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1999 J. Phys.: Condens. Matter 11 8505

(http://iopscience.iop.org/0953-8984/11/43/313)

J. Phys.: Condens. Matter **11** (1999) 8505–8510. Printed in the UK PII: S0953-8984(99)05553-8

Ultrasonic anomalies in $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ perovskites

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Received 28 June 1999

Abstract. Both the longitudinal and transverse ultrasonic sound velocities and attenuations in the single-phase polycrystalline compound $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ ($x = 0.00, 0.05, 0.10, 0.15$) have been carefully measured by a conventional pulsed echo technique at a frequency of 10 MHz, between 20 and 300 K. A dramatic increase in sound velocity, accompanied by a sharp peak in attenuation, is observed near the ferromagnetic transition temperature T_C for both longitudinal and transverse modes in all samples. This feature implies extremely strong spin–phonon coupling in this system and gives direct evidence for the spontaneous linear magnetostriction effect. At temperatures below 60 K, a dramatic softening in sound velocity accompanied by a sharp increase in ultrasonic attenuation for both longitudinal and transverse modes is observed. The analysis of the results suggests that the softening of the sound velocity for both longitudinal and transverse modes may correspond to the formation of a spin-glass state.

1. Introduction

The mixed valent $R_{1-x}A_xMnO_3$ perovskite manganates, where R and A are rare-earth and alkaline-earth elements respectively, have received much attention due to their 'colossal magnetoresistance' (CMR) near the Curie temperature [1, 2]. As is well known, the structural, transport and magnetic properties of this class of material have been studied carefully and completely. Many related physical phenomena such as the large magnetovolume effect [3], the oxygen isotope effect [4], the charge ordering transition [5] etc have been revealed recently. The most essential features may be the co-existence of metallic conductivity and ferromagnetism at low temperature. The correlation between metallic conductivity and ferromagnetism in these manganese oxides was formerly explained by Zener [6] in terms of the double exchange mechanism. Recently, Millis *et al* [7, 8] argue that double exchange alone cannot account for the magnitude of the resistivity drop below the paramagnetic to ferromagnetic phase transition temperature T_C. They suggest that electron–phonon coupling, due directly to the dynamic Jahn–Teller (J–T) type distortion of the oxygen octahedra around Mn^{3+}, must also play an important role in CMR. There is indeed much experimental evidence indicating the importance of electron–lattice coupling in these manganese oxides [3, 5, 9–11]. Recently, we found dramatic sound velocity hardening accompanied by a sharp attenuation peak in $La(Y)CaMnO_3$ near the Curie temperature for both longitudinal and transverse waves [12, 13]. Also, dramatic sound velocity softening accompanied by a big attenuation peak in $La_{0.17}Ca_{0.83}MnO_3$ near the temperature of the antiferromagnetic transition [14] was observed. These features imply extremely strong spin–phonon coupling existing in this system in addition to the previously suggested electron–phonon coupling. However, until now, the microscopic mechanism of the CMR effect remains to be resolved.

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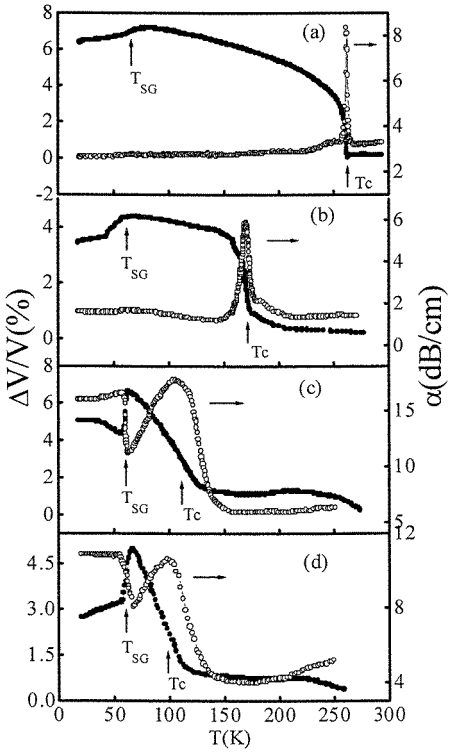

Figure 1. Temperature dependence of the ultrasonic longitudinal sound velocity and attenuation for $La_{0.67}Ca_{0.33}Mn_xZn_{1-x}O_3$: (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$.

Many experimental results [13, 15–16] have proven that the ultrasonic velocity and attenuation measurements is a very sensitive tool for monitoring systems undergoing magnetic and structural phase transitions. Here, we report our systematic study of the transport property and the longitudinal and transverse ultrasonic sound velocity and attenuation as a function of temperature in $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ ($x = 0.00$, 0.05, 0.10, 0.15) series of compounds in order to obtain more information on the microscopic mechanism of the CMR effect.

2. Experimental procedure

Polycrystalline samples $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ were prepared by the coprecipitation method. A stoichiometric amount of analytically pure starting materials La_2O_3, $CaCO_3$ and ZnO was dissolved in hot dilute nitric acid. Then, stoichiometric analytically pure $MnCl_24H_2O$ was dissolved in the solution. The solution was slowly added to the appropriate concentration solution of Na_2CO_3 that was stirred to coprecipitate. The coprecipitation solution was filtered and washed with distilled water thoroughly, baked at 120 °C for 24 hours and then calcinated at 900 °C, 1100 °C and 1200 °C with intermediate grinding respectively. Finally the product was pressed into pellets and sintered at 1260 °C for 15 hours, and cooled to room temperature at the rate of 2.5 °C min^{-1}.

The structures of $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ were determined by powder x-ray diffraction on a powder x-ray diffractometer (Japan Rigaku MAX-RD) using Cu Kα radiation ($\lambda =$ 1.5418 Å) at room temperature. Results show all samples are of single orthorhombic phase

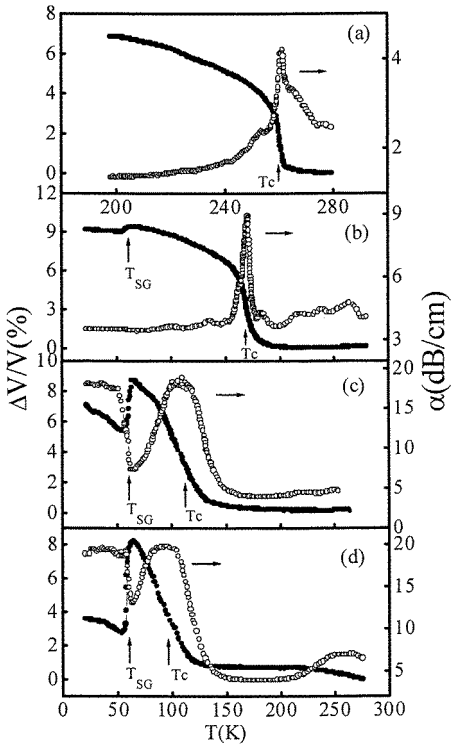

Figure 2. Temperature dependence of the ultrasonic transverse sound velocity and attenuation for $La_{0.67}Ca_{0.33}Mn_xZn_{1-x}O_3$: (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$.

with a high degree of phase purity. The electric resistance of the samples was measured as a function of temperature by the standard four-probe technique.

The specimen for ultrasonic experiments was in the form of a flat disc, 12 mm in diameter and 3.5 mm thick, and was hand-lapped to a parallelism of faces better than 2 parts in 10^4. The ultrasonic velocity and attenuation measurements were performed on the Matec-7700 series with means of a conventional pulsed echo technique. X-cut and Y-cut quartz transducers were used for the longitudinal and transverse ultrasonic excitation respectively. They were bonded to the sample surface with nonaqueous stopcock grease. All experiments were taken in a closed cycle refrigerator during the warm-up from 20 K to room temperature at the rate of about 0.25 K min^{-1}. Temperature was measured with an Rh–Fe resistance thermometer. The estimated error on temperature is ± 0.1 K.

3. Results and discussion

Shown in figures 1 and 2 are the temperature dependence of the longitudinal and transverse ultrasonic sound velocity and attenuation versus temperature for $x = 0.00$, 0.05, 0.10 and 0.15 at a frequency of 10 MHz from 20 to 300 K respectively. A dramatic sound velocity hardening ($>4\%$) accompanied by a very big attenuation peak for both longitudinal and transverse modes was observed near the ferromagnetic (FM) phase transition temperature T_C in all samples. This feature is similar in character to those observed in LaYCaMnO [12] and other ferromagnets [17, 18] near the Curie point, and is relative to the establishment of long-range magnetic order.

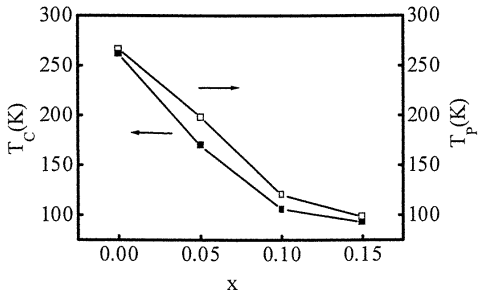

Figure 3. T_C and T_P versus Zn content x for $La_{0.67}Ca_{0.33}Mn_xZn_{1-x}O_3$.

Our ultrasonic data in $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ give further direct evidence that there exists very strong spin–phonon coupling near T_C in this system, and indicated that the type of spin–phonon coupling in $La_{0.67}Ca_{0.33}Mn_xZn_{1-x}O_3$ is due to linear (single-ion) magnetostriction rather than volume magnetostriction [19] since both the longitudinal sound velocity V_L and attenuation α_L and the transverse sound velocity V_S and attenuation α_S show anomalies near T_C. Furthermore, this ultrasonic result confirms the previous magnetostriction measurements, and gives the spontaneous ferromagnetic transition temperature T_C.

From our ultrasonic measurements shown in figures 2 and 3, we can clearly conclude that the doping of nonmagnetic ion Zn effects the magnetic property dramatically. The FM transition temperature T_C obtained from our ultrasonic measurements versus the Zn content x is plotted in figure 3. As is well known, the double exchange plays a predominant role between the neighbouring Mn^{3+} and Mn^{4+} in $La_{0.67}Ca_{0.33}MnO_3$. Therefore, when the nonmagnetic ion Zn replaces the magnetic ion Mn, the sites occupied by the Zn ion can no longer participate in the double-exchange process and thus the double exchange is weakened dramatically. On the other hand, it is high possible that the random substitution of Mn ion with Zn ion leads to the formation of ferromagnetic clusters in the LaCaMnZnO system. Thus, the FM transition temperature T_C was reduced to lower temperature with increasing Zn content.

We note that doping with nonmagnetic ion not only affects the magnetic property, but also affects the resistivity. In figure 4 we show the temperature dependence of the electric resistance for $x = 0.00$, 0.05, 0.10 and 0.15. All samples show a metal–insulator transition and the resistance peak temperature (T_P) drops dramatically with increasing Zn content. The T_P versus x curve is also plotted in figure 3. A conspicuous feature is that the spontaneous ferromagnetic transition temperature (T_C) decreases much more quickly than the resistance peak temperature (T_P) when the Zn content is 5%, and is much lower than T_P. Such is the case for $x = 0.10$ and 0.15 in which T_C is about 15 and 6 K lower than T_P respectively. This result implies that the big resistance peaks may be due to the electron–phonon coupling suggested by Millis [7], rather than the double exchange interaction [6].

Another important feature is the softening of sound velocity for both longitudinal and transverse modes observed at low temperature in $La_{0.67}Ca_{0.33}Mn_xZn_{1-x}O_3$. A dramatic softening in sound velocity was found at $T_{SG} \approx 66$ K for $x = 0$, and move to slightly lower temperature ($\approx$60 K) as Zn content increases. These kinds of downward cusp and softening in sound velocity or equivalently in the elastic constants are usually observed near the temperature of structural phase transition or the formation of glassy state where, due to the weakening of certain force constants, a particular phonon mode softens [16]. Until now, no experimental evidence indicate that the structural phase transition occurs near T_{SG} ($\approx$60 K) where dramatic sound velocity softening was observed. In fact, the spin-glass state was usually observed at low temperature in this class of material. Cai *et al* [20] observed

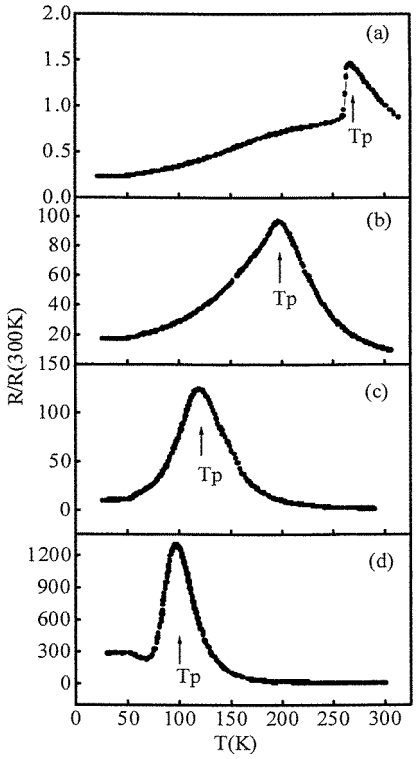

Figure 4. Temperature dependence of the electric resistance for $La_{0.67}Ca_{0.33}Mn_xZn_{1-x}O_3$: (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$.

spin-glass behaviour in $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$ at 42 K. Von Helmolt *et al* [21] observed the spin-glass property in $La_{(2-x)/3}Ba_{(1+x)/3}Mn_{1-x}Cu_xO_3$ ($x \geqslant 0.3$) at 50 K and Haupt *et al* [22] in $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ ($x = 0.2, 0.3, 0.4$) at 38 K. It is highly probable that the softening in sound velocity for both longitudinal and transverse modes is due to the formation of the spin-glass state.

The other important evidence for the formation of the spin-glass state near T_{SG} is that both the longitudinal and transverse ultrasonic attenuation below T_C are much larger than at room temperature and remain very high below T_{SG} for $x = 0.10$ and 0.15. Very similar behaviour in ultrasonic attenuation was observed in the superconductor material $La_{1.85}Ba_{0.15}CuO_4$ [23], which was attributed to the formation of a glassy state of the superconductor.

4. Conclusion

We have studied the transport and ultrasonic properties of $La_{0.67}Ca_{0.33}Mn_xZn_{1-x}O_3$ perovskite. The doping of the nonmagnetic ion Zn affects the transport and magnetic properties dramatically. The ultrasonic anomalies in sound velocity and attenuation near T_C show direct evidence for spin–phonon coupling. At low temperature, dramatic softening in sound velocity for both longitudinal and transverse modes was observed in all samples. The analysis of the results suggests that the softening of sound velocity may correspond to the formation of the spin-glass state.

Acknowledgments

This work was supported by the Chinese National Nature Science Fund, and partially supported by the Laboratory of Internal Friction and Defects in Solids.

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