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Ultrasonic study of the Jahn–Teller effect in $La_{1-x}Ca_xCoO_3$ ($0.1 \le x \le 0.2$)

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ABSTRACT

The resistivity, magnetization, longitudinal ultrasonic velocity and attenuation have been measured as a function of temperature from 20 to 300 K in the single-phase polycrystalline $La_{1-x}Ca_xCoO_3$ ($0.1 \le x \le 0.2$). It is found that with increasing Ca content, the resistivity decreases and the ferromagnetic ordering temperature shifts to higher temperature. For all samples, the velocity decreases smoothly with decreasing temperature, and then increases piercingly, accompanied with an attenuation peak. This abnormal elastic softening can be described well by the mean-field theory, which is attributed to the Jahn–Teller effect of IS Co^{3+} ions. Since the increasing ferromagnetic interaction makes the localized IS Co^{3+} ions unstable, the temperature of velocity minimum shifts to lower temperature, which suggests that the static Jahn–Teller effect is suppressed.

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1. Introduction

Recently, there has been much interest in the strongly correlated three-dimensional (3D) transition-metal oxides due to the interplay among the lattice, charge, and spin. Among them, the cobalt oxides have attracted considerable attention due to their interesting features originating from the "spin state" at the cobalt site. In undoped $LaCoO_3$, the Δ_{CF} (t_{2g}–e_g splitting) and the Hund's rule exchange energy J_{ex} is comparable, which leads to the redistribution of electrons between t_{2g} and e_g levels. The Co^{3+} ions in undoped $LaCoO_3$ are in low-spin configuration at low temperature, and they can be thermally excited to intermediate-spin (IS, $t_{2g}^5e_g^1$, $S=1$) or high-spin (HS, $t_{2g}^4e_g^2$, $S=2$) state. Earlier publications [1–4] often assume a population of the HS state whereas more recent investigations [5–10] often favor a LS → IS → HS scenario with increasing temperature. However in $La_{1-x}Ca_xCoO_3$, partial substitution of La^{3+} by Ca^{2+} stabilizes the IS stated of Co^{3+}, and magnetization measurements suggest that the spin-state transition is absent after slightly Ca doping.

In $LaCoO_3$ and $La_{1-x}Sr_xCoO_3$, the Jahn–Teller effect of IS Co^{3+} has been studied by neutron scattering pair density function analysis and fitting of the thermal expansion and magnetization [11,12]. This effect arises from one unpaired electron residing in the twofold degenerate e_g level. This occupation induces a localized lattice distortion in order to reduce the electrostatic interaction of the electron and the surrounding oxygen atoms. However, little is known on the Jahn–Teller effect in $La_{1-x}Ca_xCoO_3$. Thus, a detailed revelation of the interplay between the lattice dynamics and IS Co^{3+} in $La_{1-x}Ca_xCoO_3$ remains to be resolved.

The ultrasonic responses to the formation of the Jahn–Teller local structure in transition-metal oxides have been theoretically and experimentally studied [13,14]. In this paper, we present our systematic studies of the resistivity, magnetization, longitudinal ultrasonic velocity and attenuation as a function of temperature in single-phase polycrystalline $La_{1-x}Ca_xCoO_3$ ($0.1 \le x \le 0.2$). The Jahn–Teller effect in $La_{1-x}Ca_xCoO_3$ is well discussed.

2. Experimental procedure

The polycrystalline $La_{1-x}Ca_xCoO_3$ samples (x = 0.1, 0.12, 0.15 and 0.20) were prepared by a solid-state reaction method. Stoichiometric amount of high purity La_2O_3, $CaCO_3$ and Co_2O_3 powders were well mixed, ground and calcinated at 1000, 1100 °C in air for 15 h. Then the final powder was compacted into pellets and sintered at 1250 °C for 15 h in air.

The crystal structure of $La_{1-x}Ca_xCoO_3$ samples was characterized by powder X-ray diffraction on a powder X-ray diffractometer (Japan Rigaku MAX-RD) using Cu Kα radiation (1.5418 Å) at room temperature. The resistivity was measured by the standard four-probe technique. The field-cooled (FC) magnetization was measured in an external magnetic field of 1000 Oe using a commercial quantum device

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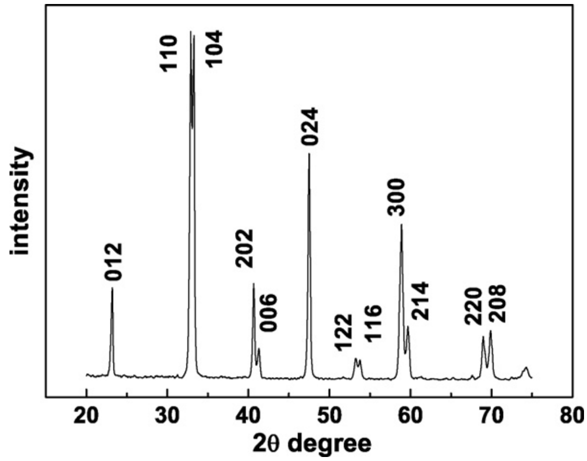

Fig. 1. XRD pattern of $La_{0.85}Ca_{0.15}CoO_3$ at room temperature.

(physical property measurement system; Quantum Design). A magnetic field of 1000 Oe has been applied at 300 K, then the sample was cooled to 10 K and the data were taken during the subsequent heating run.

The specimen for ultrasonic measurement was in the form of flat disk, and was hand-lapped to a parallelism of faces better than two parts in 10^4. X-cut quartz transducer was used for the longitudinal ultrasonic excitation. It was bonded to the sample surface with non-aqueous stopcock grease. Ultrasonic 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:

$$V = \frac{2L}{t} = 2Lf$$

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 change of sound velocity $\Delta V/V_{\min}$ was defined as:

$$\frac{\Delta V}{V_{\min}} = \frac{V - V_{\min}}{V_{\min}}$$

where $V_{\min}$ is the minimum sound velocity over the entire temperature range studied.

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

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

where V_m and V_n are the maximum amplitude (V) of the mth and the nth pulse echoes, respectively. All experiments were taken in a closed-cycle refrigerator during the warm-up from 20 to 300 K at the rate of about 0.5 K/min. The temperature was measured with a Rh–Fe resistance thermometer. The estimated error in temperature is ±0.1 K.

3. Experimental results and discussion

A typical powder X-ray diffraction pattern at room temperature is shown in Fig. 1 (for $x = 0.15$). The diffraction peaks are sharp and can be indexed with the space group $R\bar{3}c$ in the hexagonal setting.

Fig. 2 exhibits the temperature dependence of resistivity for $La_{1-x}Ca_xCoO_3$. One can see that the resistivity shows semiconductor-like transport behavior, and decreases with increasing Ca content.

The $M(T)$ curves of $La_{1-x}Ca_xCoO_3$ are shown in Fig. 3. It can be seen that the magnetic behavior of all samples is similar to ferromagnet. With increasing Ca content, both ferromagnetic ordering temperature and the absolute value of M(10 K) systematically increase monotonically. The similar magnetic behavior has been discussed by several authors in $La_{1-x}Sr_xCoO_3$. This behavior is probably due to the following reason.

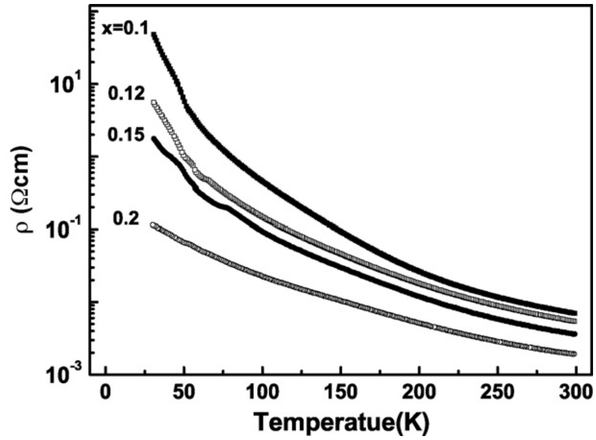

Fig. 2. The temperature dependence of resistivity for $La_{1-x}Ca_xCoO_3$.

By the pair density function analysis of neutron scattering data in $La_{1-x}Sr_xCoO_3$, Louca and Sarrao [12] has pointed out that partial substitution of La^{3+} by divalent alkaline-earth metals will bring forth to more LS Co^{4+} ($t_{2g}^5e_g^0$) ions and stabilize the neighboring Co^{3+} ions in IS state ($t_{2g}^5e_g^1$). By moving an e_g electron from Co^{3+} to a Co^{4+} ion, they share e_g electron ferromagnetically through double exchange, which induces the formation of the ferromagnetic clusters. Thus more alkaline-earth metal substitution will result in more LS Co^{4+}, strengthen the ferromagnetism and decrease the resistivity.

The temperature dependences of the relative longitudinal velocity change ($\Delta V/V_{\min}$) and attenuation (α) data are plotted in Fig. 4. For all samples, the V decreases smoothly with temperature decreasing, and then increases piercingly, accompanied with an attenuation peak. The temperature of $V_{\min}$ (T_m) as a function of x is plotted in the inset of Fig. 4. The T_m shifts to lower temperature with increasing Ca content.

From the magnetization measurements, it is known that the ferromagnetic transition occurs in all samples and the ferromagnetic ordering temperature (T_C) systematically increases monotonically. According to the Landau–Khalatnilov theory, magnetic ordering usually decreases elastic stiffness due to the magnetostriction effect, and the behavior of the elastic moduli in the vicinity of the Curie point is represented by a λ-type anomaly. The attenuation should display a maximum on the low-temperature side of the transition point. While the T_C of $La_{0.8}Ca_{0.2}CoO_3$ is about 150 K, which is much higher than the temperature of ultrasonic anomaly

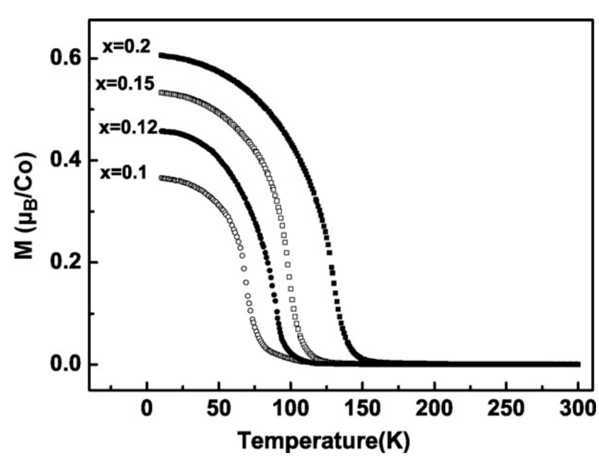

Fig. 3. The temperature dependence of magnetization for $La_{1-x}Ca_xCoO_3$.

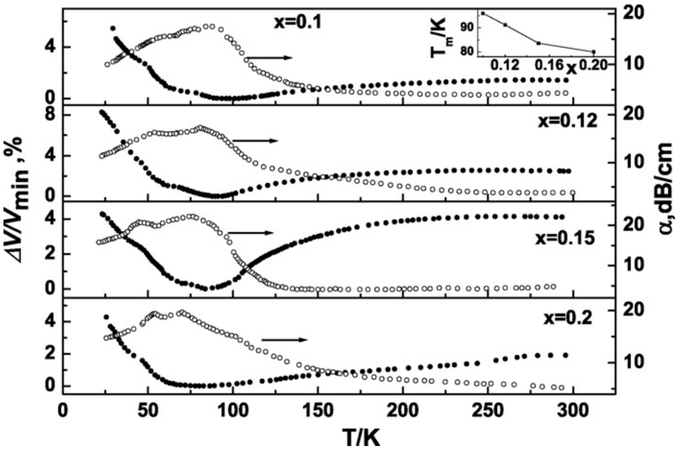

Fig. 4. The temperature dependences of relative longitudinal velocity change and attenuation for $La_{1-x}Ca_xCoO_3$. The inset is the variation of T_m with the Ca content (x).

(T_m = 80 K). Moreover, the magnitude of the relative change of velocity around T_m is much larger than that seen at typical ferromagnetic transitions. Obviously, the spin–phonon interaction due to magnetostriction alone cannot explain such large $\Delta V/V_{min}$. Therefore, we considered other alternative mechanisms which could cause the ultrasonic anomaly.

It is well known that this kind of softening in sound velocity is usually observed near the temperature of structural distortion or the formation of glassy state where, due to the weakening of certain force constants, a particular phonon mode softens. Until now, the spin-glass state in $La_{1-x}Ca_xCoO_3$ is still under discussion. From the magnetization measurements, Kriener et al. [15] pointed that for $La_{1-x}Ca_xCoO_3$, the transitions from a paramagnetic to a ferromagnetic phase exist for the entire concentration range. By neutron diffraction, Burley et al. [16] indicated that the $La_{1-x}Ca_xCoO_3$ system parallels $La_{1-x}Sr_xCoO_3$, with mixed glassy and ferromagnetic contributions. But for $x \geq 0.1$, a significant fraction of the sample adopts a ferromagnetic ground state in zero field. Moreover, the ultrasonic velocity softens from 300 K, and at this temperature, $La_{1-x}Ca_xCoO_3$ is still in paramagnetic state. Thus it seems impossible to correlate this ultrasonic anomaly with the glassy state. In fact, structural distortion was observed at low temperature in $La_{1-x}Ca_xCoO_3$. In 2004, neutron diffraction shows unequivocally that $La_{1-x}Ca_xCoO_3$ undergoes a structural phase transition, and this transition is the first-order nature. Thus it is highly probable that this ultrasonic anomaly in $La_{1-x}Ca_xCoO_3$ is caused by the structural distortion correlated with the IS Co^{3+}. The similar results were observed in $La_{1-x}Sr_xCoO_3$ which has been proved by Louca and Sarrao [12] by the pair density function analysis of neutron scattering data. Since the IS Co^{3+} ions are Jahn–Teller active, so when materials undergo co-operative Jahn–Teller phase transitions, the coupling between the Jahn–Teller ions and long-wavelength acoustic phonons will cause a lattice softening. This decrease reflects the instability of the lattice.

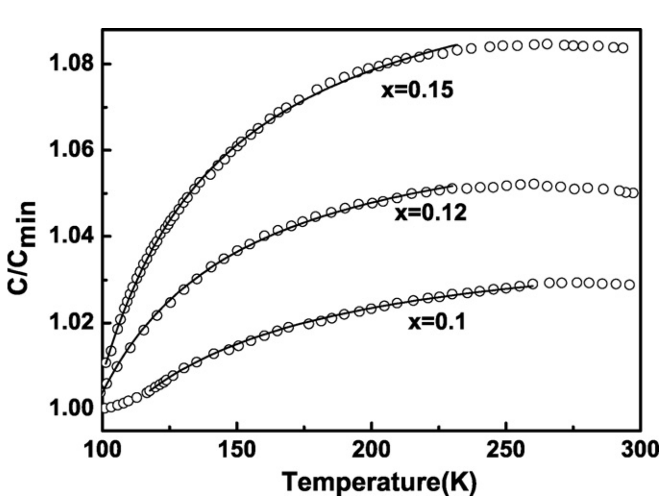

Fig. 5. The temperature dependence of the $C(T)$ for $La_{1-x}Ca_xCoO_3$ above T_{CO}. Open symbols are experimental data, solid line is the results calculated using the mean-field theory.

Table 1
Fitting parameters for longitudinal modulus, using mean-field theory at high temperature for $La_{1-x}Ca_xCoO_3$

x	λ/k_B (K)	μ/k_B (K)	C_0/C_{min}
0.1	38.6	3.0	1.04
0.12	46.1	3.4	1.07
0.15	52.3	4.5	1.11

To further verify the Jahn–Teller effect in $La_{1-x}Ca_xCoO_3$, we apply Jahn–Teller theory to $La_{1-x}Ca_xCoO_3$ ($x \geq 0.10$). The longitudinal modulus $C(T)$ can be calculated from the measurement of the V, using the formula as follows [17]:

$$C(T) = \rho V(T)$$

where ρ is the density of the sample. Through Hamiltonian calculation applying mean-field approach, Melcher and Scott [18] gave the relationship between $C(T)$ and temperature (above the Jahn–Teller transition temperature) as follows:

$$\frac{C(T)}{C_0} = \frac{T - (\lambda + \mu)/k_B}{T - \lambda/k_B}$$

where C_0 is the longitudinal modulus at absolute zero temperature, λ is the phonon exchange constant, and μ is a measure of the ion-strain coupling.

The experiment curves fitted using above equation are shown in Fig. 5. The open symbols are the experimental data and the solid line is the theoretical result. The parameters are listed in Table 1. The good agreement between experiment and theory indicates that these large ultrasonic anomalies indeed originate from the Jahn–Teller effect.

For $La_{0.8}Ca_{0.2}CoO_3$, the experiment and theory do not fit well. And we also notice that the temperature of velocity minimum of $La_{1-x}Ca_xCoO_3$ shifts to lower temperature with increasing Ca content. These phenomenons may be associated with the electron mobility. For IS Co^{3+}, the Jahn–Teller effect arises from one unpaired electron residing in the twofold degenerate e_g level. This occupation induces a localized lattice distortion in order to reduce the electrostatic interaction of the electron and the surrounding oxygen atoms. However, with the increasing Ca content, the resistivity decreases, which hints the high charge mobility. These mobile electrons introduced by the substitution of Ca ion will make the localized lattice distortion unstable, suppress the Jahn–Teller effect and result in poor theory approximation. Due to the semiconductor-like resistivity, the charge mobility decreases at low temperature. Thus the temperature of V_{min}, which represents the cooperative Jahn–Teller phase transition, shifts to lower temperature with increasing Ca content.

4. Conclusion

In conclusion, we have carefully studied the ultrasonic properties of polycrystalline $La_{1-x}Ca_xCoO_3$ ($0.1 \leq x \leq 0.2$) as a function of temperature. With Ca doping, samples undergo a substantial softening of V as well as a remarkable peak in α. This abnormal elastic softening can be described well by the mean-field theory, which is attributed to the Jahn–Teller effect of IS Co^{3+} ions. And since the increasing ferromagnetic interaction makes the localized IS Co^{3+} ions unstable, the temperature of velocity minimum shifts to lower temperature, which suggests that the static Jahn–Teller effect is suppressed.

Acknowledgment

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