

## Anharmonic oxygen vibration and mode softening in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ superconductor

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MS received 24 June 1991; revised 24 February 1992

**Abstract.** The softening of the IR active  $300\text{ cm}^{-1}$  phonon mode in Tl-2223 superconductor, around  $T_c$  has been explained by considering a sixth order polarization potential at the off-center oxygen ion site in the Tl-O plane, and by using a nonlinear lattice dynamical theory. The present theory explains, more or less satisfactorily, the unusual temperature dependence of oxygen ion vibration and frequency shifts at higher temperature. The existence of strong nonlinear electron-phonon interaction at  $T_c$  has been emphasized.

**Keywords.** Phonon-electron interactions; anharmonic lattice modes.

PACS Nos 63-20; 63-50

### 1. Introduction

After the discovery of high temperature superconductivity by Bednorz and Muller (1986) in  $(\text{La}, \text{Ba})_2\text{CuO}_4$  at 35-40 K and by Wu *et al* (1987) in YBCO at 90-100 K, a lot of interest has aroused in raising the superconducting transition temperature ( $T_c$ ) in other oxide systems (Maeda *et al* 1988; Sheng and Hermann 1988a, b; Sheng *et al* 1988). They (Sheng and Hermann 1988a, b; Sheng *et al* 1988) reported thallium-based superconductors where  $T_c$  was found to be above 100 K. General configuration of this new superconductor is  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , where  $n$  is the number of consecutive Cu-O layers (Toradi *et al* 1988).  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  (with  $n=3$ ) is one of the important superconductors in which  $T_c$  was found to be of the order of 120 K (Sheng *et al* 1988). The crystal structures of thallium-based superconductors have been studied in great detail by the neutron, electron and X-ray powder diffraction methods (Cox *et al* 1988; Hazen *et al* 1988; Hewat *et al* 1988; Shimakawa *et al* 1988).

The electron and X-ray diffraction studies (Hazen *et al* 1988) of the  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  (Tl-2223) sample reveal information about the structure and the coordination of the respective metal atoms. The structure of the Tl-2223 is based on the body centred tetragonal cell with  $a = 3.8487 \text{ \AA}$  and  $c = 35.6620 \text{ \AA}$  (at 150 K) (Cox *et al* 1988; Subramanian *et al* 1988; Toradi *et al* 1988). An important feature of the Tl-2223 structure is that the lattice parameters ( $a$  and  $c$ ) show anisotropic behaviour with respect to temperature. Also in Tl-2223, the coordination of Ca and Ba are normal; for Cu, it is the same as in other Cu-O superconductors. But the coordination of Tl ion is quite unusual (Hewat *et al* 1988). Because of the off-center position of oxygen in Tl-O plane in the form of displacements of about  $0.4 \text{ \AA}$  from the ideal position, each thallium has one short and one long interatomic bonds with oxygen which

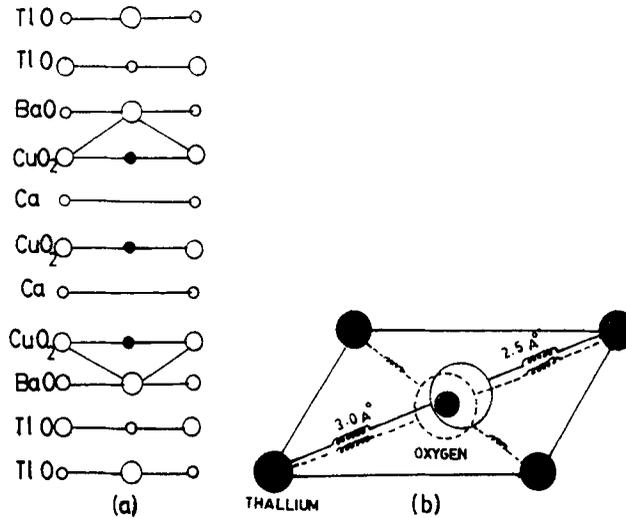


Figure 1. (a) Structural model of  $Tl_2Ba_2Ca_2Cu_3O_{10}$  superconductor. (b) A Tl-O plane where the dotted circle represents the symmetric position of oxygen atom. Difference of the bond length in between the thallium and oxygen ( $Tl_{1n} - O$ ) - ( $Tl_{1n+1} - O$ ) is about 0.4 Å.

results in increase of Tl valence (see figure 1(b)). The oxygen placed in the centre of the Tl square moves away from the higher symmetry site towards the Tl-Tl distance, reducing the Tl-O distance and thereby increasing the Tl valence from 2.16 to 6.0 (Hewat *et al* 1988).

Recently, Zetterer *et al* (1990) measured the temperature dependence of one of the infrared active phonons (near  $300\text{ cm}^{-1}$ ) in Tl-2223 superconductor. They have observed strong softening of this infrared active phonon around the superconducting transition temperature ( $\sim 112\text{ K}$ ). This mode shifts from  $306\text{ cm}^{-1}$  at 115 K to  $284\text{ cm}^{-1}$  at 95 K and then remains constant at further low temperatures. Zetterer *et al* (1990) have associated this mode softening at  $T_c$  to the anharmonic vibration of the off-center oxygen atom in Tl-O layers. These authors have not, however mentioned about the origin and nature of such anharmonicity present in the Tl-2223 superconductor. In the present paper we will, in what follows, try to explain this particular aspect, using a nonlinear lattice dynamical theory for the thallium superconductor.

It is now very well established that the polarizability of the oxygen and other chalcogen ion plays a key role in several solid state properties. The best example in this regard is the ferroelectric phase transition in perovskites (Migoni *et al* 1978; Bilz *et al* 1987). Lattice dynamically ferroelectric phase transition is described by a local on site double well polarization potential characterized by attractive electron phonon coupling term ( $g_2 < 0$ ) and a stabilizing electron two phonon term from repulsive forces between the ions modelled by a force constant ( $g_4 > 0$ ). The polarizability model has successfully explained the mode-softening in several ferroelectric systems like  $KTaO_3$ ,  $SrTiO_3$ ,  $SnTe$ , etc. (Bilz *et al* 1980). The present authors have also applied this nonlinear lattice dynamical theory to explain the temperature dependence of optical phonons in intermediate valence compound ( $Sm_{0.75}Y_{0.25}S$ ) (Chowdhury and Sanyal 1991). In addition, Kress and Sanyal (1990) have recently explained the temperature dependence of IR absorption spectra of the anharmonic oxygen vibration

in  $Si_2O$  molecule where a sixth order electron phonon coupling is proved to be dominant. Another effort is made by Bussmann Holder *et al* (1989) to establish a common origin to ferroelectricity and superconductivity in oxide systems. They indicate that the ferroelectric instability for the electron states can give rise to a superconducting state, depending on the strength of the coupling constants.

In the present paper we attribute the mode-softening of  $300\text{ cm}^{-1}$  infrared active phonon to the nonlinear polarizability of the off-center oxygen ion in the Tl–O plane of the Tl-2223 compound. Since the polarizability of the oxygen ion depends on the environment, the charge distribution of the oxygen ion is strongly influenced by one long and one short bond length between the thallium and oxygen atoms. In fact this produces a large deformation at the oxygen site resulting in strong nonlinear electron phonon interaction in the system. Necessarily such an electron phonon interactions cannot be explained in terms of either intersite  $\phi^4$  field theoretical model (Krumhansl and Schrieffer 1975) or on-site  $\phi^4$  polarizable model (Migoni *et al* 1978; Bilz *et al* 1987) as both of them give rise to structural phase transition at a particular temperature. We do not consider these approaches as no structural phase transition at  $T_c$  was found in this Tl-2223 compound (Cox *et al* 1988; Zetterer *et al* 1990).

In the present paper we consider an on-site sixth order polarization potential at the off-center oxygen ion site in the Tl–O plane. Details of the approach are given in §2. We calculate the temperature dependence of the  $300\text{ cm}^{-1}$  phonon mode and the dynamical conductivity at different temperatures and compare them with the experimental result of Zetterer *et al* (1990). The results followed by the physical interpretation of the anharmonic vibration of the oxygen ion in the Tl–O plane are given in §3.

## 2. Theory

For the present analytical treatment, the starting point of our model is one of the infrared active phonon modes near  $300\text{ cm}^{-1}$ , which is due to the anharmonic vibrations of the oxygen ion in the Tl–O plane (Zetterer *et al* 1990). Hence to a greater approximation and for qualitative analysis, it is reasonable to consider an one-dimensional linear chain of Tl–O atoms in which latter is considered to be nonlinearly polarizable (see figure 2).

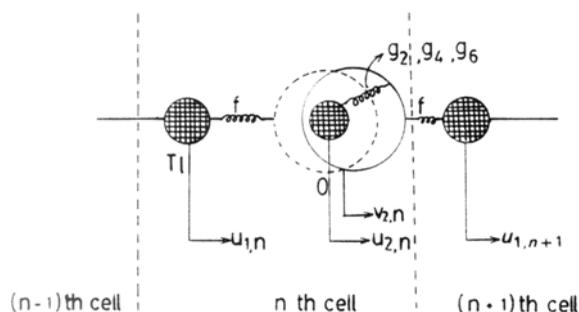


Figure 2. One-dimensional diatomic Tl–O chain.

The Hamiltonian of the diatomic Tl-O chain is

$$H = T + \phi_L + \phi_P \quad (1)$$

where

$$T = \frac{1}{2} \sum_n [m_i \dot{u}_{i,n}^2 + m_{e_j} \dot{v}_{j,n}^2] \quad (i = 1, 2; j = 2)$$

$$\phi_L = \frac{1}{2} \sum_n [f(u_{1,n} - v_{2,n})^2 + f(u_{1,n+1} - v_{2,n})^2]$$

and the anharmonicity at the oxygen site is described through a nonlinear polarization potential  $\phi_P$ , expressed as

$$\phi_P = \frac{1}{2} \sum_n [g_2(v_{2,n} - u_{2,n})^2 + \frac{1}{2} g_4(v_{2,n} - u_{2,n})^4 + \frac{1}{3} g_6(v_{2,n} - u_{2,n})^6].$$

Here,  $m_i$  and  $m_{e_j}$  are the masses of thallium, oxygen cores and the valence electrons of the oxygen atom.  $u_{i,n}$  and  $v_{j,n}$  are the displacements of the core and shell in the  $n$ th cell.  $f$  is the linear short range force constant between the shell of oxygen and the thallium core  $g_2$ ,  $g_4$  and  $g_6$  are the harmonic, quartic and sixth order force constants within the shell of oxygen ion respectively. The sixth order force constant  $g_6 < 0$  is needed to avoid the structural instability, thereby stabilizing the system (Kress and Sanyal 1990; Sanyal *et al* 1991). Due to the shift of oxygen atom by 0.4 Å in Tl-O plane, a difference in bond lengths between thallium and oxygen atom in the  $n$ th and  $(n + 1)$ th cell results. For simplicity, we have considered the force constants  $f$  to be the same in all the cells of the linear chain.

Using adiabatic approximation and defining  $w_{2,n} (= v_{2,n} - u_{2,n})$  as relative core-shell displacement of oxygen ion, we obtain a single equation of motion at the arbitrary site  $n$  for the relative shell core coordinate ( $w_{2,n} \equiv w$ ,  $x = w^2$ ) (Chowdhury and Sanyal 1991) as

$$\begin{aligned} (\alpha + \beta x + \gamma x^2) \ddot{x} - \left( \frac{\alpha \dot{x}^2}{2x} \right) + \left( \frac{1}{2} (\beta + 3\gamma x) \dot{x}^2 \right) \\ + \left( \frac{2f}{\mu} (g_2 x + g_4 x^2 + g_6 x^3) \right) = 0 \end{aligned} \quad (2)$$

with

$$\alpha = 2f + g_2, \quad \beta = 3g_4, \quad \gamma = 5g_6$$

and

$$\mu = \left( \frac{1}{m_1} \right) + \left( \frac{2}{m_2} \right)$$

is the reduced mass of the  $n$ th cell. Equation (2) can be integrated once to get the final solution as

$$\dot{x}^2 = - \left( \frac{x}{(\alpha + \beta x + \gamma x^2)^2} \right) S(x) \quad (3)$$

where

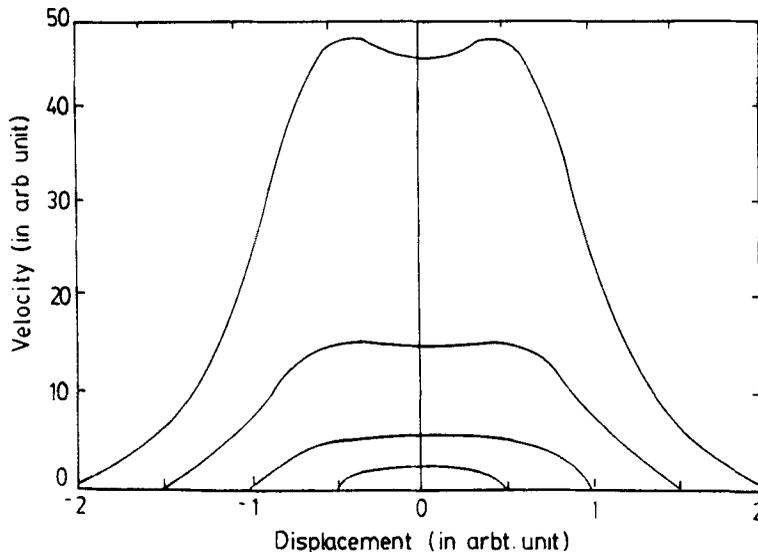
$$\begin{aligned} S(x) = x^5 + \left( \frac{5}{4} \left( \frac{g_4}{g_6} + \frac{\beta}{\gamma} \right) x^4 \right) + \left( \frac{5}{3} \left( \frac{g_2}{g_6} + \frac{\alpha}{\gamma} + \frac{g_4 \beta}{g_6 \gamma} \right) x^3 \right) \\ + \left( \frac{5}{2} \left( \frac{g_4 \alpha}{g_6 \gamma} + \frac{g_2 \beta}{g_6 \gamma} \right) x^2 \right) + \left( 5 \frac{g_2 \alpha}{g_6 \gamma} x \right) - \left( \frac{5}{4} C_0 \right) - \left( \frac{5 \lambda \beta}{4 \gamma} \right). \end{aligned} \quad (4)$$

Here  $C_0$  and  $\lambda$  have their values in terms of one of the initial roots at the turning point. Equation (3) can be integrated numerically to obtain the frequency of the oscillation as a function of initial relative displacement of the shell and core of oxygen ion which is directly related to the temperature of the system. The energy of the oscillations can be calculated in a straight-forward manner (Chowdhury and Sanyal 1991). In the present case the energy corresponds to a single well potential showing no structural phase transition.

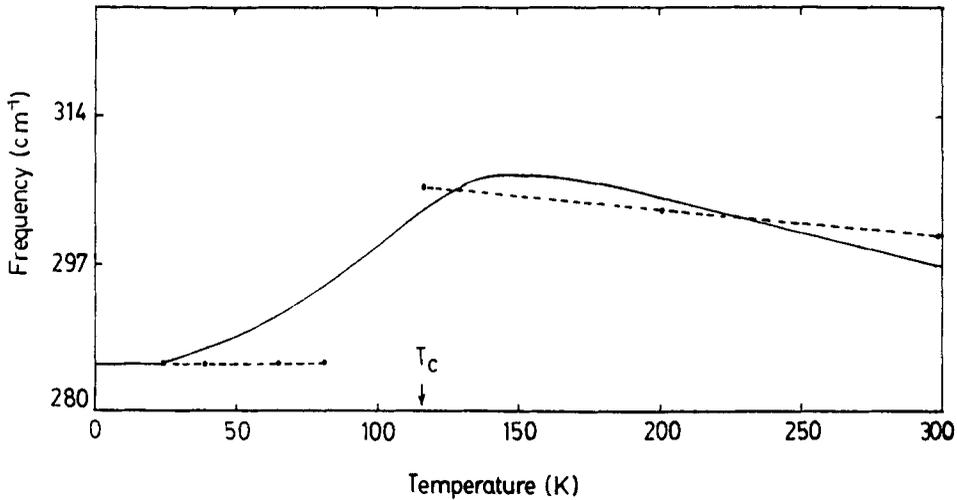
### 3. Results and discussion

As a first step of our analysis we calculate the velocity of the oscillator as a function of the initial displacement  $w_0$ , due to the anharmonic vibration at the oxygen ion site. For the choice of parameters, we consider  $-g_2 > 2f$ ,  $g_4 \ll -g_2$  and  $g_2 \gg g_6$ . The first one is reasonably valid for Tl-2223 compounds (Kulkarni *et al* 1989), while the other two are necessary to avoid the structural instability. The values of the parameters are  $f = 39.075$ ,  $g_2 = -195.35$ ;  $g_4 = 19.15$  and  $g_6 = -50.79$  ( $f$  and  $g_2$  are in  $10^2 \text{ N/m}$ ,  $g_4$  in  $10^2 \text{ N/m}^3$ ,  $g_6$  is  $10^2 \text{ N/m}^5$ ). These force constants have been obtained from the frequencies of this mode at different temperatures without exact fitting. The parameters can be justified from the shell model calculations, reported by Kulkarni *et al* (1989). Figure 3 shows the velocity of the oscillator as a function of the initial displacements. For small displacements i.e. at low temperatures, the oscillations are harmonic and the oscillator travels through the origin. As initial displacements increase tending to high temperature phase, the harmonic nature of the oscillator disappears. In this phase the oscillations become highly anharmonic which can be revealed from the nonlinear velocity distribution.

Variation of the frequency of oscillations with temperature is shown in figure 4. We have compared our results with those obtained by Zetterer *et al* (1990) from IR spectroscopy. At low temperature harmonic oscillation results and the frequency is



**Figure 3.** Velocity of the anharmonic oscillator as a function of initial relative shell-core displacements of the oxygen ion.



**Figure 4.** Frequency of oscillation of the IR active ( $\sim 300 \text{ cm}^{-1}$ ) phonon as a function of temperature. Dark circles represent the experimental frequency at different temperatures (from Zetterer *et al* 1990).

fairly constant. The harmonic region is dominated by the  $g_2$  term corresponding to the attractive electron phonon coupling. At intermediate temperature (say 50–125 K), repulsive electron two phonon interactions dominate which results in increase of frequency. At relatively high temperatures, the off-center oxygen ion experiences relatively large deformation of electron charge density resulting in a slight decrease of frequency from 125 K to 300 K. This is contributed by the sixth order anharmonic term  $g_6$ .

In contrast to the experimental results, our model does not show any sharp increase of frequency at  $T_c$ . Rather it continuously increases for a large interval of temperature. This is, we suppose, not a very serious limitation of the model, as long as it depicts qualitatively the nature of the anharmonicity in oxygen vibration. A similar continuous variation of frequency with temperature was also observed by Sawada *et al* (1987) from IR spectroscopic measurement of one of the soft phonon modes in  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  ( $x = 0.1$ ) system. Thus the origin and nature of anharmonic vibration of oxygen in both the systems seem to be similar in nature.

For the calculation of dynamical conductivity for the one dimensional Tl–O chain we use the formalism developed by Mills and Maradudin (1973) for non-interacting anharmonic oscillators and use the formula

$$\langle\langle \dot{E} \rangle\rangle = \left( \frac{q_i^2 E_i^2 \omega_i}{4m_i^2 KT} \right) Z^{-1} \sum_{n=1}^{\infty} \left( \frac{1}{n^2} \right) P_n^2(E) \left| \frac{dE}{d\omega} \right| \exp(-E/KT) \Big|_{\omega=\omega_i/n} \quad (5)$$

where  $\langle\langle \dot{E} \rangle\rangle$  is the average absorption rate per oscillator. Here  $q_i$  and  $m_i$  are the net charge and mass of the atom in the chain.  $E_i$  is the magnitude of the external electromagnetic field of frequency  $\omega_i$ ,  $Z$  is the partition function,  $T$  the temperature and  $P_n(E)$  the  $n$ th Fourier coefficient of the velocity for the mode of energy  $E$  and frequency  $\omega$ . In figure 5 we have plotted the dynamical conductivity as a function of frequency at different temperatures.

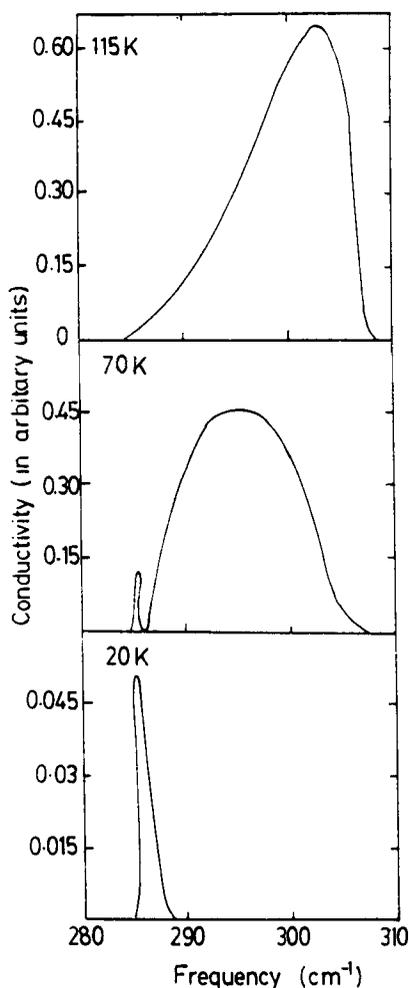


Figure 5. Dynamical conductivity curves as a function of the anharmonic frequency at different temperatures.

For harmonic oscillations at low temperature, the derivative  $dE/d\omega$  is large. Thus a single sharp peak with large intensity is obtained at low temperature. At higher temperature,  $dE/d\omega$  decreases very rapidly which gives a broad peak resulting from the anharmonic oscillations, while the harmonic peak at  $284\text{ cm}^{-1}$  loses its intensity. At further higher temperature the broad peak shifts to higher frequency side (Hrostowski and Kaiser 1957). The width and the intensity of this broad peak is mainly determined by the thermal population factor  $f = \exp(-E/KT)$ . A direct comparison of our figure 5 with figure 2 of Zetterer *et al* (1990) reveals that qualitatively our calculated results are identical to the experimental observation. Only difference, which is obvious, is that we obtain a two peak structure around the transition temperature of the mode softening while experimentally this is absent, except around 100 K where two peaks at their respective positions are observed. However, in accordance with experiment, we observe one sharp peak at low temperature at  $284\text{ cm}^{-1}$  and one broad peak around  $300\text{ cm}^{-1}$  at relatively higher temperature. This gives a qualitative relevance of our results.

The aim of the present study was however, to show that the strange and yet unexplained mode softening and large frequency shift at superconducting transition temperature in the Tl-2223 compound can be qualitatively explained by considering on-site anharmonic interactions for the off-center oxygen ion in the Tl-O plane. We have analysed the softening of the infrared active phonon at the transition temperature ( $T_c \sim 120$  K) of the  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  compound. Although the present analysis as such does not throw any light on the origin of high temperature superconductivity, it certainly emphasizes a strong nonlinear electron phonon interaction at the oxygen ion at  $T_c$ , as has been reported by Hardy and Flocken (1988) and may be a common phenomena in all perovskite superconductors.

### Acknowledgements

The authors are indebted to Dr Winfried Kress (Max Planck Institute, Stuttgart), Prof. R K Singh and Dr P K Sen for encouragement. The project is partially supported by DAE and DST research grants. One of us (NDC) is grateful to CSIR for the award of a Senior Research Fellowship.

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