Influence of Pr Substitution on Acoustic Gruneisen Parameter and Lattice Vibrational Anharmonicity Contribution in Ceramic Superconductors

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Abstract. This paper reports the effect of Pr substitution on lattice anharmonicity contribution to temperature dependent longitudinal and shear ultrasonic velocity data in (Er\(_1-x\)\(Pr_x\))Ba\(_2\)Cu\(_3\)O\(_6.9\) (\(x = 0.0, 0.1\) and 0.2) and TiSr\(_2\)(Ca\(_{1-y}\)Pr\(_y\))Cu\(_2\)O\(_7\) (\(y = 0.5\) and 1.0) superconductors. Pr was observed to influence the deviation of the elastic behaviour of both samples from the lattice anharmonicity curves at higher temperatures. The calculated effective Gruneisen parameter for the longitudinal mode (\(\gamma_{eff}^L\)) for both compounds was found to increase with Pr content, indicating increasing anharmonicity contribution. In addition, both series also showed that \(\gamma_{eff}^L\) is larger than the effective Gruneisen parameter for the shear mode (\(\gamma_{eff}^S\)) throughout the substitution. The influence of Pr substitution on \(\gamma_{eff}\) and the BCS electron-phonon coupling constant (\(\lambda\)) as well as its possible relationship to superconductivity are discussed.

1. Introduction

Ultrasonic velocity measurement is an interesting technique which is sensitive to bulk changes in elastic properties and lattice instabilities taking place in a material. Previous reports on high-temperature superconductors revealed several anomalies in the temperature dependent ultrasonic velocity profiles where a large change in velocity was normally reported at high temperatures especially above 200 K [1-3]. The percentage of velocity change was observed to be affected by oxygen content and chemical substitution. A few reports have shown that sound velocity in high-temperature superconductors is dominated by lattice anharmonicity at lower temperatures but deviated at higher temperatures [4-5]. However, it is not known if chemical substitution can affect the lattice anharmonicity contribution to elastic properties of high-temperature superconductors.

A comparison between sound velocity curve and vibrational anharmonicity curve is interesting as it allows for the lattice anharmonicity contribution to be measured. A means of assessing the anharmonic contribution to the temperature dependence of the velocity of sound for normal solids was given by Nava et. al.[6]. In this model, the change in sound velocity is given by

\[
\frac{\Delta v}{v} = -\frac{TC}{2\rho v^2} \gamma_{eff}^2
\] (1)
where $v$ is the sound velocity, $\rho$ is the mass density, $C_v$ is the specific heat per unit volume and $\gamma_{\text{eff}}$ is the effective Gruneisen parameter. The specific heat ($C_v$) in the equation above is given by

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

(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 model using equation (1) if values of $\Delta v/v$ at two different temperatures along with Debye Temperature ($\theta_D$) of a material are known. Anharmonic contribution to lattice vibration can be estimated from the computed value of the effective Gruneisen parameter ($\gamma_{\text{eff}}$) which can be calculated from the equations above. Nava et. al. successfully used the model on ultrasonic longitudinal and shear velocities of REBa$_2$Cu$_3$O$_{7-\delta}$ (RE=Y, Gd) [6].

In addition, it would be interesting to see if lattice anharmonicity contribution affects superconductivity. BCS electron-phonon coupling constant ($\lambda$) in the weak coupling limit can be computed and compared to the calculated values of Gruneisen parameter ($\gamma_{\text{eff}}$) to see if a relationship exists. This would be of particular importance as the mediating role of lattice vibrations in Cooper pair formation has regained attention [7].

This paper reports the effect of Pr substitution on lattice anharmonicity contribution to longitudinal and shear ultrasonic wave velocity in (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_6.9$ ($x = 0.0, 0.1$ and $0.2$) and TlSr$_2$(Ca$_{1-y}$Pr$_y$)Cu$_2$O$_7$ ($y = 0.5$ and $1.0$) superconductors. The possible relationship between the acoustic Gruneisen parameter and electron-phonon coupling constant ($\lambda$) will be discussed.

2. Experimental details

2.1 Sample preparation
The (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_6.9$ ($x = 0.0, 0.1$ and $0.2$) samples were prepared by mixing appropriate amounts of high purity ($\geq 99.99\%$) Er$_2$O$_3$, Pr$_6$O$_{11}$, BaCO$_3$ and CuO powders [8]. The materials were ground in a mortar and then calcined in air at around 900 $^\circ$C for 48 hours with several intermittent grindings and oven cooled. The powders were then pressed into pellets of 13 mm diameter and around 3 mm thickness. The pellets were heated at the same temperature for 24 hours and cooled to room temperature at 40 $^\circ$C per hour. The TlSr$_2$(Ca$_{1-y}$Pr$_y$)Cu$_2$O$_7$ ($y = 0.5$ and $1.0$) samples were prepared using high purity ($\geq 99.99\%$) powders of Tl$_2$O$_3$, Pr$_6$O$_{11}$, SrCO$_3$, CaO and CuO using conventional solid state and the precursor method [9]. Final sintering was around 1000 $^\circ$C in flowing O$_2$ for 3-5 minutes followed by oven cooling to room temperature.

2.2 Characterization
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$_\alpha$ 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. Details on the ultrasonic technique and sample preparation procedure can be found in our earlier publications [8,9]. Ultrasonic velocity data collected during sample heating was used for computations of the effective Gruneisen parameters and construction of anharmonicity curves.
3. Results and discussion

Powder X-ray diffraction analysis showed all (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_{3}$O$_{6.9}$ (x = 0.0, 0.1 and 0.2) samples to be single phased 123 structures [8]. Temperature dependent electrical resistance measurements for (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_{3}$O$_{6.9}$ with x = 0-0.2 exhibit metallic normal state behaviour with $T_c$ zero of 92 K, 85 K and 73 K, respectively. The oxygen content of the superconducting ErBa$_2$Cu$_{3}$O$_{6.9}$ sample was estimated based on lattice parameter values [8] using results of lattice constant versus oxygen content variation of Maletta H. et. al.[10]. The Pr substituted samples were also estimated to have an oxygen content of O$_{6.9}$ since low Pr substitution was reported not to affect the oxygen content appreciably [8]. X-ray diffraction analysis for TlSr$_2$Ca$_{1-x}$Pr$_x$Cu$_2$O$_y$ (y = 0.5 and 1.0) showed dominant 1212 phase with minor 1201 phase [9]. TlSr$_2$(Ca$_{0.5}$Pr$_{0.5}$)Cu$_2$O$_y$ was superconducting with $T_c$ zero of 77 K. Increasing Pr substitution in TlSr$_2$PrCu$_2$O$_y$ caused the sample to be insulating. Table 1 gives the zero-resistance transition temperature ($T_c$ zero), density, longitudinal velocity ($v_l$), shear velocity ($v_s$), Debye temperature ($\theta_D$) measured at 80 K, effective Gruneisen parameters ($\gamma_{eff}$) and BCS electron-phonon coupling constant ($\lambda$) for both series. A discussion of ultrasonic propagation in polycrystalline ceramics is given in ref. [11].

### Table 1. Zero-resistance transition temperature ($T_c$ zero), density, longitudinal velocity ($v_l$), shear velocity ($v_s$), Debye temperature ($\theta_D$) measured at 80 K, effective Gruneisen parameters ($\gamma_{eff}$) and BCS electron-phonon coupling constant ($\lambda$)

| Sample | $T_c$ zero (K) | Density (g/cm$^3$) ± 0.02 | $v_l$ (kms$^{-1}$) ± 0.02 | $v_s$ (kms$^{-1}$) ± 0.02 | $\theta_D$ (K) ± 5 | $\gamma_{eff}^L$ ± 0.1 | $\gamma_{eff}^S$ ± 0.1 | $\lambda$ ± 0.01 |
|--------|----------------|-----------------------------|---------------------------|---------------------------|-------------------|-------------------|-------------------|------------|
| a) ErBa$_2$Cu$_{3}$O$_{6.9}$ | 92 | 5.62 | 4.44 | 2.71 | 375 | 8.0 | 5.3 | 0.65 |
| b) (Er$_{0.5}$Pr$_{0.5}$)Ba$_2$Cu$_{3}$O$_{6.9}$ | 85 | 5.86 | 4.60 | 2.79 | 387 | 8.6 | 6.5 | 0.61 |
| c) (Er$_{0.8}$Pr$_{0.2}$)Ba$_2$Cu$_{3}$O$_{6.9}$ | 77 | 5.75 | 4.66 | 3.12 | 428 | 9.3 | 6.6 | 0.54 |
| d) TlSr$_2$(Ca$_{0.5}$Pr$_{0.5}$)Cu$_2$O$_7$ | 77 | 4.54 | 3.49 | 2.03 | 282 | 7.4 | 4.6 | 0.70 |
| e) TlSr$_2$PrCu$_2$O$_7$ | - | 4.96 | 3.50 | 2.03 | 279 | 8.6 | 4.0 | - |

Ultrasonic velocity measurements on the samples revealed different elastic response with Pr substitution. Equation (1) has been fitted to the low-temperature experimental data for both modes assuming $\gamma_{eff}$ is temperature independent using $\theta_D$ values given in Table 1. Figure 1 shows temperature dependencies of longitudinal and shear wave velocities of superconducting ErBa$_2$Cu$_{3}$O$_{6.9}$. For superconducting ErBa$_2$Cu$_{3}$O$_{6.9}$, the ultrasonic velocity for both modes (figure 1(a)) is dominated by vibrational anharmonicity below 160 K. Above 160 K, ultrasonic velocity for both modes deviates very much from the calculated anharmonicity curves. For (Er$_{0.5}$Pr$_{0.5}$)Ba$_2$Cu$_{3}$O$_{6.9}$, the ultrasonic velocity for the longitudinal (figure 2(a)) and shear modes (figure 3(a)) are also dominated by vibrational anharmonicity below 160 K, above which, both velocities start to deviate from the anharmonicity curves. On the other hand, for Er$_{0.3}$Pr$_{0.7}$Ba$_2$Cu$_{3}$O$_{6.9}$, the longitudinal velocity deviates from anharmonicity curve starting at around 180 K (figure 2(b)). However, the shear velocity starts to deviate from the vibrational anharmonicity curve at around 160 K (figure 3(b)). The Pr substitution also caused the percentage change in velocity to decrease for both modes.
Figure 1. Temperature dependencies of longitudinal wave velocities of superconducting ErBa$_2$Cu$_3$O$_{6.9}$. Inset shows the shear wave velocity versus temperature for the same sample. Fits of equation (1) to the experimental curves are shown by the broken lines.

Figure 2. Temperature dependencies of longitudinal wave velocities of (a) (Er$_{0.9}$Pr$_{0.1}$)Ba$_2$Cu$_3$O$_{6.9}$ and (b) (Er$_{0.8}$Pr$_{0.2}$)Ba$_2$Cu$_3$O$_{6.9}$. Fits of equation (1) to curve (a) and curve (b) are shown by the solid and broken lines, respectively.

For superconducting TlSr$_2$(Ca$_{0.5}$Pr$_{0.5}$)Cu$_2$O$_7$ the curves based on the anharmonicity model given by equation (1) are in good agreement with the experimental data for the longitudinal mode (figure 4(a)). Increasing Pr substitution in TlSr$_2$PrCu$_2$O$_7$ (figure 4(b)) caused the velocity curve to deviate above 180 K.
Figure 3. Temperature dependencies of shear wave velocities of (a) (Er$_{0.9}$Pr$_{0.1}$)Ba$_2$Cu$_3$O$_{6.9}$ and (b) (Er$_{0.8}$Pr$_{0.2}$)Ba$_2$Cu$_3$O$_{6.9}$. Fits of equation (1) to curve (a) and curve (b) are shown by the broken and solid lines, respectively.

Figure 4. Fits of equation (1) (broken lines) to the temperature dependencies of the longitudinal wave velocity of (a) TlSr$_2$(Ca$_{0.5}$Pr$_{0.5}$)Cu$_2$O$_7$ and (b) TlSr$_2$PrCu$_2$O$_7$. Fits of equation (1) to curve (a) and curve (b) are shown by the broken lines.

From the fitting of the anharmonicity curve to the velocity data at low temperatures, the Gruinesen parameter was computed. For superconducting ErBa$_2$Cu$_3$O$_{6.9}$, the values of \( \gamma^L \) is substantially larger than \( \gamma^S \) for all samples (Table 1). This indicates that in these samples, the longitudinal anharmonicity acoustic mode is more dominant than the shear mode anharmonicity. A similar observation was reported in Y123 [4] and Gd1113 [5]. In addition, for (Er$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{6.9}$ it was observed that both \( \gamma^L \) and \( \gamma^S \) increased with Pr content. For TlSr$_2$(Ca$_{0.5}$Pr$_{0.5}$)Cu$_2$O$_7$ and TlSr$_2$PrCu$_2$O$_7$ samples, \( \gamma^L \) was also observed to be substantially larger than \( \gamma^S \) (Table 1). This indicates that the contribution of the longitudinal mode anharmonicity is larger than the shear mode. However, a comparison between the superconducting TlSr$_2$(Ca$_{0.5}$Pr$_{0.5}$)Cu$_2$O$_7$ and non-superconducting TlSr$_2$PrCu$_2$O$_7$ showed that the superconducting sample has a larger \( \gamma^S \).

A discussion on the role of lattice anharmonicity in superconductivity of TlSr$_2$(Ca$_{1-y}$Pr$_y$)Cu$_2$O$_7$ \( (y = 0.5 \text{ and } 1.0) \) is not clear as Pr substitution caused \( \gamma^L \) to increase but at the same time \( \gamma^S \) also decreases. In addition, given the possible valence of Pr as +3 or +4, simple valence calculation shows that the average Cu valence, which is an indication of hole concentration, also decreased with the
substitution. For (Er$_{1-x}$Pr$_x$)$_2$Cu$_3$O$_7$, given the slow $T_c$ suppression rate, the valence of Pr is suggested to be 3+. Since both Er and Pr have a common valence of +3, there is no change in the average valence of Cu throughout the substitution. As such it can be suggested that the increase in both $\gamma_{\text{eff}}^x$ and $\gamma_{\text{eff}}^y$ has probably caused the decrease in $T_c$. In addition, for the (Er$_{1-x}$Pr$_x$)$_2$Cu$_3$O$_7$ further analysis involving electron-phonon coupling constant ($\lambda$) can be made. Standard BCS theory [12] in the weak coupling limit suggests $T_c$ to be dependent on electron-phonon coupling constant ($\lambda$), in addition to the Debye temperature, $\theta_D$ i.e. $T_c = 1.13\theta_D e^{-\lambda/2}$. Our results showed that the decrease in $T_c$ following an increase in $\theta_D$ as Pr is increased is also accompanied by a decrease in $\lambda$ (Table 1). Interestingly, the decrease in $\lambda$ with Pr substitution is in turn accompanied by an increase in anharmonicity which is indicated by $\gamma_{\text{eff}}$ (Table 1). Since $\gamma_{\text{eff}}$ is evaluated in the low temperature regions, it can be suggested that an increase in anharmonicity contribution may have contributed to the suppression of $T_c$. This is supported by a previous suggestion that in phonon-mediated superconductors, the presence of lattice anharmonicity does not enhance $T_c$ [13]. As such, it is suggested from this work that an increase in lattice anharmonicity contribution at low temperatures due to Pr substitution may be detrimental to electron-phonon coupling in (Er$_{1-x}$Pr$_x$)$_2$Cu$_3$O$_7$ superconductors.

4. Conclusion

In conclusion, effective Gruneisen parameters ($\gamma_{\text{eff}}$) have been computed from ultrasonic velocity data for (Er$_{1-x}$Pr$_x$)$_2$Cu$_3$O$_7$ ($x = 0, 0.1 \text{ and } 0.2$) and TlSr$_2$(Ca$_{1-y}$Pr$_y$)$_2$Cu$_3$O$_7$ ($y = 0.5$ and $1.0$) ceramics to evaluate lattice vibrational anharmonicity contribution to their elastic behaviours. Pr substitution was found to strongly influence the deviation of longitudinal and shear mode elastic response from the calculated vibrational anharmonicity curves above 160 K. For both series $\gamma_{\text{eff}}^x$ increased with Pr content and $\gamma_{\text{eff}}^y$ were also observed to be substantially larger than $\gamma_{\text{eff}}^z$. This indicates that not only the contribution of the longitudinal acoustic mode anharmonicity increased with Pr but it is also larger than the contribution for the shear mode. However, for (Er$_{1-x}$Pr$_x$)$_2$Cu$_3$O$_7$ ($x = 0, 0.1 \text{ and } 0.2$) the increase in $\gamma_{\text{eff}}$ with Pr is also accompanied by the decrease in electron-phonon coupling constant, $\lambda$ which suggests that an increase in lattice anharmonicity contribution may be detrimental to formation of Cooper pairs.

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