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EFFECTS OF OXYGEN CONTENT AND Pr SUBSTITUTION ON VIBRATIONAL ANHARMONICITY OF $ErBa_2Cu_3O_{7-\delta}$ SUPERCONDUCTORS

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ABSTRACT

The temperature dependent ultrasonic longitudinal and shear velocities propagated at 10 MHz in superconducting $(Er_{1-x}Pr_x)Ba_2Cu_3O_{6.9}$ (x = 0.0, 0.1 and 0.2) and non-superconducting $ErBa_2Cu_3O_{6.3}$ were used to evaluate effective Gruneisen parameters (γ_{eff}) for both modes. The elastic behavior of $(Er_{1-x}Pr_x)Ba_2Cu_3O_{6.9}$ (x = 0.0, 0.1 and 0.2) deviates from lattice anharmonicity theoretical curve generally above 160 K. Shear elastic response for less oxygen $ErBa_2Cu_3O_{6.3}$ is described by purely anharmonic effects throughout the temperature range of 80 K -220 K. Deviation of elastic response for the longitudinal and shear modes from vibrational anharmonicity curves is oxygen-related and may be due to a phase transition involving oxygen ordering. The calculated effective Gruneisen parameters for $(Er_{1-x}Pr_x)Ba_2Cu_3O_{6.9}$ (x = 0.0, 0.1 and 0.2) for both longitudinal and shear modes were found to increase with Pr content, indicating increasing anharmonicity. The influence of Pr substitution on BCS electron-phonon coupling constant and its relationship to vibrational anharmonicity is discussed.

Keywords: anharmonicity, Gruneisen parameter, superconductor

1. INTRODUCTION

Lattice vibrational anharmonicity is responsible for many different properties of solids as lattice modes in a real crystal are never completely harmonic. At low temperatures, anharmonicity contributes considerably to the magnitude of the elastic moduli of solids and in the absence of a relaxation

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process or phase change in the material, elastic moduli and sound velocities in solids increase with decreasing temperature. A means of assessing the anharmonic contribution to the temperature dependence of the velocity of sound for solids with normal acoustic phonon spectra was given by Nava et. al.[1]. In this model, the change in sound velocity is given by

$$\Delta v/v = -\frac{TC_v}{2\tilde{n}v^2}\tilde{a}^2_{eff} \qquad \text{eq. (1)}$$

where v is the sound velocity, ρ is the mass density, C_v is the specific heat per unit volume and γ_{eff} is the effective Gruneisen parameter. The specific heat (C_v) in the equation above is given by

$$C_v = \left(\frac{n}{V}\right)\left(3N_A k_B\right)\left[3\left(T/\theta_D\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx\right] \qquad \text{eq. (2)}$$

where N_A is the Avogadro's number, k_B is the Boltzmann constant, n is the mole number and V is the volume of the sample. The change in velocity ($\Delta v/v$) can be fitted to this theoretical model using eq. (1) if values of $\Delta v/v$ at two different temperatures along with Debye Temperature (θ_D) of a material are known. Anharmonic contribution to lattice vibration can be estimated from the computed value of the effective Gruneisen parameter (γ_{eff}) which can be calculated from the equations above.

On the other hand, elastic studies using ultrasonic waves on certain high temperature superconductors have revealed peculiar features in the temperature dependent velocity profiles. Elastic anomalies between 200 K to 230 K which is usually accompanied by a velocity hysteresis was observed during warming and cooling cycles in the RE123[1-4](RE-rare earth), Bi-2212[5] and Bi-2223[6] superconductors. These elastic anomalies and velocity hysteresis have been attributed to a phase transition involving oxygen ordering in the materials[4-7]. Previous reports have shown that in the presence of such a phase change, the elastic moduli and sound velocities originating at lower temperatures deviate from lattice vibrational anharmonicity with increasing temperature[6,8]. Near the temperatures of the phase transition, lattice anharmonicity no longer dominates the magnitude of the elastic moduli of the high-temperature superconductors. Theoretically predicted temperature dependent elastic behavior of a material is useful to determine magnitude of deviation from lattice anharmonicity-dominated elastic behavior to phase-transition dominated elastic behavior. It may also be used to compare effect of oxygen content and chemical doping on elastic properties in the lattice anharmonicity-dominated region[6]. In addition, the effect of anharmonicity on the electron-phonon coupling can be evaluated from calculated values of

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Gruneisen parameter (γ_{eff}) and BCS electron-phonon coupling constant (λ). This would be of particular interest because the effect of anharmonicity on electron-phonon coupling in high temperature superconductors is relatively unknown.

This paper reports the influence of vibrational anharmonicity on temperature dependent longitudinal and shear ultrasonic wave velocity measurements in superconducting $(Er_{1-x}Pr_x)Ba_2Cu_3O_{6.9}$ (x = 0.0, 0.1 and 0.2) and non-superconducting $ErBa_2Cu_3O_{6.3}$. The $ErBa_2Cu_3O_{7-\delta}$ is chosen because it is isostructural to the widely studied $YBa_2Cu_3O_{7-\delta}$ superconductors[9-11]. Another interesting fact is that the effect of Pr substitution on anharmonicity can be easily analyzed, as oxygen content does not change appreciably with Pr content[12]. Results of electrical measurements and structural investigations using powder X-ray diffraction are also discussed.

2. EXPERIMENTAL DETAILS

The $(Er_{1-x}Pr_x)Ba_2Cu_3O_{6.9}$ (x = 0, 0.1 and 0.2) samples were prepared by mixing appropriate amounts of high purity (≥99.99 %) Er_2O_3, Pr_6O_{11}, $BaCO_3$ and CuO powders. The materials were ground in a mortar and then calcined in air at around 900 °C for 48 hours with several intermittent grindings and oven cooled. The powders were then pressed into pellets of ~12.5 mm diameter and 3 mm thickness. The pellets were heated at the same temperature for 24 hours and cooled to room temperature at 40 °C per hour. Non-superconducting $ErBa_2Cu_3O_{6.3}$ sample was prepared by reheating the $ErBa_2Cu_3O_{6.9}$ sample at around 900 °C and quenching it immediately in liquid nitrogen. Details on the preparation of the samples have been reported earlier[7].

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 Siemens D 5000 diffractometer. The ultrasonic velocity was measured using a Matec 7700 system which utilizes the pulsed-echo-overlap technique. The sample was bonded to a quartz transducer using Nonaq stopcock grease. The longitudinal and shear velocity measurements were performed at 10 MHz in an Oxford Instrument liquid nitrogen cryostat model DN 1711 and the temperature was varied at a rate of about 1 K/min during warming and cooling. Ultrasonic velocity data collected during sample heating was used for computations of the effective Gruneisen parameters and theoretical anharmonicity curves.

3. RESULTS AND DISCUSSION

Powder X-ray diffraction patterns (not shown) showed all samples to be single phased 123. The density, porosity, zero-resistance transition temperature ($T_{c\ zero}$), onset transition temperature ($T_{c\ onset}$), and lattice parameters of the various samples

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are shown in Table 1. Temperature dependent electrical resistance measurements showed that $(Er_{1-x}Pr_x)Ba_2Cu_3O_{6.9}$ with x = 0, 0.1 and 0.2 exhibited metallic normal state behavior with $T_{c\,zero}$ of 92 K, 85 K and 73 K, respectively. The quenched $ErBa_2Cu_3O_{6.3}$ sample was non-superconducting with measurement conducted at temperatures to as low as 15 K. The oxygen content of the superconducting and non-superconducting $ErBa_2Cu_3O_{7-\delta}$ samples was estimated using results of lattice constant versus oxygen content variation of Maletta H. et. al.[11]. The Pr substituted samples were also estimated to have an oxygen content of $O_{6.9}$ since they were prepared under the same conditions and low Pr substitution was reported not to affect the oxygen content appreciably[12]. The longitudinal and shear velocities, Debye temperature (θ_D) measured at 80 K, effective Gruneisen parameter (γ_{eff}) and BCS electron-phonon coupling constant (λ) are given in Table 2. A brief discussion of ultrasonic propagation in polycrystalline ceramics has been presented earlier[7].

Ultrasonic velocity measurements on the samples revealed different elastic response with temperature. Superconducting $ErBa_2Cu_3O_{6.9}$ (Figure 1(a)) and $(Er_{0.9}Pr_{0.1})Ba_2Cu_3O_{6.9}$ (Figure 3(a)) showed thermal longitudinal velocity-hysteresis between cooling and warming. Non-superconducting $ErBa_2Cu_3O_{6.3}$ showed monotonic shear and longitudinal velocity change with temperature (Figure 1(b) and Figure 2(b)). Figures 1 to 4 show the temperature dependence of the shear and longitudinal wave velocity changes, for all samples together with the curve-fitted lines calculated using equation (1). Equation (1) have been fitted to the experimental data for both modes in the samples assuming γ_{eff} is temperature independent using θ_D values given in Table 2 and the magnitudes of two selected data points. The data points selected are boundary points of regions that give a high correlation (99.2 %-99.9 %) between the theoretical curves and the experimental data.

For superconducting $ErBa_2Cu_3O_{6.9}$, the ultrasonic velocity for both modes (Figure 1(a) and Figure 2(a)) is dominated by vibrational anharmonicity below 160 K. Above 160 K, ultrasonic velocity for both modes deviates very much from anharmonicity theoretical curves. A step-like anomaly indicating a pronounced lattice stiffening was observed for the longitudinal mode at around 230 K during heating and at around 205 K during cooling (Figure 1(a)). The step-like anomaly has been suggested to be due to a phase transition involving oxygen ordering and has been discussed in detail elsewhere[7]. From the magnitude of deviation from the idealistic behavior, the elastic response of $ErBa_2Cu_3O_{6.9}$ may be strongly influenced by the phase transition creating an anomalous region above 160 K.

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Table 1. Physical parameters measured for various samples.

Sample	Density (g/cm^3)	Porosity (%)	*Tc* onset (K)	$T_{c\,zero}$ (K)	Lattice Parameters		
					a (Å)	*b* (Å)	*c* (Å)
$ErBa_2Cu_3O_{6.9}$	5.62	19.8	94	92	3.813	3.879	11.632
$ErBa_2Cu_3O_{6.3}$	5.54	19.8	-	-	3.856	3.856	11.767
$(Er_{0.9}Pr_{0.1})Ba_2Cu_3O_{6.9}$	5.86	17.9	89	85	3.813	3.887	11.629
$(Er_{0.8}Pr_{0.2})Ba_2Cu_3O_{6.9}$	5.75	19.5	77	73	3.817	3.879	11.625

Table 2. Experimental and computed values of physical parameters of various samples.

Sample	v_l (ms^{-1})	v_s (ms^{-1})	θ_D (K)	γ_{eff}^L	γ_{eff}^S	λ
$ErBa_2Cu_3O_{6.9}$	4440	2705	375	7.98	5.28	0.65
$ErBa_2Cu_3O_{6.3}$	4306	2533	351	5.99	5.54	-
$(Er_{0.9}Pr_{0.1})Ba_2Cu_3O_{6.9}$	4598	2790	387	8.64	5.48	0.61
$(Er_{0.8}Pr_{0.2})Ba_2Cu_3O_{6.9}$	4660	3120	428	9.29	6.60	0.54

Note: The longitudinal and shear velocity values are corrected for porosity as in ref. 7.

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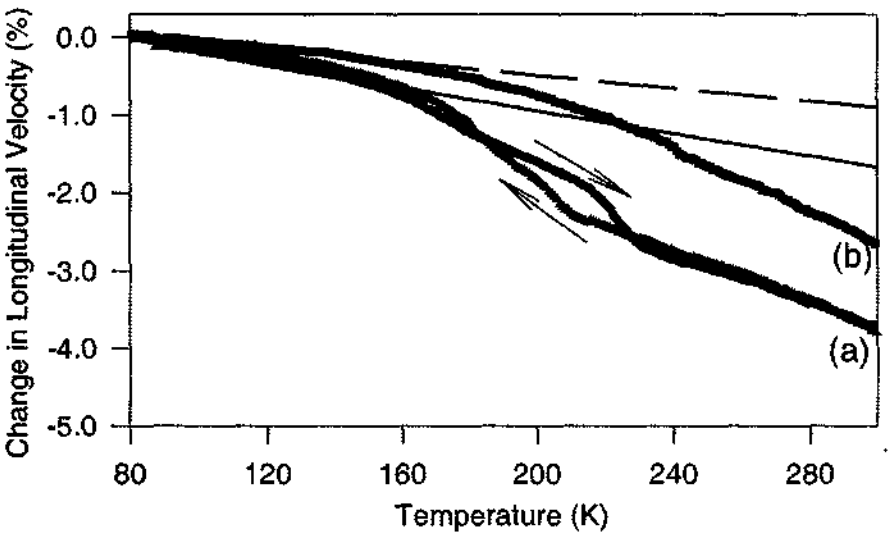

Figure 1: Temperature dependence of longitudinal wave velocities of (a) superconducting $ErBa_2Cu_3O_{6.9}$ and (b) non-superconducting $ErBa_2Cu_3O_{6.3}$. Fits of equation (1) to curve (a) and curve (b) are shown by the solid and broken lines, respectively.

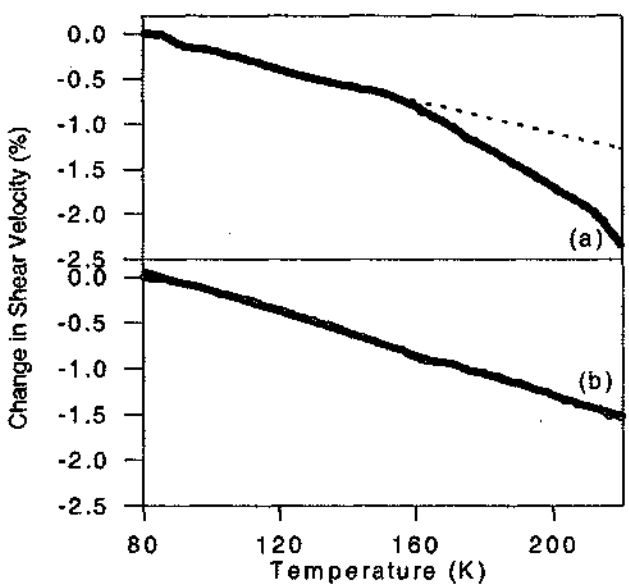

Figure 2: Temperature dependence of shear wave velocities of (a) superconducting $ErBa_2Cu_3O_{6.9}$ and (b) non-superconducting $ErBa_2Cu_3O_{6.3}$. Fits of equation (1) to curve (a) and curve (b) are shown by the broken and solid lines, respectively.

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For nonsuperconducting $ErBa_2Cu_3O_{6.3}$ the shear velocity curve (Figure 2(b)) showed an approximately linear temperature dependence and is in good agreement with the curve based on lattice anharmonicity model by Nava et. al. (eq. (1)). This indicates that shear elastic response for oxygen reduced $ErBa_2Cu_3O_{6.3}$ is dominated by purely anharmonic effects throughout the temperature range of 80 K -220 K. However, for the longitudinal mode, lattice anharmonicity dominates below 170 K. Above 170 K, the longitudinal velocity deviates from the theoretical curve.

For $(Er_{0.9}Pr_{0.1})Ba_2Cu_3O_{6.9}$, the ultrasonic velocity for the longitudinal and shear modes as shown in Figure 3(a) and Figure 4(a) respectively, are dominated by vibrational anharmonicity below 160 K, above which, both velocities start to deviate from theoretical curves. Because Pr substitution of 0.1 in $(Er_{0.9}Pr_{0.1})Ba_2Cu_3O_{6.9}$, does not cause large difference in the percent change of velocity and the velocity hysteresis compared to superconducting $ErBa_2Cu_3O_{6.9}$, the deviation from theoretical anharmonicity curves at temperatures above 160 K for both modes is probably caused by a similar oxygen ordering process [7,13].

On the other hand, for $Er_{0.8}Pr_{0.2}Ba_2Cu_3O_{6.9}$, the longitudinal velocity deviates from anharmonicity theoretical curve starting at around 190 K (Figure 3(b)). The temperature dependence of the longitudinal velocity in $Er_{0.8}Pr_{0.2}Ba_2Cu_3O_{6.9}$ exhibited a monotonic behavior with no elastic anomalies. Suppression of elastic anomalies and oxygen ordering with $Pr_{0.2}$ substitution may have enhanced longitudinal acoustic mode anharmonicity and caused deviation from theoretical curve to start at a slightly higher temperature. However, the shear velocity starts to deviate from the vibrational anharmonicity curve at around 160 K (Figure 4(b)).

The values of γ_{eff}^{L} is substantially larger than γ_{eff}^{S} for all samples (Table 2). This indicates that in these samples, the longitudinal acoustic mode anharmonicity is larger than the shear mode anharmonicity. A similar observation was observed in Y-123[6] and Gd1113[8]. In addition, we observed that both γ_{eff}^{L} and γ_{eff}^{S} increase with increase of Pr content. However, oxygen depletion causes a decrease in the value of γ_{eff}^{L} but an increase in the value of γ_{eff}^{S}. This is different from previous report[6] on Y123, where both γ_{eff}^{L} and γ_{eff}^{S} increase with increasing oxygen content. These results are not due to the changes in oxygen content of the Pr substituted samples since previous reports showed no appreciable change in oxygen content when Pr is substituted[12].

Standard BCS theory[14] in the weak coupling limit where $T_c \sim \theta_D e^{-1/\lambda}$ predicts that an increase in θ_D would accompany by an increase in T_c but this is not observed in the Pr substituted samples. However, our observation of a decrease

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in T_c following an increase in θ_D with increasing Pr content is not in contrast to the BCS theory as our results (Table 2) showed that the computed BCS electron-phonon coupling constant (λ) decreased with Pr substitution. Our results also show that the decrease in λ which indicates weakening in electron-phonon coupling with Pr substitution is accompanied by an increase in vibrational anharmonicity, which is indicated by the effective Gruneisen parameters γ_{eff} (Table 2). It was previously reported that in phonon-mediated superconductors, the presence of lattice anharmonicity does not enhance superconducting transition[15]. As such, based on our results, it is possible that lattice anharmonicity may be detrimental to electron-phonon coupling in $(Er_{1-x}Pr_x)Ba_2Cu_3O_{6.9}$ high-temperature superconductors.

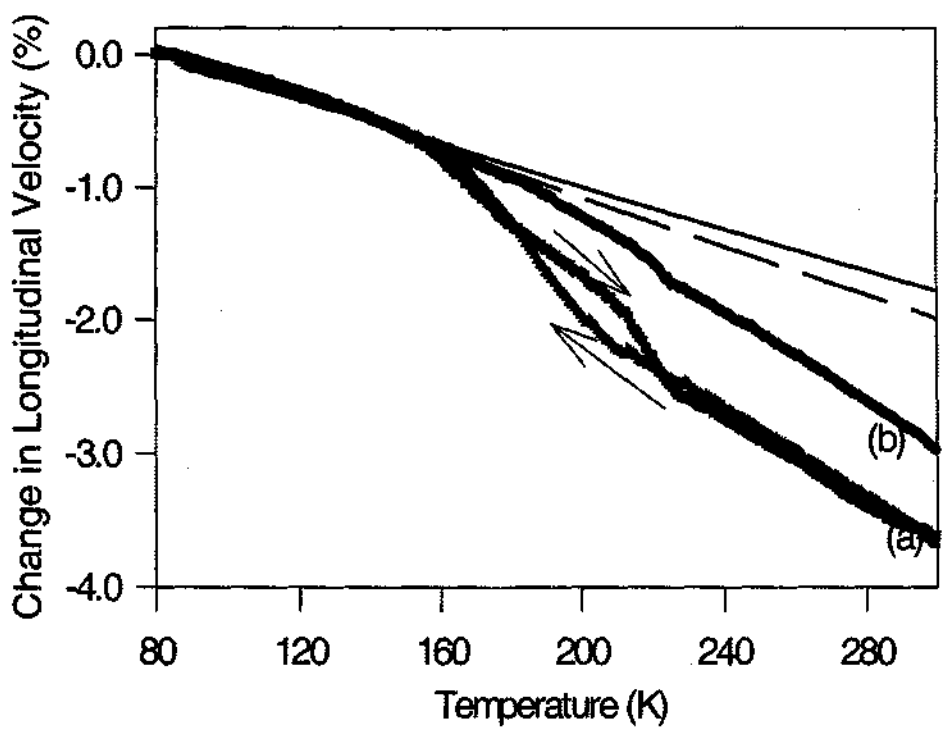

Figure 3: Temperature dependence of longitudinal wave velocities of (a) $(Er_{0.9}Pr_{0.1})Ba_2Cu_3O_{6.9}$ and (b) $(Er_{0.8}Pr_{0.2})Ba_2Cu_3O_{6.9}$. Fits of equation (1) to curve (a) and curve (b) are shown by the solid and broken lines, respectively.

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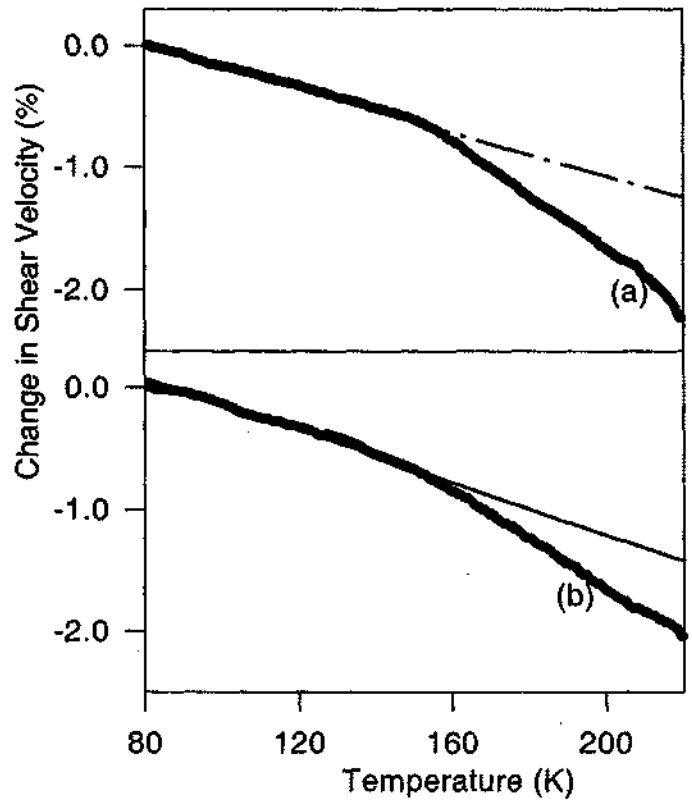

Figure 4: Temperature dependence of shear wave velocities of (a) $(Er_{0.9}Pr_{0.1})Ba_2Cu_3O_{6.9}$ and (b) $(Er_{0.8}Pr_{0.2})Ba_2Cu_3O_{6.9}$. Fits of equation (1) to curve (a) and curve (b) are shown by the broken and solid lines, respectively.

4. CONCLUSION

In conclusion, effective Gruneisen parameters (γ_{eff}) have been computed from ultrasonic velocity data for $(Er_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ to evaluate lattice vibrational anharmonicity. Deviation of elastic response for the longitudinal and shear modes from vibrational anharmonicity curves was found to be oxygen-related. Pr substitution caused γ_{eff} for both longitudinal and shear modes to increase and electron-phonon coupling constant (λ) to decrease. This indicates that an increase in anharmonicity weaken the electron-phonon coupling in the material and causes lowering of the superconducting transition temperature.

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