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THE ROLE OF PHONONS IN COLOSSAL MAGNETORESISTIVE MANGANITES AND HIGH TEMPERATURE SUPERCONDUCTING CUPRATES

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ABSTRACT

Manganites and cuprates with perovskite-like structure exhibit rich and interesting magnetic as well as electronic properties. The manganites show colossal magnetoresistive property and the cuprates show high temperature superconductivity. The underlying mechanisms in these materials are of intense pursuit worldwide. In this paper we discuss the role of phonons in the magnetic and electronic properties of these materials which are investigated using the ultrasound method. The manganites show pronounced lattice hardening and enhanced ultrasonic damping at the insulator-metallic transition temperature of 240 K. On the other hand, the two dimensional superconducting cuprates can be explained using the van Hove scenario where only a small electron-phonon coupling is necessary to achieve high transition temperature.

INTRODUCTION

The interesting properties exhibited by perovskite-like manganites and cuprates have resulted in worldwide interest. The colossal magnetoresistive (CMR) manganites show a large decrease of electrical resistivity in applied magnetic field. The cuprates on the other hand, show high temperature superconductivity of up to 134 K. These materials are intensely studied due to their potential technological applications and the need for better theoretical understanding.

The CMR property is associated with paramagnetic insulating to ferromagnetic metallic transition at the transition temperature T_c. The double exchange mechanism [1] alone is not adequate in explaining the CMR phenomenon [2]. There are many incompatibilities arising from theoretical considerations of this model when compared with experimental data such as the higher predicted T_c, very high resistivity at $T > T_c$ and the sharp drop of resistivity just below T_c [2]. The dynamic Jahn-Teller polaron due to splitting of Mn e_g states together with the double-exchange effect, make up the physics of the manganites that is producing the CMR effect [2-4].

Theoretical calculations performed using various approaches e.g. mean-field approximation, Monte Carlo stimulation, Kubo formula [5-8], which included the electron-phonon effect, produced results that are in good agreement with experimental data. More importantly, Unjong et al. [6], have shown theoretically that the existing DE model with incorporated small polaron can be improved by taking into account the effects of lattice hardening below T_c. This implies that lattice vibrations play an important role in the properties of these manganites and should be further investigated.

There have been direct experimental evidences on the important role of lattice vibrations, for example the large oxygen isotope shift effect [9] and the formation of polarons as evidenced from pair distribution function (PDF) analysis and electron paramagnetic resonance (EPR) signal [10,11].

The lattice degrees of freedom need to be understood in this material. This includes shifts in phonon frequency as observed by Kim et al. [12], sound velocity anomalies [13,14] and abrupt changes in lattice degrees of freedom [15] at T_c. These results assert the substantial role of phonons in the mechanisms of CMR.

Sound velocity and ultrasonic attenuation measurements are useful in investigating further the relation between T_c and lattice vibrations. In this paper we present ultrasonic results on $La_{1-x}Ca_xMnO_3$ with x = 0.25, 0.33, 0.45, which exhibits CMR effect in the range of doping $\sim 0.2 < x < \sim 0.5$.

CuO_2 planes play a major role in the electronic properties of layered cuprate superconductors. Substitution of non-magnetic impurities such as Zn should have a significant effect on the electronic properties of these *d*-wave superconductors. Previous studies on Zn doped $YBa_2Cu_3O_7$ superconductors showed Zn atoms mainly take the Cu(2) sites in the CuO_2 planes and such substitution may be useful in understanding the mechanism of superconductivity in these materials. Zn^{2+} as a non-magnetic ion, disrupts the local antiferromagnetic correlation of Cu(2) spin and thereby induces a localized paramagnetic moment shared by four neighbouring Cu(2) sites.

Electron-phonon coupling also strongly influences the electronic properties of high T_c cuprate superconductor and must be included in any microscopic theory. Various recent experimental results point towards the important role of phonons in the mechanism of these superconductors [for example 16,17]. The observation of a peak in the density of states near E_F has been reported in various cuprates [18,19]. A number of theoretical studies have been reported along this idea [20-23]. Ultrasonic studies can be useful to determine the lattice dynamics in materials. In this paper, we report results of ultrasonic studies on $ErBa_2(Cu_{3-x}Zn_x)O_{7-\delta}$ (x = 0, 0.01 and 0.05).

EXPERIMENTAL DETAILS

$La_{1-x}Ca_xMnO_3$ samples with x = 0.25, 0.33 and 0.45 were prepared using solid-state reaction method. Stoichiometric proportions of La_2O_3, $CaCO_3$ and MnO_2 (purity > 99.9 %) are mixed and ground thoroughly, and calcined in air at 1150 °C for 24 hrs with intermediate grinding. The resultant powders were then pressed into pellets of ~13 mm diameter and ~2 mm thickness. The pellets were sintered in air at 1200 °C for 10 hrs and slow-cooled to room temperature at a rate of 3 °C/min.

The $ErBa_2(Cu_{3-x}Zn_x)O_{7-\delta}$ (x = 0, 0.01 and 0.05) samples were prepared by mixing appropriate amounts of high purity (≥ 99.99 %) Er_2O_3, $BaCO_3$, CuO and ZnO powders. The powders were calcined in air at around 900 ^oC for 48 h with several intermittent grindings and oven cooled. The powders were then pressed into pellets with approximately 13 mm diameter and 3 mm thickness. The pellets were sintered at 900 ^oC for another 24 h and oven cooled.

Electrical resistance (d.c.) measurements were carried out using the four-point probe technique with silver paint contacts. The samples were also examined by X-ray powder diffraction with CuK_α radiation using a Siemens D5000 diffractometer. Scanning electron microscope (SEM) micrographs were recorded using a Philips XL30 scanning electron microscope.

Ultrasonic velocity was measured using a Matec 7700 system which utilizes the pulsed-echo-overlap technique. The sample was bonded to the transducer using Nonaq stopcock grease. The ultrasonic waves were propagated along the direction of pressing using an X-cut (longitudinal) or Y-cut (shear) quartz transducer with a fundamental frequency of 10 MHz. The measurements were performed in an Oxford Instruments liquid nitrogen cryostat, model DN 1711 and the temperature was changed at a rate of about 1 K min^{-1} during warming and cooling. No thermal expansion correction was made.

ROLE OF PHONONS IN MANGANITES

Polycrystalline materials can be treated as isotropic elastic media having two independent elastic stiffness moduli i.e. longitudinal modulus $C_L = \rho v_l^2$, shear modulus $\mu = \rho v_s^2$, with ρ is mass density, v_l is longitudinal velocity and v_s is shear velocity. The acoustic Debye temperature, θ_D can be calculated using the standard formula, $\theta_D = \left(\frac{h}{k}\right)\left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}} v_m$ where $\frac{3}{v_m^3} = \frac{1}{v_l^3} + \frac{2}{v_s^3}$, h is the Planck's constant, k is the Boltzmann's constant, N is the number of mass point, V is the atomic volume and v_m is the mean sound velocity.

Temperature-dependent electrical resistivity measurements (Figure 1) show the expected insulator to metallic transition (T_{IM}), a feature that corresponds to CMR properties. The x = 0.25 sample showed T_{IM} at 260 K, x = 0.33 at 240 K and x = 0.45 at 150 K. The x = 0.25 sample showed a sharp resistivity peak, while the x = 0.33 showed a broader transition from insulating to metallic phase with the fall-off in resistivity occurred in a larger temperature range. For x = 0.45 sample, a large resistivity hysteresis was observed during cooling and warming.

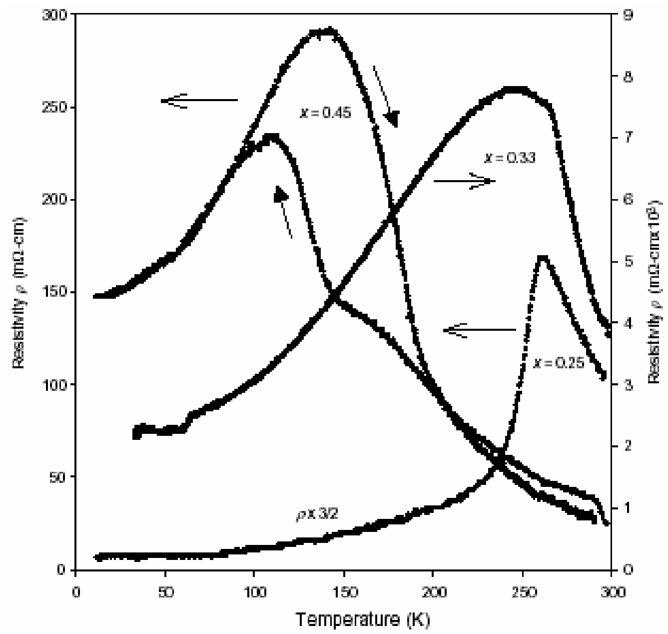


Figure 1. Resistivity versus temperature curves for $La_{1\_x}Ca_xMnO_3$ with x = 0.25, 0.35 and 0.45 [26].

Figure 2 shows ultrasound results for x = 0.33 sample [26]. A slight deviation in shear velocity curve was observed at around 210 K. This is followed by an increase in attenuation with a peak at around 220 K. The longitudinal velocity also deviates from its normal curve at around 220 K with increase in temperature. This feature is also followed by a sudden increase in attenuation to give a broad maximum around this temperature region. The anomalies observed in both shear and longitudinal velocities observed just below T_{IM} are associated with changes related to charge carriers. The percent change in sound velocity is much larger in these CMR samples compared to the high temperature superconducting cuprates for the same temperature range. A notable feature of the attenuation is that it began to increase suddenly at around 180 K as temperature is increased. Figure 3 shows the results from a model by Min and Lee [27] that included the phonon factor in the double exchange mechanism in which lattice hardenings at T_c and a decrease is attenuation below T_c is expected.

All samples showed decrease in attenuation below the transition temperature. This is consistent qualitatively with previous theoretical results on phonon damping [5]. For x = 0.25 and 0.33 samples, observations of lattice hardening below T_c, in both longitudinal and shear modes, accompanied by a peak in attenuation, suggests the close interplay between charge carriers and lattice degrees of freedom. The lattice hardening was explained as due to the change in electron screening below T_c caused by the double exchange factor [24]. The hardening of phonon frequency below T_c was justified in a theoretical prediction based on a model combining the double exchange and the lattice polaron [5,6].

The Debye temperature is highest for the x = 0.33 void-free (θ_D = 555 K), and non-void free (θ_D = 497 K) sample. This is consistent with values reported for $La_{1-x}Sr_xMnO_3$ material measured using heat capacity measurements [28].

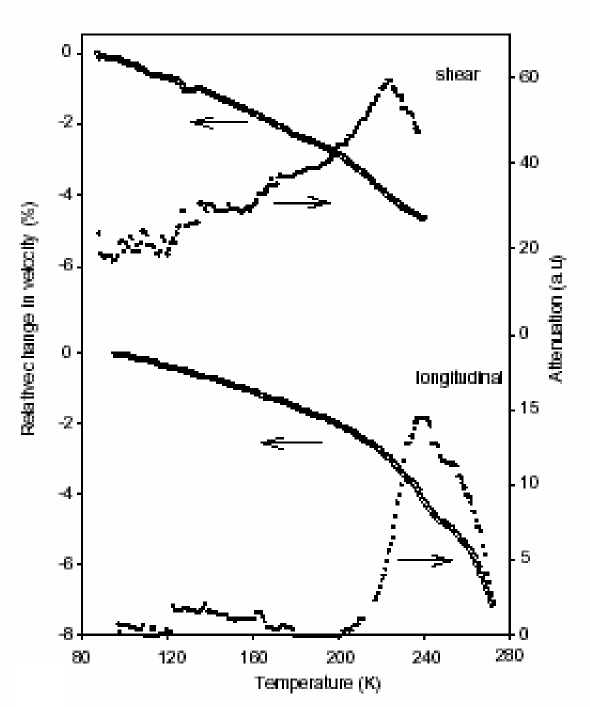
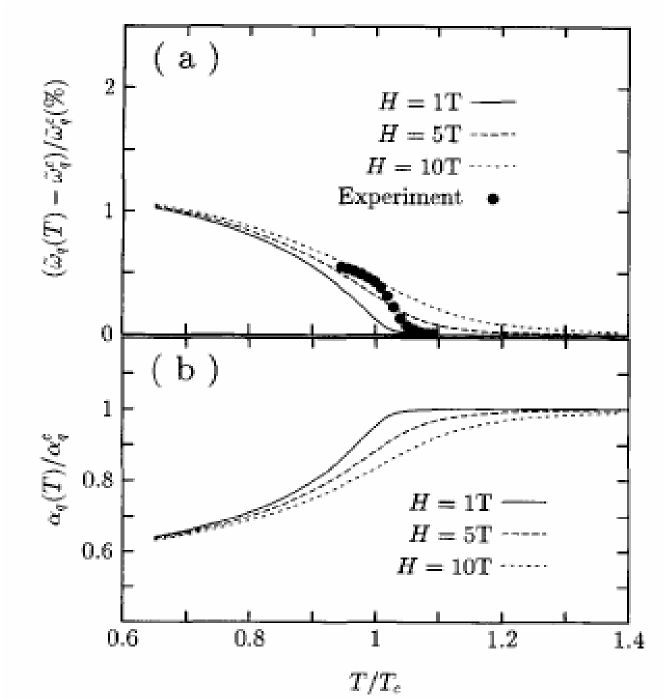


Figure 2. Temperature-dependence of longitudinal and shear velocities with their attenuation of $La_{1-x}Ca_xMnO_3$ for x = 0.33 [26].



Figur 3. (a) The phonon frequency shifts (for various magnetic field strengths. (b) The phonon damping constants [27].

ROLE OF PHONONS IN HIGH T_c CUPRATES AND THE VAN HOVE SCENARIO

Temperature dependent electrical resistance of $ErBa_2(Cu_{3-x}Zn_x)O_{7-\delta}$ with x = 0, 0.01 and 0.05 exhibit metallic normal state behavior and superconducting transition $T_{c\ onset}$ (onset critical temperature) of 93 K, 86 K and 76 K, respectively. As previously discussed, Zn^{2+} substitution caused an increase in the c-lattice parameter and expanded the space between CuO_2 layers. This indicates that the distance between CuO_2 layers play an important role in the mechanism of superconductivity.

Scanning electron micrographs shows the existence of voids and pores indicating the degree of porosity in all the samples. No significant variation in microstructure was observed by SEM between all the samples. The ultrasound wavelength λ (=v/f) is around 300 – 500 μm and this is much larger than the average grain size in our samples.

From the calculated Debye temperature, the electron-phonon coupling constant, λ can be calculated by using BCS theory in the case of weak coupling limit as $T_c = 1.13\theta_D e^{-1/\lambda}$. The van Hove scenario is an extension of the BCS theory. It takes into account the anisotropic structure of the cuprates. Van Hove has shown that there exit a singularity in the density of states, N(ε) near the Fermi level in a two dimensional system (Figure 4). N(ε) can be written as $N(\varepsilon) = N_O \ln\left|\frac{E_F}{\varepsilon - E_F}\right|$ where N_o is a constant and E_F is the energy [29].

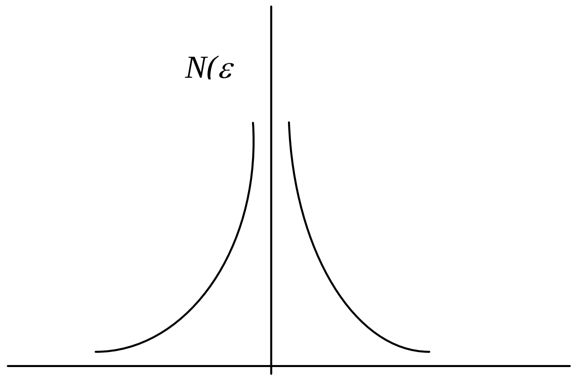


Figure 4. Density of states in two dimensional system of the van Hove scenario.

The transition temperature in the van Hove scenario can be written as $T_c = 2.72 T_F e^{-1/\sqrt{\lambda}}$, where $T_F = E_F/k$ (E_F is the Fermi energy) with T_F is $10\theta_D$ for high T_c material in the weak coupling limit [23].

The calculated electron-phonon coupling constant from van Hove scenario is $\lambda_{Hove} \sim 0.041 - 0.043$ for all samples which is close to the value found in $YBa_2Cu_3O_{7-\square}$ ($\square = 0.042$) from Raman scattering data [30]. It can be concluded that in the two-dimensional cuprate superconductors, the electron-phonon coupling constant is very small. If electron-phonon is playing a role in the Cooper pair formation in the cuprate superconductors, then this small momentum transfer is pivotal for the pair formation. The Debye temperature measured at 80 K, electron-phonon coupling constant, λ calculated using the BCS theory and the van Hove scenario are given in Table 1.

Table 1. Transition temperature (T_c), Debye temperature (θ_D) measured at 80 K, electron-phonon coupling constant of the BCS theory (λ_{BCS}) and the van Hove scenario (λ_{Hove}) of $ErBa_2Cu_3O_{7-\delta}$, $ErBa_2(Cu_{2.99}Zn_{0.01})O_{7-\delta}$ and $ErBa_2(Cu_{2.95}Zn_{0.05})O_{7-\delta}$. The values in brackets are not corrected for porosity [31].

Zn content (x)	T_c (K)	θ_D (K)	λ_{BCS}	λ_{Hove}
$x = 0$	93	471 (428)	0.57 (0.61)	0.041 (0.043)
$x = 0.01$	86	398 (356)	0.60 (0.65)	0.043 (0.045)
$x = 0.05$	78	388 (360)	0.58 (0.61)	0.042 (0.045)

CONCLUSIONS

Sound velocity and ultrasonic attenuation measurements in the temperature range of 80 to 270 K have been performed on $La_{1-x}Ca_xMnO_3$ in the CMR doping region of $0.25 < x < 0.45$. The elastic properties of $La_{1-x}Ca_xMnO_3$ (x = 0.25, 0.33, 0.45) along with the characteristic acoustic temperature θ_D derived from the sound velocity measurements are presented. For x = 0.25 and 0.33 samples, observations of lattice hardening below T_c, in both longitudinal and shear modes, accompanied by a peak in attenuation, suggests the close interplay between charge carriers and lattice degrees of freedom. The lattice hardening was explained as due to the change in electron screening below T_c caused by the double exchange factor.

The x = 0.45 sample however, exhibits a peculiar behavior in both resistivity and sound velocity changes indicating other mechanism involved besides the paramagnetic-insulator to ferromagnetic-metallic transition. We suggest that both the thermal velocity and resistivity hysteresis, and the velocity anomalies at 160 and 180 K in the x = 0.45 sample are related to the occurrence of ferromagnetic conducting region and charge-ordered state.

We also report the effect of zinc substitution on superconducting $ErBa_2(Cu_{3-x}Zn_x)O_{7-\delta}$. We found that the critical temperature decreases with increasing Zn content. Zn substitution also increases the cell volume by expansion of the c-lattice parameter. A more direct method is necessary to probe the role of electron-phonon coupling in these materials. However, from these ultrasonic results, we suggest that the two-dimensional van Hove scenario is a viable candidate for the mechanism of superconductivity in the cuprates.

In conclusion, from these results we suggest that phonons are important in the CMR phenomenon where a lattice hardening was observed at the transition followed by a decrease in the attenuation. This is consistent with the model that incorporates double exchange mechanism with phonon. High temperature superconductivity in the cuprates can be explained by the small electron-phonon coupling that is consistent with the van Hove scenario.

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