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Magnetic and Electrical Properties of $(La_{1-x}\ Ca_x)\ MnO_3$

Abstract: Samples of polycrystalline $(La_{1-x}Ca_x)MnO_3$, where x takes values ranging from 0.005 to 0.3, have been studied experimentally. Specimens were carefully prepared in the stoichiometric forms by changing the oxygen partial pressure conditions for each value of x. For specimens having x smaller than 0.1, the Néel temperature T_N is almost constant, 141°K, while the paramagnetic Curie temperature θ increases as x increases. On the other hand, for specimens in which x is greater than 0.1, both T_N (or T_c) and θ are almost equal and increase with the value of x. The Mn^{55} NMR spectra associated with Mn^{3+} and Mn^{4+} ions were observed in specimens having x smaller than 0.175, while motionally narrowed Mn^{55} spectra were observed where the values of x were 0.2 or 0.3. All the experimental results could be qualitatively explained by postulating that the d holes at the sites around Ca^{2+} ions contribute to both the electrical conduction and the magnetic interaction. The ferromagnetic interaction induced by mobile d holes can not be ascribed to the double-exchange interaction, if this interaction has the usual form $b \cos(\theta/2)$.

Introduction

The distorted-perovskite type oxides $(La_{1-x}Ca_x)MnO_3$, where x takes values ranging from 0.005 to 0.3, are interesting since the electrons that carry the electrical current are considered to contribute mainly to the magnetic interaction. The host crystal, $LaMnO_3$, is an insulator.[1] It has been found very recently that this crystal is a weak ferromagnet with a Néel temperature of 141°K.[2] Crystals doped with a small amount of Ca^{2+} (substituting for La^{3+} in $LaMnO_3$) are semiconducting[1] and ferromagnetic.[3,4] The correlation between the electrical conduction and the induction of the ferromagnetic interaction was first noticed experimentally by Jonker and van Santen,[1,3] and simply explained as a double-exchange* interaction by Zener.[5] A detailed theoretical treatment for the double-exchange interaction was given by Anderson and Hasegawa,[6] and the interaction was used by de Gennes[7] to explain the magnetic properties of $(La_{1-x}Ca_x)MnO_3$.

In this study, we have observed how the ferromagnetic moments are induced; the correlation with the electrical conduction is noticed particularly in the low Ca concentration range.

Experiments

• *Specimen preparation and x-ray study*

By controlling the ratio of gases, CO_2 to H_2, properly stoichiometric (from chemical analysis for Mn^{3+}, Mn^{4+} and total oxygen) specimens of the series $(La_{1-x}Ca_x)MnO_3$ were obtained.[2] The crystallographic structures at room temperature are cubic, orthorhombic and monoclinic for decreasing values of x. In the monoclinic phase, the angle between the a and b axes deviates slightly ($<1°$) from 90°. The phase transition temperature obtained by x-ray diffraction study is shown in Fig. 1 as a function of x. Also, a marked induced anisotropy was observed for a narrow range of composition around $x = 0.17$ upon cooling from room temperature to liquid nitrogen temperature in a magnetic field. This indicates that the cooperative Jahn-Teller distortion associated with the orthorhombic-to-cubic transition may be influenced by the magnetic ordering if it occurs below T_c. A detailed explanation of this effect will be found in the literature.[2]

• *Magnetization*

The results of magnetization measurements are shown in Fig. 2. For specimens with x smaller than 0.1, the Néel temperature T_N is almost constant, 141°K, while the paramagnetic Curie temperature θ increases with the value of x. The spontaneous magnetization at 77°K, M_s, is almost unchanged. These facts suggest the creation of some ferromagnetic regions in the host crystal which do not interact with each other. For specimens with x greater than 0.1, the Curie temperature and spontaneous magnetization increase with the value of x; θ is almost equal to T_c. This shows that ferromagnetic interaction begins to dominate over the antiferromagnetic interaction in pure $LaMnO_3$.

• *NMR*

The Mn^{55} NMR frequency spectra, which are shown in Fig. 3, were obtained by the spin-echo technique. For

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* The term double-exchange originates from the assumption that the electron moves between only two equivalent sites.[5,6]

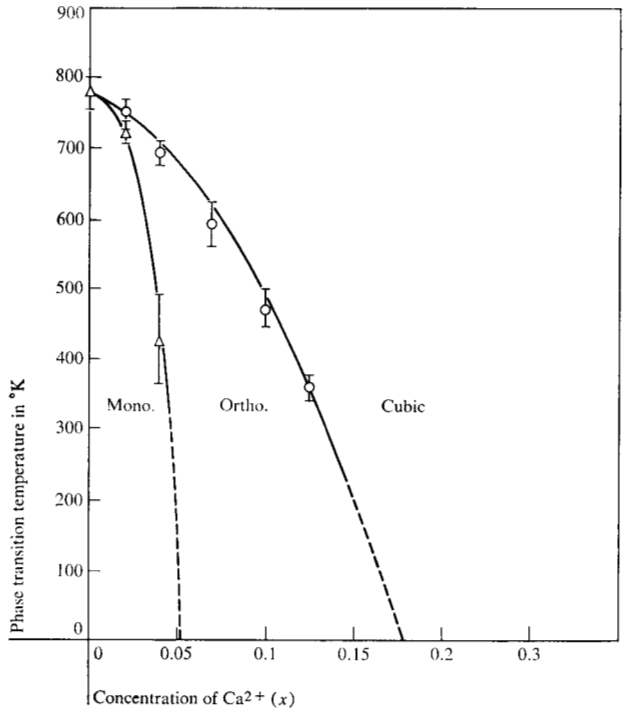


Figure 1 Phase transition temperatures, from monoclinic to orthorhombic structure and from orthorhombic to cubic structure, as functions of the Ca concentration.

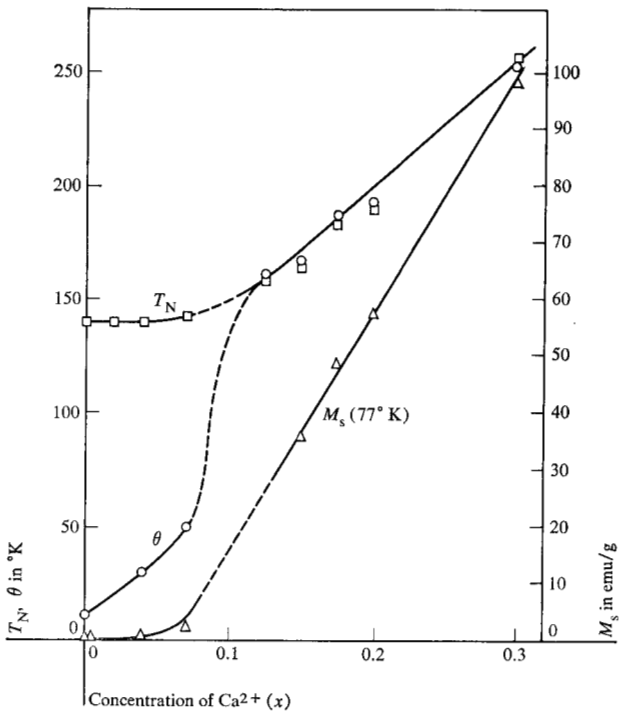


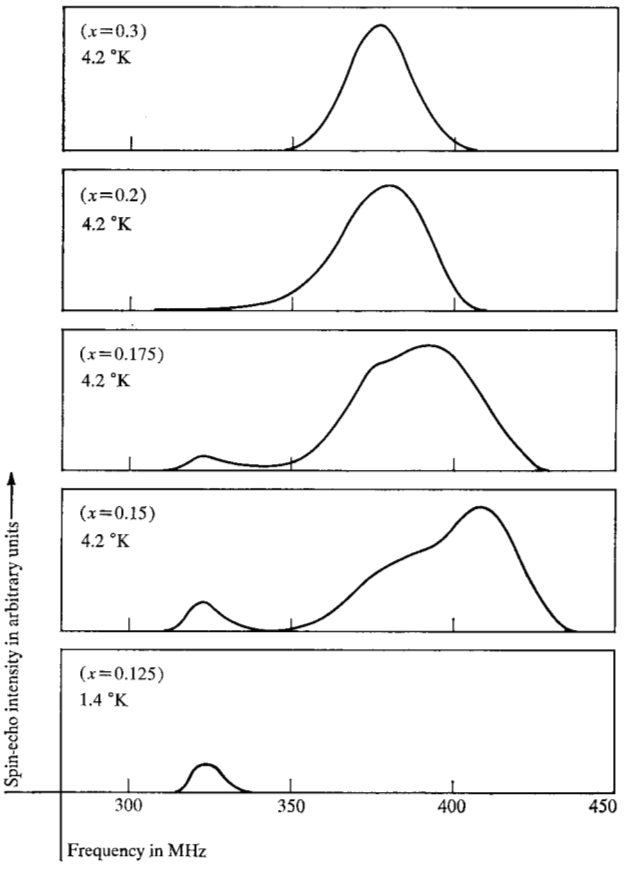
Figure 2 Ca concentration dependence of T_N (or T_c), θ_p and M_s; T_N (or T_c) is defined as the temperature at which the spontaneous magnetization appears.

specimens having x smaller than 0.175, the spectra obtained may be divided into two parts. One is the relatively broad spectrum on the higher frequency side and the other is on the lower frequency side with a center resonance of 323 MHz. From comparison of the resonances at Mn^{3+} and Mn^{4+} ions in other oxides, the higher frequency spectrum can be ascribed to the Mn^{55} NMR associated with Mn^{3+} ions and the lower frequency one to Mn^{4+} ions.[2] For specimens having x equal to 0.2 or 0.3, only one spectrum is obtained. This can be assigned to the Mn^{55} NMR associated with motionally narrowed states.[2] This identification is consistent with the conductivity measurement for $(La_{1-x}Sr_x)MnO_3$ by Van Santen and Jonker,[1] who observed that the conduction is very high in this high Ca concentration region.

Discussion

$LaMnO_3$ is a weak ferromagnet and an insulator. If La^{3+} ions are replaced by Ca^{2+} ions, then the d holes appear to be mobile among the equivalent manganese positions around Ca^{2+} ions, an effect which results in the reconfiguration of the oxygen ions. The oxygen ions around the manganese ion with a hole relax the distorted octahedron to a regular one, since Mn^{4+} is not a Jahn-Teller ion. In this state the translation of the d hole always accompanies the reconfiguration of the oxygen ions. At the same time, the moments of the Mn ions, through which the hole moves, prefer to be ferromagnetically

Figure 3 NMR frequency spectra at 4.2°K and 1.4°K.



oriented.[5] For the case of low Ca concentration (the values of x being smaller than 0.1), the hole is strongly bound to the sites around a Ca^{2+} ion but cannot move, at the lower temperature, to a site on which there is a La^{3+} ion. Thus a ferromagnetic "molecule" is created. T_N is almost invariant since the mobile holes are confined to separated molecules, and M_s does not increase proportionately. For values of x greater than 0.1, the ferromagnetic molecules begin to interact since the holes can move in the whole crystal through the sites neighboring Ca^{2+} ions. At the same time, the translational energy from one site to another around a Ca^{2+} ion decreases with the value of x, since the Jahn-Teller stabilization energy decreases as is shown in Fig. 1. Thus, the exchange rate of a hole between the sites becomes more rapid as x increases. As a result, for specimens having x equal to 0.2 and 0.3, motional narrowing was observed, as shown in Fig. 3.

It is concluded that the strength of the ferromagnetic interaction increases with increasing x. T_c and θ become nearly equal, as the interaction between the ferromagnetic molecules also becomes ferromagnetic.

According to the above picture, the static conductivity should be expected to change abruptly at a value of x approximately equal to 0.1. This was observed for $(La_{1-x}Sr_x)MnO_3$ by van Santen and Jonker.[1]

The appearance of the ferromagnetic interaction is consistent with the idea of the double-exchange interaction. However, in $(La_{1-x}Ca_x)MnO_3$ the mobile hole does not move between only two equivalent sites, so the idea of the double-exchange interaction should be applied cautiously to $(La_{1-x}Ca_x)MnO_3$. The particular form of the interaction,[6] $b \cos(\theta_{ij}/2)$, is derived only when the electron (or hole) is assumed to move between two equivalent sites.[8] The double-exchange interaction is not applicable to the explanation of the magnetic properties of $(La_{1-x}Ca_x)MnO_3$ if the interaction is represented by the above form.

References

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