Ultrasonic evidence for magnetoelastic coupling in $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ perovskites

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The longitudinal and transverse ultrasonic velocities and attenuations of single-phase polycrystalline colossal magnetoresistance compound $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ have been measured at a frequency of 10 MHz, between 50 and 300 K. At the ferromagnetic and insulator-metal phase-transition temperature T_c, a dramatic increase in sound velocity accompanying an attenuation peak was observed in both the longitudinal and transverse modes. This simultaneous occurrence of magneton, electron, and lattice ordering features implies strong spin-phonon coupling and electron-phonon coupling, known to exist for the octahederally coordinated d^4 ion and originating in the Jahn-Teller effect. [S0163-1829(99)04717-7]

The compounds $La_{1-x}A_xMnO_3$ (A represents a divalent alkali element such as Ca, Sr or Ba, etc.) have attracted much recent attention due to their ''colossal magnetoresistance'' (CMR) near the Curie temperature existing in the range of $0.2 \leqslant x \leqslant 0.5$.[1,2] The most essential features of their magnetic and transport properties are the coexistence of metallic conductivity and ferromagnetism at low temperature. The correlation between metallic conductivity and ferromagnetism in these manganese oxides was formerly explained by Zener[3] in terms of the double-exchange mechanism. Recently, Millis *et al.*[4,5] argue that double-exchange alone cannot account for the magnitude of 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-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.[6–10] For instance, near T_c, dramatic changes are observed in the lattice degree of freedom, the anomalous lattice expansion,[6] the shift of phonon frequency,[8] and the anomalous sound velocity hardening,[10] which all reflect that the lattice is closely related to the electronic and magnetic properties. However, detailed understanding of the interplay between the lattice dynamics and the electronic and magnetic properties remains to be resolved. In this paper we present the measurements of longitudinal and transverse ultrasonic velocities and attenuations in $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ polycrystalline samples between 50 and 300 K. Very dramatic increases of sound velocities and anomalous attenuation peaks in both longitudinal and transverse modes were found at T_c. This result gives direct evidence for magnetoelastic coupling and is useful for understanding the microscopic origin of the colossal magnetoresistance (CMR) effect.

The polycrystalline sample $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ was prepared by the coprecipitation method. Stoichiometric amount of analytically pure starting materials La_2O_3, Y_2O_3, and $CaCO_3$ was dissolved in hot dilute nitric acid. Then, stoichiometric analytically pure $MnCl_2 \cdot 4H_2O$ was dissolved in the solution. The solution was slowly added to the enough saturation solution of $(NH_4)_2CO_3$ which is stirred to coprecipitate. The coprecipitation solution was filtered, and washed with distilled water for several times, baked at 120 °C for 24 h and then calcinated at 900, 1100, and 1200 °C with intermediate grind, respectively. Finally the product was pressed into pellets and sintered at 1260 °C for 15 h, and cooled to room temperature at the rate of 2.5 °C/min.

The structure of $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ was determined by powder x-ray diffraction on a powder x-ray diffractometer (Japan Rigaku MAX-RD) using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) at room temperature. Result shows the sample is in the single orthorhombic phase.

The electric resistance of the sample was measured as a function of temperature by the standard four-probe technique. The result is displayed in Fig. 1 where a very sharp cusp is observed at $T_c = 155$ K. The sample shows semiconductor behavior above T_c and metallic behavior below T_c, which agrees with other reports very well.[6,11]

The specimen for ultrasonic experiment was in the form of flat disk, 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 by 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 50 K to room temperature at the rate of about

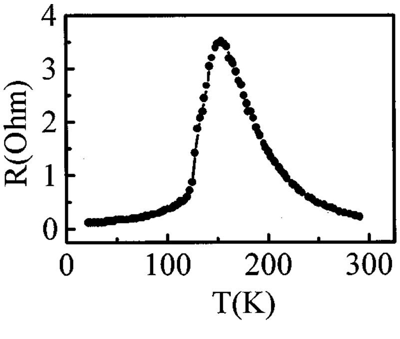

FIG. 1. Temperature dependence of the electric resistance in zero field for $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$.

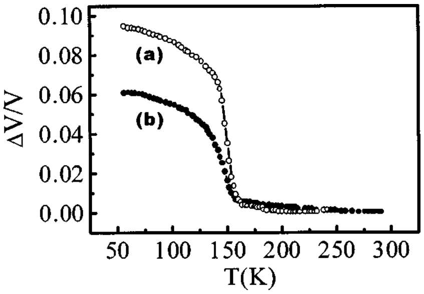

FIG. 2. Temperature dependence of the relative change of the ultrasonic sound velocity for $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ (a) transverse, (b) longitudinal.

0.25 K/min. Temperature was measured with a Rh-Fe resistance thermometer. The estimated error on temperature is ±0.1 K. The temperature variation of the ultrasonic path length of the specimen was calculated by using the data of thermal expansion given by Ibara.[6]

The longitudinal and transverse ultrasonic velocities and attenuations as a function of temperature were plotted in Figs. 2 and 3 for the $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ polycrystalline compound. Both the longitudinal and transverse ultrasonic velocities show nearly temperature-independent behavior above T_c, but increase steeply as temperature is lowered below T_c. The relative change of sound velocity ($\Delta V/V$) around T_c is about 5% for the longitudinal wave and 8% for transverse wave, respectively. Correspondingly, the longitudinal and transverse ultrasonic attenuations (α_l and α_s) display sharp peaks at 150 K, which is slightly lower than T_c (155 K). This feature is in qualitative accord with the Landau-Khalatnikov theory.[12] The longitudinal ultrasonic attenuation displays another peak centered about 260 K where no correlative anomalous phenomena were observed in transport properties and sound velocity. A similar behavior was observed in polycrystalline terbium[13] and europium,[14] and was attributed to the possible formation of short-range order in the paramagnetic state, preceding the magnetic order-disorder transition.

The anomalies in the ultrasonic velocity and attenuation of $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ near the ferromagnetic phase-transition temperature T_c, as seen on other ferromagnets,[15,16] show clear evidence for strong spin-phonon coupling. As is well known, the spin-phonon interaction is due to magnetostriction, and the effective elastic coupling will depend on the type of interaction.[17] If the coupling is due primarily to volume magnetostriction, longitudinal velocities should be anomalous and transverse velocities should not. On the other hand, for single-ion (linear) magnetostriction, there should be coupling to the transverse as well as longitudinal modes. The same ultrasonic anomalous behavior observed in both longitudinal and transverse modes indicates that the spin-phonon coupling in $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ is due to single-ion magnetostriction rather than volume magnetostriction.

We note that the feature of longitudinal sound velocity of $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ around the ferromagnetic (FM) phase transition is very similar in character to that observed in $La_{0.67}Ca_{0.33}MnO_3$.[10] But, the magnitude of the relative change of velocity ($\Delta V/V$) for $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ below T_c is almost more than double that of $La_{0.67}Ca_{0.33}MnO_3$, and much larger than that seen at typical FM transitions.[13,18] Obviously, the spin-phonon interaction due to magnetostriction alone cannot explain such large $\Delta V/V$ of $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ below T_c. From the report of Ibarra,[6] we see that no changes in crystal structure were observed above and below T_c in this compound. Thus it is quite possible that the large hardening of sound velocity below T_c is partly related to electron-phonon coupling which was predicted by Millis *et al.*[4,5] Using the Hamiltonian of small polarons with a strong electron-phonon interaction, Min *et al.*[19,20] have investigated the anomalous behaviors of sound velocity in CMR manganese oxides. They calculated a sound velocity hardening below the ferromagnetic transition temperature, which is due to T-dependent electron screening coming from the double-exchange interaction. Their calculation result is qualitatively similar to the observation of Ramirez *et al.*[10] with a calcium compound and ours with a yttrium-doped compound. The difference in quantity between them can account for the intensity of electron-phonon coupling.[5] According to Millis's calculation, the substitution of Y for La decreases the effective d-d overlap and increases the electron-phonon interaction. It also can lead to the increasing of sound velocity hardening.

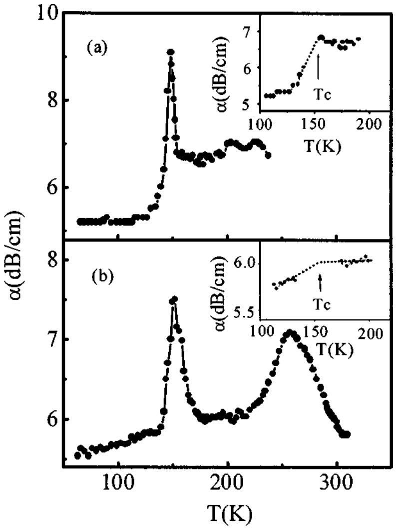

FIG. 3. Temperature dependence of the ultrasonic attenuation for $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ (inset is the temperature dependence of the ultrasonic attenuation background) (a) transverse, (b) longitudinal.

The other important evidence for electron-phonon coupling is the anomaly decrease of the attenuation background at temperature below T_c (see the inset of Fig. 3). For a typical magnetic material, attenuation usually slightly increases with decreasing temperature due to the scattering of the magnetic domain. On the contrary, in $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ both longitudinal and transverse attenuation backgrounds are approximately temperature independent above and below T_c, and decrease drastically at T_c. This behavior is quite similar in character to that observed at the superconducting transition which was attributed to the formation of a superconductivity energy gap.[21] According to Millis's theory, there is also a gap open in the electron spectral function at $T > T_c$ for strong electron-phonon coupling. This gap makes the resistance rise as T is lowered to T_c. Below T_c, resistance drops sharply as the gap closes and metallic behavior is restored.

The abrupt decrease in ultrasonic attenuation background at T_c must also relate to this gap. It is impossible to calculate this gap quantitatively since our data is obtained from a polycrystalline sample. Furthermore, data from a single crystal with different directions would be valuable to further clarify the nature of this transition.

In conclusion, we have studied the ultrasonic properties in perovskite $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ ceramic. The results show direct evidence for electron-phonon and spin-phonon coupling at the ferromagnetic phase transition. It is suggested that the spin-phonon coupling is due to single-ion magnetostriction and the electron-phonon may originate from the dynamic Jahn-Teller effect.

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