferromagnetic signal below 270 K is induced by the impurity phase, $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, and that the spontaneous magnetization does not depend on temperature, modified susceptibility-temperature curves can be obtained by subtracting the signal due to the impurity phase from the experimental signal. The modified magnetic susceptibility curves are given in Fig. 4. The experimental data were obtained in the field cooled mode under a magnetic field of 1.5 T. As shown in this figure, the susceptibilities for $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ samples with $x=0.01$ – 0.1 abruptly increase below 150 K though the degree of the increment depends on the value of x . This feature of the temperature dependence of susceptibility remains unchanged under different magnitudes of magnetic field, i.e., 0.001 and 0.05 Oe. The largest value of the susceptibility is obtained at 5 K for each sample. The M - H curves for all the samples were measured at 5 K. Using the curves, effective magnetic moments, μ_{eff} , per Mn ion are calculated, and the results are given in Fig. 5. This figure indicates that $(\text{Ca}_{0.9625}\text{La}_{0.0375})_2\text{MnO}_4$ has the largest value of μ_{eff} , i.e., $0.3 \mu_B/\text{Mn}$.

The following observations indicate that $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ with $x=0.01$ – 0.1 is a weak ferromagnet: (1) the temperature range in which $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ ($x=0.01$ – 0.1) shows spontaneous magnetization corresponds to the temperature range where antiferromagnetism appears in Ca_2MnO_4 ; (2) the spontaneous magnetic moments are small, i.e., less than $0.3 \mu_B$; (3) the shape of the M - H curves

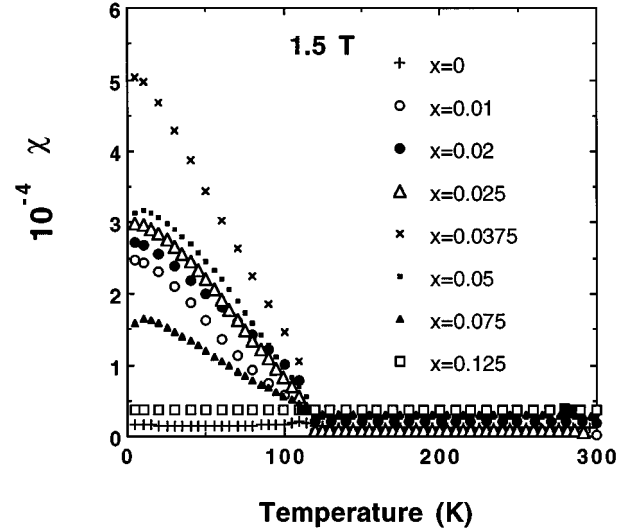


FIG. 4. Temperature dependence of the volume susceptibility, χ , (cgs) for $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ in a magnetic field of 1.5 T.

indicates that $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ ($x=0.01$ – 0.1) have both ferromagnetic and paramagnetic characteristics below 115 K. Therefore, it is possible that the magnetic spins of Mn ions are antiferromagnetically ordered below 115 K in Ca_2MnO_4 and the magnetic spins may be canted by electrons which are introduced by La substitution or doping. The canted spin causes weak ferromagnetism. As previously discussed, the electrical conduction in $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ with $x=0.01$ – 0.1 is of the variable-range hopping mechanism below 115 K. This means that a finite density of states appears in the mobility gap in $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ with $x=0.01$ – 0.1 and the electrons in the mobility gap could cause hopping conduction and induce weak ferromagnetism.

The observation for La doping in the present study is quite consistent with those reported for Y,⁶ Sn,⁷ and F (Ref. 8) doping: canted spin states were observed in all the cases and a hopping conduction mechanism was presumed for Y doping.

B. $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$

Single phase samples of $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ were obtained with compositions $x=0$ – 0.075 . The lattice parameters of the

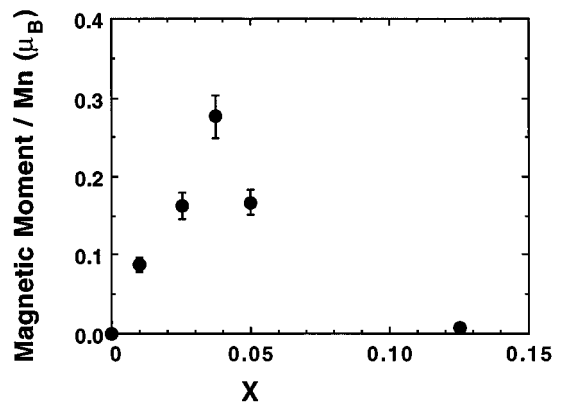


FIG. 5. The dependence of magnetic moment per Mn ion on x for $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ at 5 K.

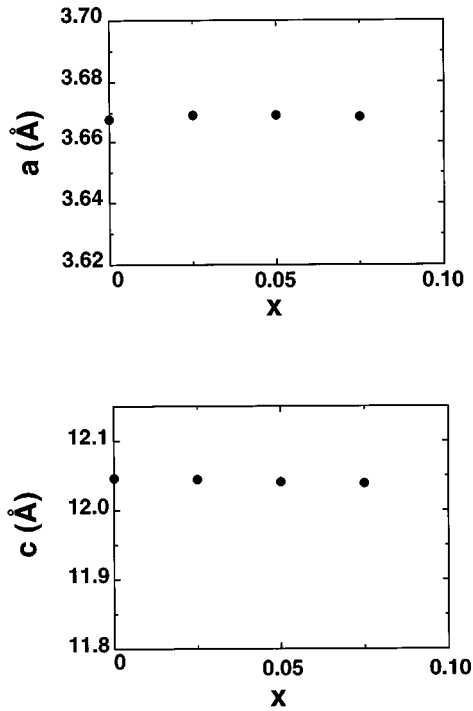


FIG. 6. Tetragonal unit-cell parameters, a and c , vs the Na content, x , for $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$.

phase are not affected by the amount of substituted Na, as shown in Fig. 6. This may be explained from the sizes of calcium and sodium. From the authors' knowledge, there is no data available for the effective ionic radius of Ca with a coordination of 5, which is relevant to the compound, Ca_2MnO_4 . We can still gain a fair estimation of the effective ionic radii using the results with a coordination of 6. The effective ionic radius of Ca with a coordination of 6 is 1.00 Å and that of Na is 1.02 Å.¹² Therefore, large shifts in the lattice parameters with dopant addition is not necessarily expected. In the present work, we assume that the holes are doped by replacing Ca^{2+} by Na^+ ions. The results of electrical conductivity measurements for $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ as a

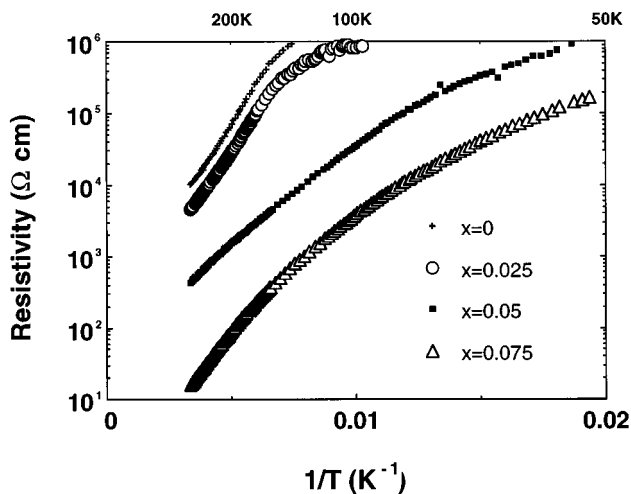


FIG. 7. Temperature dependence of the electrical resistivity for $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$.

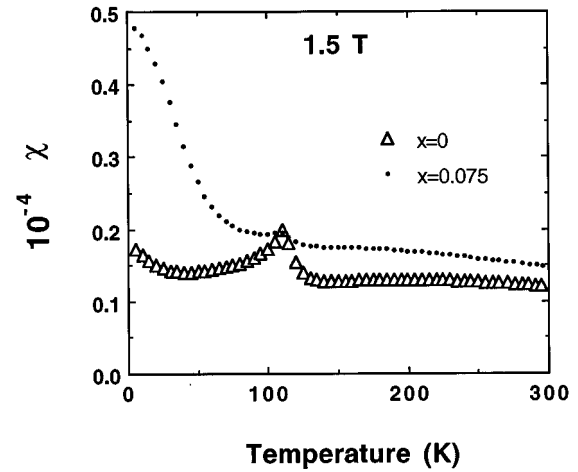


FIG. 8. Temperature dependence of the volume susceptibility, χ , (cgs) for $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ in a magnetic field of 1.5 T.

function of temperature are shown in Fig. 7. Although the activation energies obtained from the data in Fig. 7 remain nearly constant, the absolute value of the electrical resistivity monotonically decreases with increasing the content of Na ions at given temperatures. This decrease in resistivity implies that Na ions create impurity levels in the electronic states of Ca_2MnO_4 . As the dopant increases, more holes are available to carry the charge and as a result, the resistivity of the samples decreases as a function of the amount of a dopant.

The temperature dependence of the susceptibility is plotted in Fig. 8 as a function of the Na content. It is seen that $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ has a spontaneous magnetization at low temperatures as for the case of $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$, though the magnetic moments are much smaller. The magnetic moments of the spontaneous magnetization at 20 K are calculated using Eq. (2) and plotted with respect to the Na content in Fig. 9. The moment increases monotonically as x increases up to $x=0.075$. A significant difference between $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ and $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ is seen in the temperature dependence of the susceptibility. As shown in the previous section, the general behavior of the temperature dependence of the magnetic susceptibility for

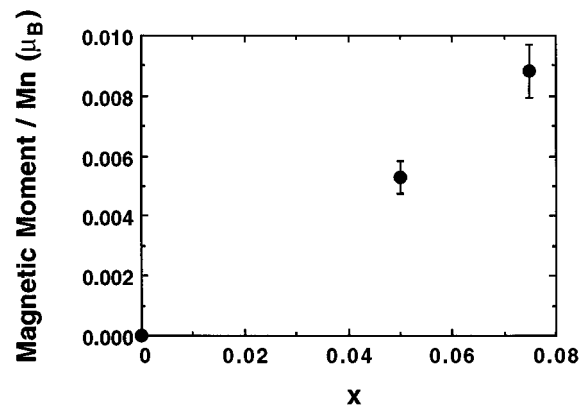


FIG. 9. The dependence of the magnetic moment per Mn ion on x for $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ at 20 K.

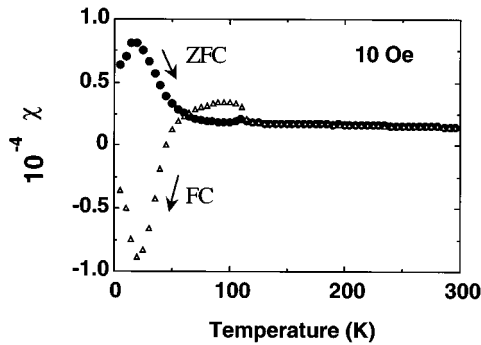


FIG. 10. Temperature dependence of the volume susceptibility, χ , (cgs) in a magnetic field of 10 Oe in both zero-field-cooled (ZFC) and field-cooled (FC) modes for $(\text{Ca}_{0.925}\text{Na}_{0.075})_2\text{MnO}_4$.

$(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ is not affected by the magnitude of the applied magnetic field. However, for the $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ system, the temperature dependence of the magnetic susceptibility depends on the magnitude of the applied magnetic field. In particular, the magnetic susceptibility of $(\text{Ca}_{0.925}\text{Na}_{0.075})_2\text{MnO}_4$ turns negative below 40 K at low magnetic fields, e.g., 10 Oe, as shown in Fig. 10. Shown in the same figure is the temperature dependence of the susceptibility for this sample in both the zero-field-cooled (ZFC) and field-cooled (FC) mode. This clearly shows that $(\text{Ca}_{0.925}\text{Na}_{0.075})_2\text{MnO}_4$ is not superconducting because the susceptibility never becomes negative in the ZFC mode. If the sample is ferrimagnetic and the magnetization is measured under the application of an external field, there is a possibility that the magnetization changes sign. The temperature dependence of magnetization depends on the sign of $\lambda(\alpha+1) - \mu(\beta+1)$, where λ and μ are proportion of Mn ions in *A* and *B* sites, α and β the factors which express the intensity of intrasite interactions relative to the intersite interactions.¹³ For example, if the magnetization of the *A* site is more easily affected by thermal vibration than that of the *B* site, the sign of $\lambda(\alpha+1) - \mu(\beta+1)$ may change.¹³ This type

of temperature dependence was first reported by Gorter.¹⁴ Therefore, the susceptibility vs temperature curve indicates that $(\text{Ca}_{0.925}\text{Na}_{0.075})_2\text{MnO}_4$ is ferrimagnetic.

IV. CONCLUSION

Electrical and magnetic properties of $(\text{Ca}_{1-x}\text{A}_x)_2\text{MnO}_4$, where *A* = La or Na, were studied using single-phase samples of $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ with $x=0-0.125$. Ca_2MnO_4 was found to be antiferromagnetic below 115 K. When La is doped to the Ca site, i.e., electrons are doped, for the samples with $x=0.01-0.1$, the antiferromagnetically ordered magnetic moment is canted and exhibits spontaneous magnetization below 115 K. The maximum spontaneous magnetization of $0.3 \mu_B$ was obtained at 5 K for the sample $(\text{Ca}_{0.9625}\text{La}_{0.0375})_2\text{MnO}_4$. Thermal activation mechanisms are dominant in the electrical conduction at temperatures above 115 K for all the samples, while the hopping electron mechanism is dominant at temperatures below 115 K for $(\text{Ca}_{1-x}\text{La}_x)_2\text{MnO}_4$ with $x=0.01-0.0375$.

For the case of Na doping, i.e., hole doping, single phase samples of $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ were obtained for $x=0-0.075$. When Na is doped to the Ca site, $(\text{Ca}_{1-x}\text{Na}_x)_2\text{MnO}_4$ exhibits spontaneous magnetization below 115 K. $(\text{Ca}_{0.925}\text{Na}_{0.075})_2\text{MnO}_4$ shows the maximum spontaneous magnetization of $0.009 \mu_B$ at 20 K. Thermal activation and hopping electron mechanisms dominate the electrical conduction mechanism above 115 K and below 115 K, respectively. When a low magnetic field (<30 Oe) is applied, the magnetic susceptibility of $(\text{Ca}_{0.925}\text{Na}_{0.075})_2\text{MnO}_4$ is negative at temperatures below 40 K, indicating that $(\text{Ca}_{0.925}\text{Na}_{0.075})_2\text{MnO}_4$ is ferrimagnetic.

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