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Ultrasonic behaviours near different phase transitions in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

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Abstract. The ultrasonic longitudinal and transverse sound velocities in the single-phase polycrystalline compound $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.33, 0.63, 0.73, 0.83$) have been measured by a conventional pulse-echo-overlap technique at a frequency of 10 MHz, between 50 K and 300 K. Dramatic anomalies in sound velocity for both longitudinal and transverse modes were observed near the temperature of the ferromagnetic transition (T_C), charge-ordering transition (T_{CO}), and antiferromagnetic transition (T_N). The detailed form of the sound velocity anomalies is somewhat different near different phase transitions. The results imply a strong spin–phonon coupling.

1. Introduction

Hole-doped manganese oxides of perovskite-type $\text{R}_{1-x}\text{A}_x\text{MnO}_3$, where R and A are a trivalent rare earth and a divalent alkaline earth, respectively, have attracted considerable attention due to their special structural, magnetic, and electronic properties, as well as their potential applications in magnetic memory devices and sensors [1–5]. In this system, the interplay and competition between spins, doped charge carriers (holes), the degree of freedom of orbitals, and lattice structures lead to a variety of phase transitions [6–8]. For the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system, the $x = 0$ and 1 end members of the solid dilution, LaMnO_3 and CaMnO_3 , are insulators at all temperatures and their magnetic ground state is antiferromagnetic (AFM), as expected for spins interacting via the superexchange interaction when the metal–oxygen–metal bond angle is close to 180° [9]. Between $0.2 < x < 0.45$, the system is a ferromagnetic (FM) metal at low temperatures, and displays colossal magnetoresistance (CMR) effects near T_C . In a narrow region of composition around $x = 0.50$, a competition between two types of magnetic order was observed [10]. At higher doping levels ($0.5 < x \leq 1.0$), the system is AFM at low temperature with different magnetic structure [11], and a real-space charge-ordering (CO) phase transition was observed by electron diffraction [12, 13], which is usually associated with a phase transition to the AFM state. Recently, anomalies in sound velocity were observed near the temperature of FM and CO/AFM phase transitions [12, 14, 15], which indicates that the sound velocity anomaly can be a very sensitive and useful tool to monitor different types of phase transitions in this system. In this paper, we present a systematic study of the longitudinal and transverse ultrasonic sound velocities as a function of temperature on

$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.33, 0.63, 0.73, 0.83$) samples in order to gain more insight into the microscopic origin of different types of phase transitions.

2. Experimental procedure

Polycrystalline samples $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.33, 0.63, 0.73, 0.83$) were prepared by a coprecipitation method. A stoichiometric amount of analytically pure starting materials La_2O_3 and CaCO_3 was dissolved in hot dilute nitric acid. Then, stoichiometric, analytically pure $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in the solution. The solution was slowly added to the appropriate concentration solution of $(\text{NH}_4)_2\text{CO}_3$ which was stirred to coprecipitate. The coprecipitation solution was filtered, washed with distilled water several times, baked at 120°C for 24 h, and then calcinated at 1000°C , 1100°C , and 1200°C with intermediate grinding. Finally, the product was pressed into pellets and sintered at 1260°C for 18 h, and cooled to room temperature at the rate of $2.5^\circ\text{C min}^{-1}$.

The crystal structures of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ samples were determined by powder x-ray diffraction on a powder x-ray diffractometer (Japan Rigaku MAX-RD) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The x-ray diffraction patterns of the samples are shown in figure 1. All samples are single phase with no detectable secondary phases. The diffraction peaks are sharp and can be indexed based on a pseudo-cubic perovskite structure.

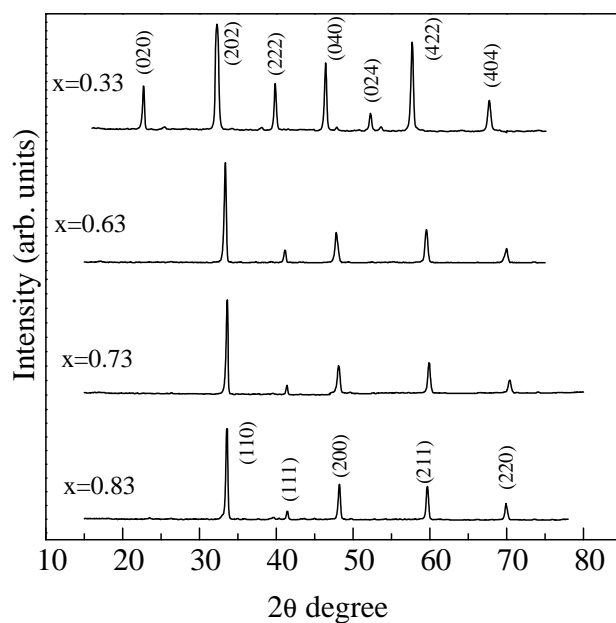


Figure 1. X-ray diffraction patterns of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ samples ($x = 0.33, 0.63, 0.73, 0.83$).

The specimens for ultrasonic measurements were in the form of a flat disc, 12 mm in diameter and 3.5–4.0 mm thick, and were hand-lapped to a parallelism of faces better than 2 parts in 10^4 . The thicknesses of the specimens were measured on a calibrated micrometer stand to within $\pm 1 \times 10^{-3}$ mm. X-cut and Y-cut quartz transducers were used for the longitudinal and transverse ultrasonic excitation, respectively. They were bonded to the specimen surface with water-free Nonaq stopcock grease. All measurements were made in a closed-cycling refrigerator during the warm-up from 50 K to room temperature at the rate of about 1.0 K min^{-1} .

Temperature was measured with an Rh–Fe resistance thermometer. The estimated error of temperature was ± 0.1 K.

Ultrasonic sound velocity and attenuation measurements were made on the Matec-7700 series at a frequency of 10 MHz by means of a conventional pulse-echo-overlap technique. The sound velocity V was found through the following relationship:

$$V = 2L/t = 2Lf$$

where L is the thickness of the specimen, t is the sound velocity transit time determined from the distances between corresponding cycles of two successive echoes, and $f(=1/t)$ is the trigger frequency displayed on a Sabtronics model 8000C frequency counter.

The relative ultrasonic attenuation was calculated from the exponential decay of the echoes, and can be expressed as

$$\alpha = \frac{-20}{2(m-n)L} \lg \frac{V_m}{V_n}$$

where V_m and V_n are the maximum amplitude (voltage) of the m th and the n th pulse, respectively. Attenuation was continuously recorded, and the data were presented directly onto a 4" taut band meter and a built-in strip chart recorder during the dynamic pulsed ultrasonic experiments on the model 2470B automatic attenuation recorder.

3. Results and discussion

The temperature dependences of the longitudinal sound velocity for $x = 0.33$ and 0.63 at a frequency of 10 MHz are shown in figure 2(a). A dramatic hardening in longitudinal sound velocity was observed for $x = 0.33$ and $x = 0.63$ below the FM transition temperature T_C and CO transition temperature T_{CO} . This feature is in good agreement with that observed by Ramirez *et al* [12], and was attributed to the strong coupling of sound to the internal energy and electron–phonon coupling via the Jahn–Teller effect, respectively. To gain more information about the microscopic origin of the FM and CO transitions, we measured the transverse sound velocity for $x = 0.33$ and $x = 0.63$ in the temperature range from 50 K to 300 K. The results are shown in figure 2(b). For $x = 0.33$, a similar hardening in transverse sound velocity was observed below T_C . This simultaneous occurrence of the sound velocity anomalies and the establishment of long range magnetic order at T_C suggests that there exists strong spin–phonon coupling near T_C . It is very interesting to note that the unexpected anomalies in transverse sound velocity were observed at T_C and T_{CO} for $x = 0.33$ and 0.63 . It should be remembered that transverse waves, propagating through the crystal lattice, do not generate localized variations in density and do not distort the Fermi surface. This is in contrast to the behaviour of the longitudinal wave [16]. The same behaviour of the sound velocities of the longitudinal and transverse waves for $x = 0.33$ and 0.63 seem to indicate that the lattice hardening in $x = 0.63$ below T_{CO} is somehow related to the spin–phonon coupling, in addition to the previously proposed electron–phonon coupling. In fact many magnetic measurements evidenced that the CO transition is accompanied by a phase transition to the AFM state [12, 17, 18].

To complete the ultrasonic characterization near the CO/AFM transition, we performed a series of sound velocity measurements for $x = 0.73$ and 0.83 in the temperature region 50–300 K. The data are plotted in figure 3(a) and (b). Both the longitudinal and transverse sound velocities increase dramatically below T_{CO} and T_N , which is similar in character to as observed for $x = 0.63$. According to the phase diagram proposed by Schiffer *et al* [8], the AFM phase transition should be expected for $x = 0.83$. It seems that the anomalies in sound velocity, observed for $x = 0.63$, 0.73 and 0.83 , are related to the AFM transition, and imply a

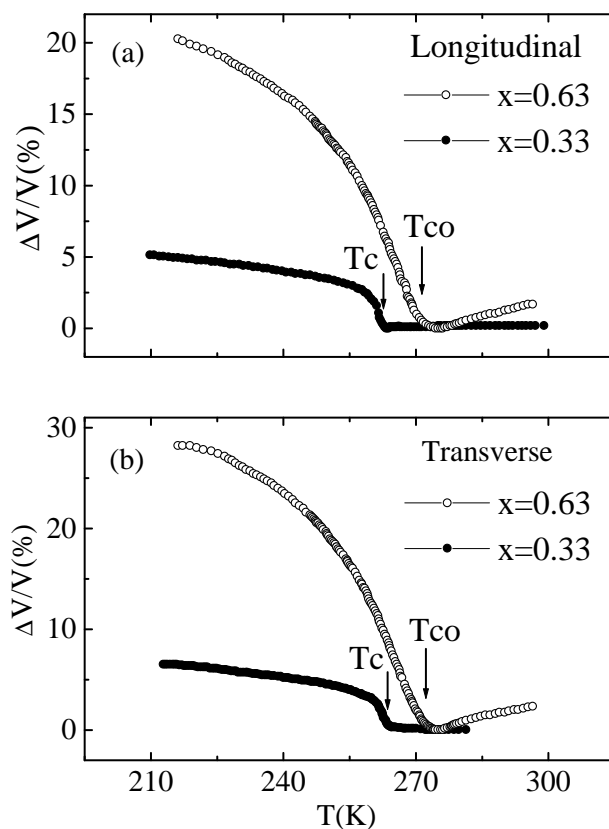


Figure 2. Temperature dependences of the longitudinal (a) and transverse (b) ultrasonic sound velocities for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$.

strong spin–phonon interaction near T_{CO} and T_N . It is worth noting that the fractional increase in sound velocity observed in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ below T_N is much larger than that observed in a conventional AFM transition [19, 20].

The other important feature in figures 2 and 3 is the different behaviour of the sound velocities above the temperatures of different types of phase transitions. For $x = 0.33$, the sound velocity is nearly temperature independent above T_C . However, considerable softening was observed near T_{CO} for $x = 0.63$ and $x = 0.73$, as the transition was approached from higher temperatures. Similar softening in sound velocity above T_N was observed for $x = 0.83$; however, the fraction of velocity softening is much larger (15%) than that for $x = 0.63$ and $x = 0.73$. The differences in behaviour of the sound velocities above phase transitions are probably related to different types of magnetic transitions. For $x = 0.33$, the ground state is known to be FM order. On the other hand, Wollman and Koehler [11] found CE-type AFM order for $0.5 \leq x \leq 0.75$ and C-type AFM order for $x = 0.8$ in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ by neutron powder diffraction. CE-type order is developed by the coherent stacking of octants of the C- and E-type structures. C-type order consists of ferromagnetic chains. It may be possible that the AFM structure of the present $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ crystals change from CE-type in the CO region to C-type in the AFM region. Furthermore, the substantial softening in sound velocity for $x = 0.83$ indicates that the critical fluctuations of the order–disorder type, associated with the C-type AFM order, are much larger than that of other types of magnetic transitions.

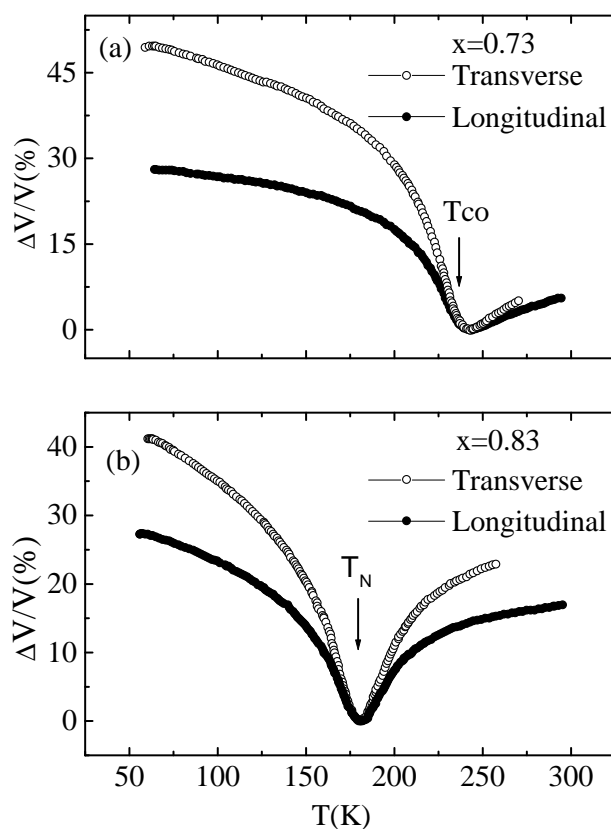


Figure 3. Temperature dependences of the longitudinal and transverse sound velocities for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$: (a) $x = 0.73$; (b) $x = 0.83$.

4. Conclusion

In conclusion, we have measured the longitudinal and transverse ultrasonic sound velocities of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.33 \leq x \leq 0.83$) as a function of temperature. Anomalies in both longitudinal and transverse sound velocities were observed near the temperature of the ferromagnetic transition, charge-ordering transition, and antiferromagnetic transition. It is suggested that these anomalies of sound velocity are due to the spin-phonon interaction, and the differences in behaviour of the sound velocity near T_C , T_{CO} , and T_N are due to different types of magnetic transitions.

Acknowledgments

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References

- [1] Jin S, Tiefel T H, McCormack M, Fastnacht R A, Ramesh R and Chen L H 1994 *Science* **264** 413
- [2] Von Helmolt R, Wecker J, Holzapfel B, Schultz L and Samwer K 1993 *Phys. Rev. Lett.* **71** 2331

- [3] Chahara K, Ohno T, Kasai M and Kozono Y 1993 *Appl. Phys. Lett.* **63** 1990
- [4] Gu J Y, Ogale B, Rajeswari M, Venkatesan T, Ramesh R, Radmilovic V, Dahmen U, Thomas G and Noh T W 1998 *Appl. Phys. Lett.* **72** 1113
- [5] Rao R A, Lavric D, Nath T K, Eom C B, Wu L and Tsui F 1998 *Appl. Phys. Lett.* **73** 3294
- [6] Urushibara A, Morimoto Y, Arima T, Asamitsu A, Kido G and Tokura Y 1995 *Phys. Rev. B* **51** 14 103
- [7] Mahendiran R, Tiwary S K, Raychaudhuri A K and Ramakrishnan T V 1996 *Phys. Rev. B* **53** 3348
- [8] Schiffer P, Ramirez A P, Bao W and Cheong S W 1995 *Phys. Rev. Lett.* **75** 3336
- [9] Goodenough J B 1976 *Magnetism and the Chemical Bond* (Huntington: Krieger)
- [10] Anderson P W and Hasegawa H 1955 *Phys. Rev.* **100** 675
- [11] Wollman E O and Koehler W C 1955 *Phys. Rev.* **100** 545
- [12] Ramirez A P, Schiffer P, Cheong S W, Chen C H, Bao W, Palstra T T M, Gammel P L, Bishop D J and Zegarski B 1996 *Phys. Rev. Lett.* **76** 3188
- [13] Mori S, Chen C-H and Cheong S-W 1998 *Nature* **392** 473
- [14] Zhu C F and Zheng R K 1999 *Phys. Rev. B* **59** 11 169
- [15] Fujishiro H, Fukase T and Ikebe M 1998 *J. Phys. Soc. Japan* **67** 2582
- [16] Gottlieb M, Garbuny M and Jones C K 1970 *Physical Acoustic* vol VII, ed W P Mason and R N Thurston (New York: Academic) p 2
- [17] Bao W, Axe J D, Chen C H and Cheong S-W 1997 *Phys. Rev. Lett.* **78** 543
- [18] Kawano H, Kajimoto R, Yoshizawa H, Tomioka Y, Kuwahara H and Tokura Y 1997 *Phys. Rev. Lett.* **78** 4253
- [19] Berlincourt D and Jaffe H 1958 *Phys. Rev.* **111** 143
- [20] Leisure R G and Moss R W 1969 *Phys. Rev.* **188** 840