Journal of Alloys and Compounds, 211/212 (1994) 292–295
JALCOM 138

Acoustic absorption in high-temperature superconductors due to pseudo-Jahn–Teller centres

L. Mihailov, A. Manov and A. Vavrek
Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia (Bulgaria)

Abstract

The temperature dependence of the acoustic absorption of $YBa_2Cu_3O_{7-\delta}$ and $La_{2-x}Sr_xCuO_4$ up to 100 K is calculated using the two-well tunnelling systems theory. The presence of tunnelling systems in high-T_c superconductors due to the pseudo-Jan–Teller effect, which specifies the tunnelling systems' parameters, is assumed in the calculations. The relaxation times related to the microprocesses of the absorption are determined by the reaction rate method. The relaxation processes connected with non-radiative transitions as well as phonon-assisted tunnelling are taken into account. The results obtained are in good agreement with the experimental measurements. The present work supports the assumption that the tunnelling systems in high-T_c superconductors exist, originated from the pseudo-Jahn–Teller effect.

1. Introduction

Acoustic experiments at audio frequencies are well suited to the study of different kinds of relaxation process at low temperatures [1–3] and phase transitions at higher temperatures (above ~100 K) [4]. Experimentally, the low-temperature behaviour of acoustic absorption in high-T_c materials is quite similar to that in amorphous solids [1–3]. The tunnelling model is found to be most suitable for explaining the dependences of the relative variation of sound velocity $\delta v/v$ and of the internal friction Q^{-1} on T in amorphous solids. Tunnelling systems were supposed to exist in high-T_c superconductors (HTSC), which could explain the initial increase and the "plateau" in $Q^{-1}(T)$ dependencies at temperatures up to several K [1–3]. In addition, the tunnelling model could be an explanation for an experimentally observed controversial linear term in the low-temperature heat capacity [5], as well as dielectric losses [6], but this does not bring the issue to a close.

2. Model

Proceeding from the vibronic model based on the pseudo-Jahn–Teller effect (PJTE), the temperature dependence of the internal friction Q^{-1} is explained. We assume that there exist two types of hole states in HTSC: itinerant states, which are characteristic of Zhang–Rice singlets [7]; and local polarizable states, which secure the pairing of Zhang–Rice singlets [8,9]. These local states are described through PJTE.

The pseudo Jahn–Teller adiabatic potential forms a dual branched surface along the promoting-mode coordinate Q (Fig. 1) [10]:

$$E_{U/L} = \tfrac{1}{2}(KQ^2 \pm \sqrt{(2GQ+\Delta)^2 + E_{gu}^2}) \quad (1)$$

where E_{gu} is the energy gap between two appropriate hole states $|g\rangle$ and $|u\rangle$ (for example, $|g\rangle = |2p_{x,y,z}\rangle$ of the apex oxygen O(A) (Fig. 2) and $|u\rangle = |3d_{3z^2-r^2}\rangle$ of the in-plane copper Cu(P)); $K = M\Omega^2$ is the spring constant of the promoting mode with reduced oscillator mass M and bare-phonon frequency Ω; $G = (2V_M/r_0^2)P_{gu}$

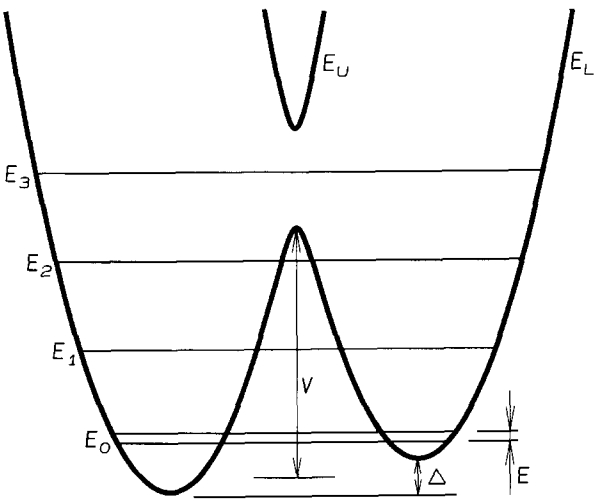

Fig. 1. Double-well potential energy $E_L(Q)$ with difference between the levels E, barrier height V and asymmetry Δ, and vibronic levels $E_i = (i+\frac{1}{2})\hbar\Omega$.

SSDI 0925-8388(94)00138-3

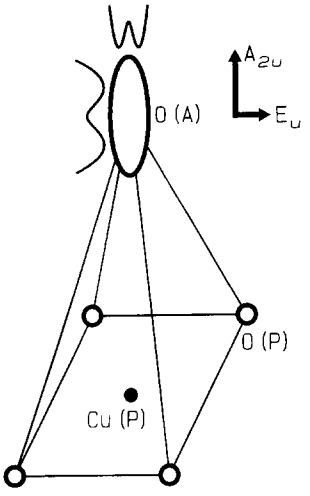

Fig. 2. Polarized apex oxygen atom O(A), promoting both charge transfer along the c axis and hole–dipole interactions through A_{2u}, E_u mode-coupling. Polarization of O(A) in off-site positions (large thermal ellipsoids) is due to vibronic potential energy E_L.

is the electron-mode coupling constant; V_M is the Madelung's potential at the apex site; r_o is the O(A)–Cu(P) bond length; $P_{gu}=\langle g|r|u\rangle$ is the transition dipole moment; and Δ is the asymmetry energy due to mixing perturbations that are not inherent to the PJTE.

The small value of Δ ($\Delta \ll \hbar\Omega$) allows the use of symmetric potential characteristics. The lower branch type (single or double well) is determined by the gap parameter $\mu=E_{gu}/4E_{JT}$, where $E_{JT}=G^2/2K$ is the Jahn–Teller energy. At $\mu<1$ the lower branch $E_L(Q)$ is double-well and Ω renormalizes to $\Omega_r=\Omega\sqrt{1-\mu^2}$.

The vibronic model predicts phase diagrams of T_c *vs.* in-plane hole concentration p [8, 9] as well as optical infrared spectra [8, 11]. The basic quantities needed for the calculation are E_{gu} and E_{JT}. E_{gu} is determined by fitting of infrared spectra [11] and E_{JT} is found through P_{gu}, calculated by fitting of phase diagrams [9].

In terms of Q^{-1} the relaxation absorption can be expressed by the non-equilibrium oscillating part δc of the elastic constant [12]:

$$Q^{-1}=\mathrm{Im}\left(\frac{\delta c}{c_0}\right)=\frac{\beta n D^2\,\mathrm{sech}^2(\beta E)}{4\rho v^2}\,\frac{\omega\tau}{1+\omega^2\tau^2} \qquad (2)$$

where n is the concentration of tunnelling systems; $\beta=\frac{1}{2}kT$; $c_0=\rho v^2$, ρ being the mass density; τ is the corresponding relaxation time; $D=2\gamma\Delta/E$ is the deformation potential; $\gamma=\partial\Delta/\partial F$, F being the field of thermal phonons; $E=\sqrt{\Delta^2+\Delta_0^2}$ is the energy separation between the two levels; and Δ_0 is the tunnelling splitting of the symmetric tunnelling system ($\Delta=0$). Δ_0 is computed in the framework of the vibronic model [8, 9, 13]:

$$\Delta_0=\Delta_1+\delta\Delta$$

$$\Delta_1=\frac{2E_{JT}\mu(1-\mu)}{\sinh(\xi_0^2)},\quad \delta\Delta=\frac{2E_{JT}\mu(I-1+\mu^{-1})}{\sinh(\xi_0^2)}$$

$$I=\frac{1}{\sqrt{\pi}}\int_{-\infty}^{+\infty}\sqrt{C(\xi)}\,\exp(-\xi^2)(1-S\exp(2\xi\xi_0))\,\mathrm{d}\xi$$

where $C(\xi)=1+\xi^2\hbar\Omega_r/2E_{JT}\mu^2$, $S=\exp(-\xi_0^2)$ and $\xi_0^2=(2E_{JT}/\hbar\Omega_r)(1-\mu^2)$.

The rates of several processes that contribute to Q^{-1} have to be taken into account [10, 14–17]: The rates τ_d^{-1} of the one-phonon or direct processes, τ_{R1}^{-1} of two-phonon or first-order Raman processes, and "reaction rate" $\tau_{NRT}^{-1}=\tau_0^{-1}+\tau_{sub}^{-1}+\tau_{over}^{-1}$ of non-radiative transitions are [10, 15, 16]

$$\tau_d^{-1}=AE\,\Delta_0^2\coth(\beta E),\quad \tau_{R1}^{-1}=R\,\frac{\Delta_0^2}{E^2}\,T^7$$

$$\tau_0^{-1}=\frac{E_r}{2\pi\hbar}\exp\left(\frac{-E_r}{\hbar\Omega}\right)$$

$$\tau_{sub/over}^{-1}=\frac{2\beta}{\hbar}\sinh(\beta\hbar\Omega)\kappa_{sub/over}\times\exp(-2\beta V)(1-\exp(\Delta/kT))$$

$$V=E_{JT}+\frac{E_{gu}^2}{16E_{JT}}-\frac{E_{gu}}{2}$$

$$\kappa_{sub}=2\beta\hbar\Omega\sum_{i=1}^{m}\frac{\exp(2\beta(V-E_i))}{1+\exp(P_i)}$$

$$P_i=\frac{2\sqrt{2K}}{\hbar\Omega}\int_{-Q_t}^{+Q_t}\sqrt{E_L(Q)-E_i}\,\mathrm{d}Q$$

$$\kappa_{over}=\frac{\vartheta\pi}{\sin(\vartheta\pi)}+\vartheta\sum_{i=1}^{\infty}\frac{(-1)^i}{i-\vartheta}$$

where $E_r=4E_{JT}$ is the reorganization energy; $A=\gamma^2/2\pi\hbar^4\rho v^5$; $\vartheta=(\beta\hbar\Omega/\pi)(4E_{JT}/E_{gu}-1)$; $E_i=(i+\frac{1}{2})\hbar\Omega)$; m is the number of sub-barrier levels; and $\pm Q_t$ are the turning points used in the quasi-classical approximation [10]. τ_{over}^{-1} and τ_{sub}^{-1} apply for the overbarrier and sub-barrier non-radiative transitions respectively. According to the reaction-rate method [15], τ_0^{-1} represents the tunnelling processes at $T=0$ and has to be compared with $\tau_d^{-1}(T=0)$. The additional sub-barrier transition takes into account the rate of the tunnelling processes related to the sub-barrier vibronic levels with quantum numbers $i\neq 0$. In our calculation τ_{over}^{-1} is caused by the thermal activation, and the excited states of the tunnelling system are included in the calculation scheme for non-radiative transitions. Thus the overall relaxation constant τ^{-1} in eqn. (2) is a sum of the relaxation constants mentioned above:

$$\tau^{-1}=\tau_D^{-1}+\tau_{R1}^{-1}+\tau_{sub}^{-1}+\tau_{over}^{-1}.$$

3. Results and discussion

The tunnelling model is based on two important assumptions [17]: (i) the existence of tunnelling systems and (ii) the distribution of Δ and Δ_0. Hunklinger [18] has successfully described the $Q^{-1}(T)$ dependence in vitreous silica using a Gaussian distribution of the tunnelling parameter $\lambda = \ln(\hbar\Omega/\Delta_0)$. Applying the tunnelling model formalism, we have shown [16, 19] that the peculiarities in the acoustic absorption in $YBa_2Cu_3O_{7-\delta}$ (YBCO) and $La_{2-x}Sr_xCuO_4$ (LaSCO) for temperatures up to 100 K could be explained in principle as absorption in an ensemble of tunnelling systems. Our conclusion was that the experimentally observed peak is narrower and higher than the computed one using a Hunklinger-style Gaussian distribution of λ. The fit improves on using a rectangular distribution.

Unlike the tunnelling model, in which tunnelling systems are not specified, the vibronic model specifies two-level entities: small pseudo-Jahn–Teller polarons. In this paper we have done calculations with a δ-function distribution of λ. The $Q^{-1}(T)$ dependencies are shown in Fig. 3. Except for Δ and $\gamma = \partial\Delta/\partial F$, all the data are either taken from experiment, or are consistent with phase diagrams and infrared spectra.

The appropriate modes of O(A) are bending, E_u, and stretching, A_{2u} [20]. Taking into account the semi-axes ratio of the experimental thermal ellipsoids [21] (x, y-size/z-size is approx. $\frac{2}{3}$ for YBCO and approx. $\frac{3}{2}$ for LaSCO, which may be inferred from the graphs), we use the linear combination of these modes: $\Omega_r = \frac{2}{5}E_u + \frac{3}{5}A_{2u} = 510$ cm^{-1}, $\Omega = 630$ cm^{-1} for YBCO and $\Omega_r = \frac{3}{5}E_u + \frac{2}{5}A_{2u} = 538$ cm^{-1}, $\Omega = 575$ cm^{-1} for LaSCO.

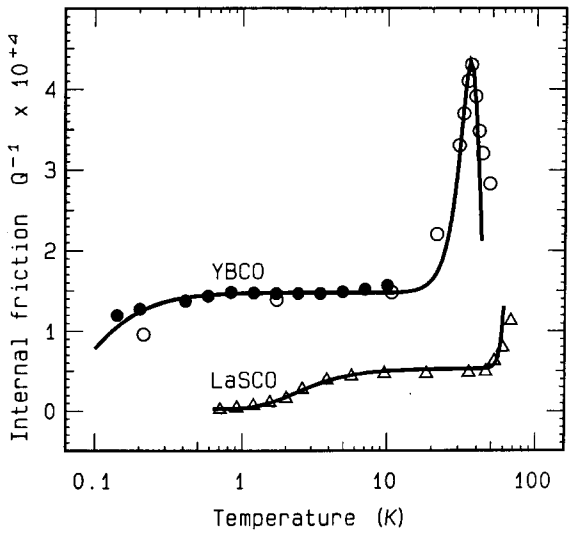

Fig. 3. Internal friction fits for YBCO (1.05 MHz) and LaSCO (700 Hz). Experimental points are taken from [1] (○), [2] (●) and [3] (△).

We use $\rho = 2.9$ g cm^{-3} [2], $v = 6400$ m s^{-1} [22], $M = 8$ atomic mass units, $R = 5\times10^{-4}$ s^{-1}, $E_{gu} = 1.5$ eV [11] and $P_{gu} = 0.45$ eÅ [9], $E_{JT} = 0.64$ eV for YBCO ($R = 1.5\times10^{-5}$ s^{-1}, $E_{gu} = 0.9$ eV [11], $P_{gu} = 0.34$ eÅ [9], $E_{JT} = 0.69$ eV for LaSCO). The value of R, which determines the first-order Raman processes, is not essential for the calculation, because of the small contribution of these processes.

We set $n = p_{O(A)}\,\delta p\,p_{lag}$, where $p_{O(A)}$ is the concentration of the O(A) atoms (17.32 nm^{-3} for YBCO and 10.58 nm^{-3} for LaSCO [9]), δp was interpreted as fraction of biholes over doped Cu(P)-site pairs (9% for YBCO and 22% for LaSCO) [9] and p_{lag} is the critical concentration at which superconductivity arises from the insulating phase (0.08 eV for YBCO and 0.06 eV for LaSCO).

The fitting values are quite reasonable: $\Delta = 1.8\times10^{-5}$ eV, $D = 2\gamma\Delta/E = 0.36$ eV for YBCO and $\Delta = 5\times10^{-4}$ eV, $D = 1.4$ eV for LaSCO. We consider in more detail the fit for YBCO (the fit for LaSCO is tentative). We obtained $\Delta_0 = 1.125\times10^{-6}$ eV ($E = 1.804\times10^{-5}$ eV) and $V = 0.1097$ eV; hence there is one vibronic level below the barrier for YBCO (four levels for LaSCO). As to the tunnelling rate, the values of $\tau_0^{-1} = 3.58$ s^{-1} and $\tau_d^{-1}(T=0) = 3.23$ s^{-1} are quite close. We may estimate the Arrhenius frequency ω_a from the Arrhenius law $\tau_a^{-1} = \omega_a \exp(-2\beta E_a)$ as well, which gives $\omega_a = 527$ cm$^{-1} \approx \Omega$ at $E_a = V - \hbar\Omega/2 = 0.0707$ eV.

According to the tunnelling model, acoustic absorption is relevant to the interaction between the acoustic wave and the thermal phonons' ensemble by the medium of asymmetry modulation. This interaction is fulfilled by the deformation potential. This thesis is corroborated by our fits, which indicate the existence of asymmetry. We obtain quite reasonable deformation potentials for that sort of oxides.

In accordance with our previous work, the plateau is caused by the distribution of parameters of tunnelling systems (as in glasses), for which successfully $\omega\tau \approx 1$ [16] is fulfilled. In this case Q^{-1} in the plateau regime is independent of ω. The narrowing of the distribution of λ into the δ-function leads to the formation of the plateau in the region $10^2 \geqslant \omega\tau \geqslant 1$, while the maximum corresponds to $\omega\tau = 1$. This causes the dependence $Q^{-1} \propto \omega^{-1}$ in the plateau regime, unlike the experimental and theoretical situation in glasses. Unfortunately we do not have experimental results for the dependence of $Q^{-1}(\omega)$ in the plateau regime for these materials under these conditions.

It is seen from Fig. 3 that the experimentally observed acoustic absorption in HTSC could be successfully explained by the present model, which assumes the existence of tunnelling systems (pseudo-Jahn–Teller polarons) in these materials, with parameters that are fixed (or distributed in a narrow range) parameters.

The relaxation processes that account for the phonon-assisted tunnelling (direct processes) are responsible for the plateau appearance, while the non-radiative transitions (and first-order Raman processes) form the peak at higher temperatures. It is remarkable that there is also a feature at approx. 35 K in the experimental dielectric losses for YBCO. A peak at approx. 100 K in the ultrasonic attenuation for LaSCO is observed [23, 24] at frequencies 10 MHz and 24 MHz respectively.

4. Conclusions

The temperature dependence of the acoustic absorption of YBCO and LaSCO up to 100 K has been calculated using the two-well tunnelling systems theory. The relaxation times used in the calculations were determined by the reaction rate method. This method was applied to the tunnelling system due to PJTE, present in HTSC, which specifies tunnelling system parameters.

The results obtained by our calculations of acoustic absorption in YBCO and LaSCO show that the fitting curves are very close to the experimentally observed ones. Moreover, the results offer the possibility of estimating the asymmetry Δ and the deformation potential D for YBCO and LaSCO as well. All this encourages the conclusion that tunnelling systems HTSC exist, originating from PJTE.

Acknowledgments

Thanks are due to the referee for constructive criticism. The authors would like to acknowledge enlightening conversations with M. Georgiev, M. Borissov and M. Ivanovich.

References

1 M. Nunez Regueiro, P. Esquinazi, M.A. Izbizky, C. Duran, D. Castello and J. Luzuriaga, *Ann. Phys. Fr., 13* (1988) 401.
2 C. Duran, P. Esquinazi, C. Fainstein and M. Nunez Regueiro, *Solid State Commun., 65* (1988) 957.
3 P. Esquinazi, C. Duran, C. Fainstein and M. Nunez Pegueiro, *Phys. Rev. B, 37* (1988) 545.
4 G. Cannelli, M. Canali, R. Cantelli, F. Cordero, S. Ferraro, M. Ferretti and F. Trequattrini, *Phys. Rev. B, 45* (1992) 931.
5 S.E. Stupp and D.M. Ginsberg, *Physica C, 158* (1989) 299.
6 G.A. Samara, W.F. Hammetter and E.L. Venturini, *Phys. Rev. B, 41* (1990) 8974.
7 F.C. Zhang and T.M. Rice, *Phys. Rev. B, 37* (1988) 3759.
8 L. Mihailov, M. Ivanovich and M. Georgiev, *J. Phys. Soc. Jpn., 62* (1993) 2431.
9 M. Borissov, M. Dimitrova, M. Georgiev, A. Manov, L. Mihailov and A. Vavrek, Institute of Solid State Physics, Jubilee collection, World Scientific, Singapore, 1994, p. 307.
10 M. Georgiev and A. Manov, *Czech. J. Phys. B, 38* (1988) 83.
11 A. Vavrek, M. Borissov and L. Mihailov, *C.R. Acad. Bulg. Sci., 43* (1990) 33.
12 P.A. Doussineau, C. Frenois, R.G. Leisure, A. Levelut, J.Y. Prieur, *J. Phys. (Paris), 41* (1980) 193.
13 M. Georgiev and M. Borissov, *Phys. Rev. B, 39* (1989) 11624.
14 J. Jäckle, *Z. Phys., 257* (1972) 212.
15 S.G. Christov, *Collision Theory and Statistical Theory of Chemical Reactions. Lecture Notes in Chemistry,* Vol. 18, Springer, Berlin–Heidelberg–New York, 1980, p. 184.
16 L. Mihailov, A. Vavrek, M. Borissov, M. Georgiev and A. Manov, in J.M. Marshall, N. Kirov and A. Vavrek (eds.), *Electronic and Optoelectronic Materials for the 21st Century, Varna, Bulgaria, 1992,* World Scientific, Singapore, 1993, p. 606.
17 W.A. Phillips, *Amorphous Solids – Low Temperature Properties. Topics in Current Physics,* Vol. 24, Springer, Berlin–Heidelberg–New York, 1981, p. 1.
18 S. Hunklinger, *Acta Phys. Slovaka, 40* (1990) 14.
19 A. Vavrek, M. Borissov, A. Manov and B. Filipova, *C.R. Acad. Bulg. Sci., 43* (1990) 35.
20 R. Feile, *Physica C, 159* (1989) 1.
21 J.D. Jorgensen, *Jpn. J. Appl. Phys., 26, Suppl. 26-3* (1987) 2017.
22 V.G. Bariahtar, V.N. Variuhin and A.B. Nazarenko, *Sverhprovodimost (Russ.), 3* (1990) 1145.
23 Y. Horie, Y. Terashi, H. Fukada, T. Fudami and S. Mase, *Solid State Commun., 64* (1987) 501.
24 K. Fossheim, T. Laegreid, E. Sandvoid, F. Vassenden, K.A. Müller and J.G. Bednorz, *Solid State Commun., 63* (1987) 531.