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Ultrasonic Study on Jahn-Teller Distortions in $La_{1/3}Sr_{2/3}CoO_3$

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(Dated: Received on April 27, 2007; Accepted on May 24, 2007)

The longitudinal ultrasonic velocity (V_l), attenuation (α_l), magnetization and resistivity of single phase polycrystalline $La_{1/3}Sr_{2/3}CoO_3$ were measured as a function of temperature from 20 K to 300 K. The resistivity shows metallic behavior in the whole temperature range and a kink at 235 K was observed, which coincides with the ferromagnetic transition temperature (Tc). As the temperature cools down from Tc, the V_l softens conspicuously at beginning and reaches a minimum at 120 K. After that the V_l dramatically stiffens below 120 K accompanied by a wide attenuation peak. The analysis of the results suggests that these ultrasonic anomalies may correspond to local lattice distortions via the Jahn-Teller effect of intermediate spin Co^{3+}.

Key words: $La_{1/3}Sr_{2/3}CoO_3$, Ultrasonic velocity and attenuation, Jahn-Teller effect

I. INTRODUCTION

Magnetic oxides with perovskite crystal structures have proven to be a fertile research area for physicists, solid state chemists, and materials scientists, due to the fascinating array of superconducting, magnetic, and electronic properties they exhibit. These properties play an important role in high temperature superconductivity [1], colossal magnetoresistive manganites [2,3], ferroelectricity [4,5], co-incident metal-insulator transition [6,7], charge and orbital ordering [8,9], and phase separation [10,11]. The study of these phenomena has reawakened interest in the Jahn-Teller effect in solids. This effect removes the orbital degeneracy and plays an important role in many interesting physical phenomena through the interplay of orbital and spin degrees of freedom with lattice. Thus, the understanding of Jahn-Teller effect is an important issue in the present studies of transition metal oxides. The study of the cobalt perovskite, $La_{1-x}Sr_xCoO_3$, is therefore very useful, since this system exhibits complex Jahn-Teller effects that are intermediate to the static effects of the manganites and the dynamic effects observed in cuprates.

$La_{1-x}Sr_xCoO_3$ attracts much attention of researchers due to the possibility of application in magnetic media, cathode materials, catalysts, etc. Moreover, the $La_{1-x}Sr_xCoO_3$ system is interesting because of its unusual properties, such as the spin state transitions of the Co ions [12-14], and the complex Jahn-Teller effect [15-17]. The former effect is due to the fact that the crystal field splitting of the Co d states (E_{CF}) and the Hund's rule exchange energy (E_{EX}) are comparable, meaning that the energy gap between the t_{2g} and e_g states is rather small. For $LaCoO_3$, this gap is of the order of 10 meV [18], so $LaCoO_3$ is diamagnetic below 90 K and paramagnetic above this temperature, which is associated with the spin state transition of Co^{3+} between a low spin (LS $t_{2g}^6e_g^0$ with S=0) and an intermediate spin (IS $t_{2g}^5e_g^1$ with S=1) states. Partial substitution of La^{3+} with Sr^{2+} in $LaCoO_3$ introduces formally Co^{4+} ions and stabilizes the neighboring IS Co^{3+}, thus the spin transition disappears [19,20]. As reported by Itoh *et al.* [21], the magnetic diagram shows a spin-glass phase for $0<x\leq0.18$ and cluster-glass one for $x>0.18$. The second unusual property is related to the IS Co^{3+}, which is distinct since it is Jahn-Teller active due to the double degeneracy of the e_g orbitals and would induce lattice distortions. From the pair density function analysis [17], Louca *et al.* has confirmed this fact in the paramagnetic insulating phase. They found that the spin activation of Co^{3+} ions induces local static Jahn-Teller distortions. And in the ferromagnetic metal (FMM) phase, static Jahn-Teller distortions are absent for $x\leq0.3$. For $x>0.3$, on the other hand, static Jahn-Teller distortions reappear since the concentration of charges is so high that propagation occurs through well connected LS Co^{4+} without destroying the Jahn-Teller effect at some IS Co^{3+} sites. However, this supposition needs more experimental support.

As a sensitive tool, ultrasonic technique has been proven to be particularly successful in studying systems with electron-phonon coupling, spin-phonon coupling, and phase transition. In previous works, the ultrasonic responses to the formation of the Jahn-Teller distortion in manganites near the charge ordering and ferromagnetic transitions have been experimentally studied [22,23]. In this work, we present systematic studies of the longitudinal ultrasonic velocity and attenuation as a function of temperature in $La_{1/3}Sr_{2/3}CoO_3$ in order to gain more insight into the relationship between the Jahn-Teller effect and ferromagnetic metal state.

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II. EXPERIMENTS

The polycrystalline sample of $La_{1/3}Sr_{2/3}CoO_3$ was prepared by a solid state reaction method. Stoichiometric amount of 4N purity La_2O_3, $SrCO_3$, and Co_2O_3 powders were well mixed, ground and calcinated in the air for 15 h at 1000, 1100, and 1200 ° C, respectively. The final obtained powder was pressed into pellets at 300 MPa and then sintered at 1250 °C in air for 20 h, and cooled to room temperature at a rate of 1 °C/min.

The crystal structure was characterized using a Japan Rigaku MAX-RD powder X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å) at room temperature. The resistivity was measured by the standard four-probe technique (2000 multimeter, 220 programmable current source, Keithley Instruments Inc., USA). For magnetization measurement, the sample was initially cooled in 100 Oe to 5 K, then the field cooled (FC) magnetization was measured under 100 Oe as the sample was heated up to 300 K by a commercial quantum device (SQUID; Quantum Design MPMSXL).

The specimen for ultrasonic measurement was in the form of flat disk, 4.5-5.2 mm thick, and was hand-lapped to a parallelism of faces better than 2 parts in 10^4. The longitudinal ultrasonic velocity and attenuation measurements were performed on the Matec-7700 series by means of a conventional pulsed echo technique. An X-cut quartz transducer was used for the longitudinal ultrasonic excitation. It was bonded to the sample surface with nonaqueous stopcock grease. All experiments were performed in a closed-cycle refrigerator during the warm-up from 20 K to 300 K at the rate of about 0.25 K/min. Temperature was measured with an Rh-Fe resistance thermometer. The estimated error on temperature is ±0.1 K.

The sound velocity V was found through the following relationship:

$$V = 2L/t = 2Lf \quad (1)$$

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 change of the sound velocity $\Delta V/V$ is defined according to the following equation:

$$\frac{\Delta V}{V} = \frac{V_l - V_{lmin}}{V_{lmin}} \quad (2)$$

where V_{lmin} (in unit of m/s) is the minimal longitudinal ultrasonic velocity in the temperature ranging from 20 K to 300 K.

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

$$\alpha = \frac{-20}{2(m-n)L} \lg \frac{V_m}{V_n} \quad (3)$$

where V_m and V_n are the maximum amplitude (voltage) of the mth and the nth pulse, respectively.

The thickness of the specimen was measured on a calibrated micrometer stand to within ±0.001 mm, with the transit time in nanosecond resolution. The absolute percentage error in velocity measurement is ±0.1%, and the relative error is 10^{-6}.

III. RESULTS AND DISCUSSION

The X-ray diffraction pattern of $La_{1/3}Sr_{2/3}CoO_3$ at room temperature is shown in Fig.1. The sample is of single phase with no detectable secondary phases. The diffraction peaks are sharp and can be indexed based on a cubic perovskite structure, which is consistent with other reports [24].

Figure 2 exhibits the temperature dependences of resistivity and magnetization for $La_{1/3}Sr_{2/3}CoO_3$. It is found that the resistivity shows metallic behavior in the whole temperature range. A kink around 235 K is also observed, which coincides with the FM transition temperature.

The origin of the metallic behavior in cobaltite is still controversial although many authors proposed a double exchange (DE) mechanism. This model was initially introduced by Zener to explain the simultaneous occurrence of ferromagnetism and metallic conductivity in the manganate [25]. However, the metallic behavior above Tc in $La_{1/3}Sr_{2/3}CoO_3$ is in contrast with the typical DE model, where the hopping of e_g electrons between two neighbor ions is allowed when their localized spins are in parallel configuration. For example, in manganites, the DE model between Mn^{3+} and Mn^{4+} results in the metallic behavior below Tc. This probably implies that the Hund's rule coupling in Co ions is rather weak, so that the e_g electrons can hop quite freely between Co sites without a need of parallel localized spins or high magnetizing fields. In fact, a kink in resistivity around Tc is a common feature for an itiner-

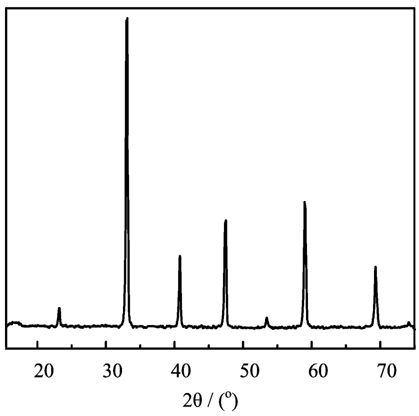

FIG. 1 XRD pattern of $La_{1/3}Sr_{2/3}CoO_3$ at room temperature.

DOI:10.1088/1674-0068/21/02/136-140

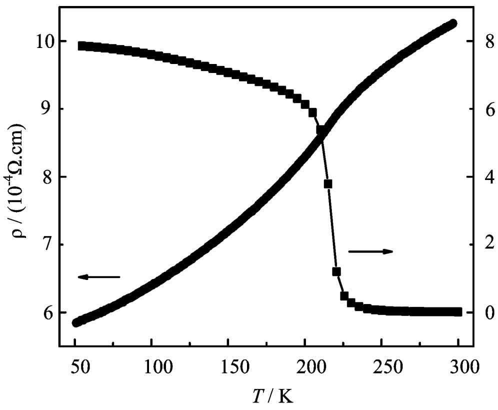

FIG. 2 Temperature dependences of resistivity and magnetization for $La_{1/3}Sr_{2/3}CoO_3$.

ant ferromagnet because of the reduction of scattering from spin disorder in the FM state [26].

Figure 3 shows the temperature dependences of the longitudinal ultrasonic velocity and attenuation for $La_{1/3}Sr_{2/3}CoO_3$ at a frequency of 10 MHz. A steady increase with decreasing temperature, from 300 K to Tc, is observed. Upon cooling down from Tc, the velocity softens conspicuously and dramatically stiffens below 120 K, which is accompanied by a wide attenuation peak. The relative change of the velocity is more than 1.5%.

To investigate the origin of these ultrasonic anomalies, we explored several possibilities. The first consideration is the magnetic transition. As is known, the thermal fluctuations of the spins become large near the magnetic transition point and may produce an appreciable scattering of the phonons, resulting in a significant coupling between the spins and the phonons. According to the Landau Khalatnikov theory [27,28], the behavior of the elastic modulus in the vicinity of the Curie point is represented by a λ type anomaly and the attenuation exhibits a peak on the low-temperature side of the Curie point. However, in our ultrasonic measurements, with decreasing temperature below the Curie point, the ultrasonic velocity decreases in magnitude exhibiting a big valley around 120 K and the attenuation displays a wide peak at 75 K, which is much lower than Tc. Thus it seems impossible to correlate these ultrasonic anomalies with the magnetic transition. In fact, another small attenuation peak centered about 235 K was observed, which was probably due to the spin-phonon coupling.

The second probability is the spin state transition of Co^{3+} between a low spin state and an intermediate spin state. From the ultrasonic measurements of single crystal $LaCoO_3$, Murata *et al.* has observed a lattice softening around 100 K, which is explained by spin state transition. This transition would lead to an abrupt decrease in DC susceptibility at 50-100 K. However, no magnetization decrease was found in our sample. This result hints that no spin state transition occurred. This

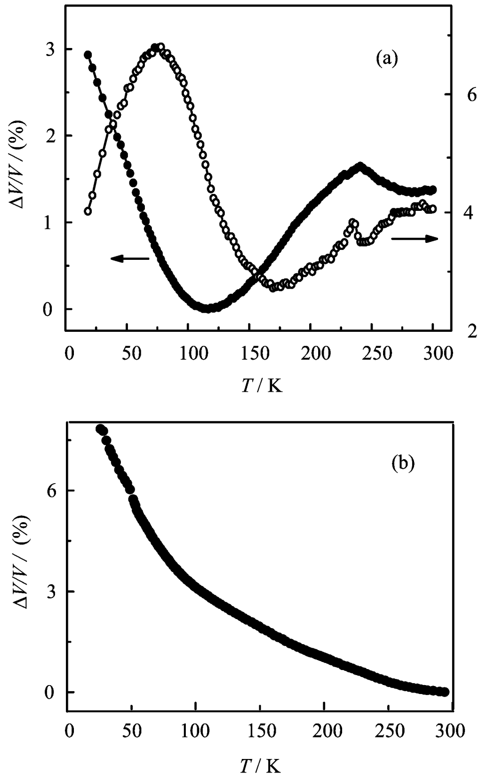

FIG. 3 (a) Temperature dependence of longitudinal ultrasonic velocity and attenuation for $La_{1/3}Sr_{2/3}CoO_3$. (b) The temperature dependence of the longitudinal ultrasonic velocity for $La_{0.8}Sr_{0.2}CoO_3$.

fact is in agreement with other reports [19,20]: partial substitution of La^{3+} with Sr^{2+} in $LaCoO_3$ introduces formally Co^{4+} and stabilizes the neighboring IS Co^{3+}, thus the spin transition disappears. It should be noted that the remarkable lattice softening no longer exists in $La_{0.9}Sr_{0.1}CoO_3$. Therefore, the spin state transition is not the origin of the ultrasonic anomaly found in the sample.

According to acoustics theory, the softening in sound velocity is usually observed near the temperature of the formation of glassy state where, due to the weakening of certain force constants, a particular phonon mode softens [29]. This conclusion was confirmed in $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ perovskite [23]. In $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$, at temperature below 60 K, a dramatic softening in sound velocity is observed, which is suggested to correspond to the formation of a glassy state. To compare the ultrasonic anomalies in $La_{1/3}Sr_{2/3}CoO_3$ with that caused by a typical glassy state in similar cobalt perovskite, we determined the temperature dependence of the ultrasonic velocity for $La_{0.8}Sr_{0.2}CoO_3$ whose ground state is a cluster glassy state [21] (Fig.3(b)). As is known, $La_{0.8}Sr_{0.2}CoO_3$ undergoes FM transition at about 200 K. It can be seen that the sound velocity increases steadily with the decreasing temperature, and no softening is observed in

DOI:10.1088/1674-0068/21/02/136-140

the whole temperature range. This ultrasonic property is totally different from that of $La_{1/3}Sr_{2/3}CoO_3$. Thus, it is suggested that the ultrasonic could not be explained only based on the glassy state.

Since the magnetic transition, spin state transition and glassy state could not result in the ultrasonic anomalies in $La_{1/3}Sr_{2/3}CoO_3$, it seemed that the local lattice distortion may be an alternative mechanism. In fact, the ultrasonic responses to the formation of the lattice distortions have been theoretically and experimentally studied. For example, the ultrasonic velocity softening was observed in Terbium below the ferromagnetic transition accompanied by a rhombic distortion of the crystal lattice [30]. In perovskite transition metal oxides, the lattice distortion always arises from the Jahn-Teller effect. As is known, in many charge ordered manganites [22], a softening above charge ordering transition temperature (Tco) and dramatic stiffening below Tco are observed from the ultrasonic velocity measurement, and the relative change of sound velocity around Tco is greater than that caused by a typical antiferromagnetic spin fluctuations. This is interpreted by the electron-phonon coupling originated from the Jahn-Teller effect of Mn^{3+} in octahedral MnO_6 coordination, which arises from one unpaired electron residing in the two-fold degenerate e_g level. This occupation favors one certain e_g electron orbital and may occur as long rang orbital ordering phenomenon. This ultrasonic feature is similar in character to that of our samples, which implies that the Jahn-Teller effect may also play an important role in $La_{1/3}Sr_{2/3}CoO_3$. However, the question is: which kind of Co ions is Jahn-Teller active?

In $La_{1/3}Sr_{2/3}CoO_3$, the valence states of Co ions are +3 and +4. For Co^{4+}, its ground state is low spin ($t_{2g}^5e_g^0$), which means that it does not necessarily remove the degeneracy to lower its symmetry. So it is not Jahn-Teller active. For Co^{3+}, its IS state ($t_{2g}^5e_g^1$) is stabilized by the neighboring Co^{4+} through the size effects and covalency, thus it is Jahn-Teller active due to the double degeneracy of the e_g orbitals and maybe result in ultrasonic anomalies in $La_{1/3}Sr_{2/3}CoO_3$ at low temperature. In fact, this local static lattice distortions along with broadening of the phonon modes have been observed in $La_{1-x}Sr_xCoO_3$ (x >0.3) from the pair density function analysis [17] of neutron diffraction data because of the weakened charge lattice interactions.

According to the Jahn-Teller theory, the coupling of the electronic states of the ions to the long-wavelength acoustic phonons will cause one or more elastic constants to undergo an anomalous decrease as the phase transition is approached [31]. This decrease reflects the instability of the lattice. This theory result is qualitatively similar to our observation. Therefore the anomalies of ultrasonic velocity and attenuation in $La_{1/3}Sr_{2/3}CoO_3$ at low temperature possibly originate from the Jahn-Teller effect.

It is worth noting that this Jahn-Teller effect occurs in the ferromagnetic metal state. This is strange since an LS Co^{4+} and an IS Co^{3+} dynamically share an e_g electron, through the double exchange mechanism and the itinerant electrons which would make the localized lattice distortion unstable. This probably results from the fact that in $La_{1/3}Sr_{2/3}CoO_3$, the concentration of charges is so high that propagation occurs through well connected LS Co^{4+} without destroying the Jahn-Teller effect at some IS Co^{3+} sites. For a cubic lattice, the site percolation limit is 0.31. From the pair density function analysis in $La_{1-x}Sr_xCoO_3$, Louca *et al.* pointed out that for x<0.3, the static Jahn-Teller distortions are absent. For x>0.3, which is beyond the site percolation limit, the static Jahn-Teller distortions reappear [17].

IV. CONCLUSION

In conclusion, the longitudinal ultrasonic velocity, attenuation, magnetization and resistivity of single phase polycrystalline $La_{1/3}Sr_{2/3}CoO_3$ were measured as a function of temperature from 20 K to 300 K. The resistivity shows metallic behavior in the whole temperature range. An anomaly with an increase of the slope $d\rho/dT$ was detected at 235 K, which coincides with the ferromagnetic transition temperature. As the temperature cools down from Tc, the ultrasonic velocity softens conspicuously and reaches its minimum at 120 K, before dramatically stiffening below 120 K accompanied by a wide attenuation peak. It is suggested that these ultrasonic anomalies may originate from the local lattice distortions via the Jahn-Teller effect of IS Co^{3+}.

V. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No.10774136).

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DOI:10.1088/1674-0068/21/02/136-140