Generalized Grüneisen parameters and the low temperature thermal expansion of high-T_c superconductor Bi$_2$Sr$_2$CaCu$_2$O$_8$

Generalized Grüneisen parameters and the low temperature thermal expansion of high-T_c superconductor Bi₂Sr₂CaCu₂O₈

K P Jayachandran and C S Menon

School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam,
Kerala 686 560, India

Abstract

The anisotropy of low temperature thermal expansion of Bi₂Sr₂CaCu₂O₈ (Bi 2212) is analysed theoretically using quasiharmonic theory of thermal expansion. Vibrational anharmonicity as determined by the generalized Grüneisen parameters (GPs) γ_j' and γ_j'' of the various normal mode frequencies of the lattice has been studied. γ_j' refers to change in frequencies due to a uniform areal strain perpendicular to the c-axis and γ_j'' to the change in frequencies due to a uniform areal strain along the c-axis of the Bi 2212 crystal. The generalized GPs are calculated using the second-order elastic constants (SOECs) and third-order elastic constants (TOECs). The SOECs and TOECs are calculated using deformation theory. The strain energy density ϕ is estimated by taking into account the interactions of nine nearest neighbours of each atom in the unit cell of Bi 2212. The energy density thus obtained is compared with the strain-dependent lattice energy from the continuum model approximation to obtain the complete set of non-vanishing SOECs and TOECs of Bi₂Sr₂CaCu₂O₈. Generally, γ_j'' exhibits higher values than γ_j'. Thus the crystal is more anharmonic along the c-axis than in the ab-plane. The longitudinal acoustic mode γ_3'' is the most anisotropic of all the mode gammas. The transverse acoustic mode γ_1' attains negative values from $\theta = 25°$ to $55°$, where θ is the angle made by the direction of wave propagation with the c-axis of the crystal Bi₂Sr₂CaCu₂O₈. The low temperature limit of the effective Grüneisen functions $\overline{\gamma}_{\parallel}(0)$, which is parallel to the c-axis of Bi 2212, is almost double the value of $\overline{\gamma}_{\perp}(0)$. Hence the discrepancy in the vibrational anharmonicity along the c-axis and along the CuO₂ plane persists even at low temperatures. The low temperature limit of the volume lattice thermal expansion γ_L is calculated from mode Grüneisen gammas. γ_L has been obtained as 4.2 for Bi₂Sr₂CaCu₂O₈. The low temperature limit γ_L is positive and therefore, we expect the volume lattice thermal expansion to be positive down to absolute zero in Bi₂Sr₂CaCu₂O₈. At low temperatures, the acoustic wave velocities in high-T_c superconductors increase their value due to the freezing out of optical phonons. This can be a reason for the higher value of the low temperature limit of Grüneisen gammas in Bi₂Sr₂CaCu₂O₈.

1. Introduction

The thermal expansion of a solid arises strictly due to the anharmonicity of the crystal lattice, the nonlinearity of interatomic forces with respect to atomic displacements. Usually the anharmonic properties are described in terms of Grüneisen parameters (GPs) γ, which quantify the volume or strain dependence of the lattice vibrational frequencies. γ is important in characterizing high-T_c oxide superconductors, appearing in the volume dependence of superconducting transition temperature T_c with the electron–phonon enhancement factor to control T_c [1, 2]. High-T_c superconductors which are highly anisotropic especially along the c-axis direction are expected to exhibit interesting variation in GPs. It is well known that GPs depend much on oxygen concentration in high-T_c superconductors [3, 4]. γ is related to high pressure properties of materials such as bulk modulus and pressure derivatives of elastic moduli. A difficulty has arisen in determining GPs for many of the high-T_c superconductors because of the wide variation in the bulk modulus measured by different methods and on different specimens [5]. Generally, the ultrasonic velocities have led to values of bulk moduli which are much smaller than those determined by x-ray diffraction or neutron diffraction under pressure. One obvious case of discrepancy is that most specimens are highly porous assemblies of small platelets, usually extended in the ab-plane but short in the c-direction with voids. Since the individual platelets are also anisotropic and smaller than the wavelength of the ultrasonic waves, extrapolation of the data to a non-porous isotropic medium is open to question.

In this paper, we have calculated the generalized isothermal GPs γ_j' and γ_j'' for the acoustic modes, of $Bi_2Sr_2CaCu_2O_8$ using the quasiharmonic theory of thermal expansion. The crystal structure of Bi 2212 is orthorhombic although the lattice parameter a is very close in magnitude to the lattice parameter b. Hence, to a good approximation, the crystal structure can be regarded as being tetragonal. The generalized GP γ_j' refers to the change in frequencies due to a uniform areal strain perpendicular to the c-axis and γ_j'' to the change in frequencies due to a uniform longitudinal strain along the c-axis of $Bi_2Sr_2CaCu_2O_8$. For evaluating γ_j' and γ_j'', the SOECs and TOECs are determined using deformation theory [6, 7]. From this, the low temperature limit of the Grüneisen functions, γ_L, is calculated. The procedure to calculate the low temperature limit is also given.

2. Theory

In the harmonic approximation, the atoms in a solid are assumed to oscillate symmetrically about their equilibrium positions which remain unaltered irrespective of the temperature. Therefore, $\gamma = 0$ for a harmonic solid. Hence deviations of γ from zero can be interpreted as a direct measure of anharmonicity. The thermal expansion of a solid, therefore, is a property arising strictly due to the anharmonicity of the lattice.

2.1. Quasiharmonic theory of thermal expansion

In the quasiharmonic approximation, the oscillations are still assumed to be harmonic in nature but the frequencies are taken to be functions of the strain components in the lattice. The strained state of the lattice is specified fully by the six strain components η_{rs} ($r, s = 1, 2, 3; \eta_{rs} = \eta_{sr}$).

A normal mode with frequency $\omega(\boldsymbol{q}, j)$ makes a contribution $F(\boldsymbol{q}, j)$ to the total vibrational free energy F_{vib}, given by

$$F(\boldsymbol{q}, j) = k_B T[\tfrac{1}{2} Y + \log(1 - e^{-Y})] \qquad (1)$$

where $Y = \hbar\omega(q, j)/k_B T$, $\hbar = h/2\pi$, h being the Planck constant, k_B is the Boltzmann constant, T is the absolute temperature and q is the wavevector of the jth acoustic mode. The total vibrational free energy is, therefore,

$$F_{\text{vib}} = \sum_{q,j} F(q, j)$$
$$= k_B T \sum_{q,j} [\tfrac{1}{2} Y + \log(1 - e^{-Y})]. \tag{2}$$

The thermal expansion coefficients α_{lm} of the crystal are obtained as

$$V\alpha_{lm} = -\left[\frac{\partial^2 F_{\text{vib}}}{\partial \sigma_{lm} \partial T}\right]_{T,\sigma',\sigma}$$
$$= \sum_{q,j} \sum_{rs} S_{lm,rs} \gamma_{rs}(q, j) k_B C_E[\omega(q, j), T]. \tag{3}$$

Here,

$$\alpha_{lm} = \left(\frac{\partial \eta_{lm}}{\partial T}\right)_\sigma$$

σ_{lm} are the components of the stress tensor, $S_{lm,rs}$ are the compliance coefficients relating η_{rs} and σ_{lm} and

$$\gamma_{rs}(q, j) = -\left[\frac{\partial \log \omega(q, j)}{\partial \eta_{rs}}\right]_T. \tag{4}$$

Here, γ_{rs} are the generalized GPs of the normal mode frequencies. In equation (3), the subscript σ' means that all other σ_{ik} are to be held constant while differentiating with respect to σ_{lm} and subscript σ means that all σ_{lm} are held constant. $C_E[\omega(q, j)T] = Y^2 e^{-Y}/(1 - e^{-Y})^2$ is the Einstein specific heat function. In the quasiharmonic approximation, the GPs are assumed to be constants independent of temperature.

It is more advantageous to choose such strains that do not alter the crystal symmetry, instead of choosing any arbitrary strain, while defining GPs. For $Bi_2Sr_2CaCu_2O_8$ there are two principal thermal expansion coefficients, namely $\alpha_\parallel$, which is the linear expansion coefficient parallel to the c-axis, and $\alpha_\perp$, which is the linear thermal expansion coefficient perpendicular to the c-axis. Here, it is convenient to use the following strains for the determination of the thermal expansion.

 (i) A uniform longitudinal strain ε'' along the c-axis. Then all the η_{rs} are zero, except $\eta_{33} = \varepsilon'' = d \log c$, where c is the axial length.
(ii) A uniform areal strain ε' in the basal plane perpendicular to the c-axis. Then $\eta_{11} = \eta_{22} = \tfrac{1}{2} dA/A = \varepsilon'/2$, where A is the area of the basal plane of the crystal. All other η_{rs} vanish.

Therefore

$$\gamma_{33}(q, j) = \gamma''(q, j) = \frac{-\partial \log \omega(q, j)}{\partial \log c}$$

and

$$\frac{1}{2}[\gamma_{11}(q, j) + \gamma_{22}(q, j)] = \gamma'(q, j) = \frac{-\partial \log \omega(q, j)}{\partial \log A}. \tag{5}$$

From equation (3), we now obtain

$$V\alpha_{33} = V\alpha_\parallel = \sum_{q,j} [2S_{13} \gamma'(q, j) + S_{33} \gamma''(q, j)] k_B C_E(\omega(q, j))$$

and

$$V\alpha_{11} = V\alpha_{22} = V\alpha_\perp = \sum_{q,j} [(S_{11} + S_{12})\gamma'(\boldsymbol{q}, j) + S_{13}\,\gamma''(\boldsymbol{q}, j)]k_B C_E(\omega(\boldsymbol{q}, j)). \tag{6}$$

The effective Grüneisen functions are defined as

$$\overline{\gamma}_\perp(T) = [(C_{11}^S + C_{12}^S)\alpha_\perp + C_{13}^S\alpha_{||}]V/C_p$$
$$\overline{\gamma}_{||}(T) = [2C_{13}^S\alpha_\perp + C_{33}^S\alpha_{||}]V/C_p. \tag{7}$$

The C_{ij}^S are the adiabatic elastic constants, C_p is the specific heat at constant pressure and V is the volume of the crystal.

Comparing equations (7) with (6), we obtain

$$\overline{\gamma}_\perp(T) = \left(\sum_{q,j} \gamma'(\boldsymbol{q}, j)C_E[\omega(\boldsymbol{q}, j), T] \right)\left(\sum_{q,j} C_E[\omega(\boldsymbol{q}, j), T] \right)^{-1}$$
$$\overline{\gamma}_{||}(T) = \left(\sum_{q,j} \gamma''(\boldsymbol{q}, j)C_E[\omega(\boldsymbol{q}, j), T] \right)\left(\sum_{q,j} C_E[\omega(\boldsymbol{q}, j), T] \right)^{-1}. \tag{8}$$

The expressions (8) give the temperature dependence of the effective Grüneisen function.

In the low temperature limit, only the low frequency acoustic modes make a contribution to the specific heat. The number of such normal modes in the jth acoustic branch is proportional to $v_j^{-3}(\theta, \phi)$, where $v_j(\theta, \phi)$ is the velocity of the jth acoustic mode travelling in the direction (θ, ϕ). The GP $\gamma(\boldsymbol{q}, j)$ depends only on the branch index j and the direction (θ, ϕ). It is independent of the magnitude of the wavevector $\boldsymbol{q}$. The effective lattice Grüneisen functions $\overline{\gamma}_\perp(T)$ and $\overline{\gamma}_{||}(T)$ approach the limits defined below, at low temperatures:

$$\mathop{\text{Lt}}_{T\to 0} \overline{\gamma}_\perp(T) = \overline{\gamma}_\perp(0) = \left(\int \sum_{j=1}^3 \gamma_j'(\theta, \phi)v_j^{-3}(\theta, \phi)\,\text{d}\Omega \right)\left(\int \sum_{j=1}^3 v_j^{-3}(\theta, \phi)\,\text{d}\Omega \right)^{-1}$$
$$\mathop{\text{Lt}}_{T\to 0} \overline{\gamma}_{||}(T) = \overline{\gamma}_{||}(0) = \left(\int \sum_{j=1}^3 \gamma_j''(\theta, \phi)v_j^{-3}(\theta, \phi)\,\text{d}\Omega \right)\left(\int \sum_{j=1}^3 v_j^{-3}(\theta, \phi)\,\text{d}\Omega \right)^{-1} \tag{9}$$

where $\gamma_j'(\theta, \phi)$ and $\gamma_j''(\theta, \phi)$ are the GPs for the acoustic modes propagating in the direction (θ, ϕ). Calculations of the low temperature limit of $\overline{\gamma}_\perp(T)$ and $\overline{\gamma}_{||}(T)$ are possible knowing the pressure derivatives of the SOECs or the TOECs of the crystal.

2.2. Procedure to obtain the low temperature limit of the Grüneisen function (γ_L)

The low temperature limits of the effective Grüneisen functions $\overline{\gamma}_\perp(0)$ and $\overline{\gamma}_{||}(0)$ of a uniaxial crystal depend on the generalized GPs $\gamma_j'(\theta, \phi)$ and $\gamma_j''(\theta, \phi)$ of the acoustic modes propagating in different directions in the crystal. In this section, a method of calculation of the GPs for the high-T_c superconductors $Bi_2Sr_2CaCu_2O_8$, from higher order elastic constants is presented.

A medium is said to be homogeneously strained if the components of the strain tensor η_{ij} do not vary from point to point in the medium. Let the co-ordinates of the lattice point in the strained state be X_i ($i = 1, 2, 3$). When the lattice is given infinitesimal displacements u_i from the strained state, the resulting state is referred to by the co-ordinates $x_i = X_i + u_i$; the equation of motion is

$$\rho\ddot{x}_j = \frac{\partial}{\partial x_k}\tau_{kj} \tag{10}$$

where ρ is the density in the strained state and τ_{kj} is the stress tensor. The condition of equilibrium requires that the stress tensor be symmetric, i.e.

$$\tau_{jk} = \tau_{kj}. \tag{11}$$

We have for the Jacobian J

$$\frac{\partial}{\partial x_k}\left(\frac{1}{J}\frac{\partial x_k}{\partial a_p}\right) = 0. \tag{12}$$

Using equations (10) and (11), Thurston and Brugger [8] arrive at the following wave equation in a homogeneously strained lattice in terms of the displacements u_i:

$$\rho_0 \ddot{u}_j = A^S_{jk,pm}\frac{\partial^2 u_k}{\partial a_p \partial a_m} \tag{13}$$

where J in equation (12) is defined as

$$J = \mathrm{Det}\left(\frac{\partial x_i}{\partial a_j}\right) \tag{14}$$

with a_i $(i = 1, 2, 3)$ being the position co-ordinates of a lattice point in the unstrained state. In equation (13), ρ_0 is the density of the crystal before deformation and

$$A^S_{jk,pm} = \delta_{jk}\bar{t}_{pm} + \frac{\partial X_j}{\partial a_q}\frac{\partial X_k}{\partial a_i}\left(\overline{\frac{\partial \bar{t}_{pm}}{\partial \eta_{mi}}}\right) \tag{15}$$

where

$$\bar{t}_{pm} = \left(\overline{\frac{\partial U}{\partial \eta_{pm}}}\right)_S. \tag{16}$$

The overbar denotes that the quantities have to be evaluated in the homogeneously strained state of the lattice. δ_{jk} is the Kronecker delta symbol and ηs are the Lagrangian strains. U is the internal energy of the lattice which is a function of entropy S and Lagrangian strain components η_{ij}. U can be expanded in powers of the strain parameters about the unstrained state as

$$U = U_0 + \frac{1}{2!}\sum_{ijkl} C_{ij,kl}\eta_{ij}\eta_{kl} + \frac{1}{3!}\sum_{ijklmn} C_{ij,kl,mn}\eta_{ij}\eta_{kl}\eta_{mn} + \cdots. \tag{17}$$

The linear term in strain is absent because the unstrained state is one where U is a minimum. $C_{ij,kl}$ and $C_{ij,kl,mn}$ are the SOECs and TOECs defined as

$$C_{ij,kl} = \left[\frac{\partial^2 U}{\partial \eta_{ij}\partial \eta_{kl}}\right]_{0,S} \tag{18}$$

$$C_{ij,kl,mn} = \left[\frac{\partial^3 U}{\partial \eta_{ij}\partial \eta_{kl}\partial \eta_{mn}}\right]_{0,S}. \tag{19}$$

Here, the derivatives are to be evaluated at equilibrium configuration and at constant entropy. The elements of the position co-ordinates dx_i are related to da_i by the equation [9]

$$dx_i = \frac{\partial x_i}{\partial a_j}\,da_j = \sum_{j=1}^{3}\left(\delta_{ij} + \varepsilon_{ij}\right)da_j \tag{20}$$

where ε_{ij} are deformation parameters.

Using equations (17) and (20), we obtain $A^S_{jk,pm}$ in equation (15) to the first order in ε_{jk} as

$$A^S_{jk,pm} = C_{pj,mk} + \sum_{rs}\left(C_{pj,mk,rs} + C_{pm,rs}\delta_{jk}\right)\varepsilon_{rs} + \sum_q C_{pq,mk}\varepsilon_{jq}\sum_q C_{pj,mq}\varepsilon_{kq}. \tag{21}$$

The plane wave solution in strained co-ordinates is

$$u_j = u_j^0 \exp i\omega \left(t - \frac{n_i X_i}{W} \right) \tag{22}$$

where W is the actual velocity of the wave in the strained state and ω the frequency of the wave in the strained state. n_i are the direction cosines of wave propagation and t is the time. u_j, the displacements in equation (22), can be expressed as

$$u_j = u_j^0 \exp i\omega \left(t - \frac{N_i a_i}{v} \right) \tag{23}$$

where v is the natural velocity and N_i are the direction cosines of the wave in the unstrained state. Let λ_0 be the wavelength of a given wave in the unstrained state travelling along a direction having direction cosines N_i. After deformation, the wavelength of the elastic wave changes to λ; the wave propagation direction also is changed and the corresponding direction cosines are n_i. The frequency of the wave changes from ω_0 to ω. In the unstrained state, the actual velocity W_0 in the direction N is

$$W_0 = \frac{\omega_0 \lambda_0}{2\pi}. \tag{24}$$

In the strained state, the actual velocity W of the wave is

$$W = \frac{\omega \lambda}{2\pi} \tag{25}$$

and the natural velocity of the wave is

$$v = \frac{\omega \lambda_0}{2\pi}. \tag{26}$$

The ratio ω/ω_0 directly gives v/W_0 without involving the changes in the dimensions.

Substituting u_j from equation (23) in (13), we get

$$\rho_0 v^2 u_j^0 = \sum_{pm} A_{jk,pm}^S N_p N_m u_k^0. \tag{27}$$

The three linear homogeneous equations (27) corresponding to $j = 1, 2, 3$ can be solved only if

$$\text{Det} \left| \rho_0 V^2 \delta_{jk} - \sum_{pm} A_{jk,pm}^S N_p N_m \right| = 0 \tag{28}$$

where

$$D_{jk} = \sum_{pm} A_{jk,pm}^S N_p N_m \tag{29}$$

giving the three natural velocities for any direction of wave propagation. The GPs $\gamma_j'(\theta, \phi)$ and $\gamma_j''(\theta, \phi)$ for the jth acoustic mode propagating in the direction (θ, ϕ) can be defined as

$$\gamma_j'(\theta, \phi) = -\frac{\partial \log \omega(q, j)}{\partial \log A} = -\frac{\partial \log v_j(\theta, \phi)}{\partial \log A} \tag{30}$$

and

$$\gamma_j''(\theta, \phi) = -\frac{\partial \log \omega(q, j)}{\partial \log c} = -\frac{\partial \log v_j(\theta, \phi)}{\partial \log c} \tag{31}$$

where A is the area of the basal plane of the crystal and c is the lattice parameter. $v_j(\theta, \phi)$ is the natural velocity of the jth acoustic mode propagating in the direction (θ, ϕ), referred to the c-axis as the z-axis when the lattice is homogeneously strained by a uniform areal

strain $\varepsilon' = d \log A$ in the plane perpendicular to the c-axis and a uniform longitudinal strain $\varepsilon'' = d \log c$ along the c-axis respectively. To the first order in ε_{ij}, the uniform longitudinal strain ε'' corresponds to ε_{33} and the uniform areal strain ε' is equivalent to $\varepsilon_{11} = \varepsilon_{22} = \frac{1}{2}\varepsilon'$. The other components of ε_{ij} vanish. Expanding equation (29) using (21) for tetragonal class of crystals we get the non-vanishing terms as

$$
\begin{aligned}
D_{xx} = {} & [C_{11}N_x^2 + C_{66}N_y^2 + C_{44}N_z^2] + \frac{\varepsilon'}{2}[(C_{111} + C_{112} + 3C_{11} + C_{12})N_x^2 \\
& + (2C_{166} + 2C_{66} + C_{12} + C_{11})N_y^2 + (C_{155} + C_{144} + 2C_{44} + 2C_{13})N_z^2] \\
& + \varepsilon''[(C_{113} + C_{13})N_x^2 + (C_{366} + C_{13})N_y^2 + (C_{344} + C_{33})N_z^2] \\
D_{yy} = {} & [C_{66}N_x^2 + C_{11}N_y^2 + C_{44}N_z^2] + \frac{\varepsilon'}{2}[(2C_{116} + C_{11} + 2C_{66} + C_{12})N_x^2 \\
& + (C_{112} + C_{111} + C_{12} + 3C_{11})N_y^2 + (C_{144} + C_{155} + 2C_{13} + 2C_{44})N_z^2] \\
& + \varepsilon''[(C_{366} + C_{13})N_x^2 + (C_{113} + C_{13})N_y^2 + (C_{344} + C_{33})N_z^2] \\
D_{zz} = {} & [C_{44}(N_x^2 + N_y^2) + C_{33}N_z^2] + \frac{\varepsilon'}{2}[(C_{155} + C_{144} + C_{11} + C_{12})N_x^2 \\
& + (C_{144} + C_{155} + C_{11} + C_{12})N_y^2 + (2C_{133} + 2C_{13})N_z^2] \\
& + \varepsilon''[(C_{344} + C_{13} + 2C_{44})(N_x^2 + N_y^2) + (C_{333} + 3C_{33})N_z^2] \\
D_{xy} = {} & [(C_{12} + C_{66})N_x N_y] + \left[\frac{\varepsilon'}{2}(2C_{166} + 2C_{112} + 2C_{12} + 2C_{66})N_x N_y\right] \\
& + [\varepsilon''(C_{366} + C_{123})]
\end{aligned}
$$

(32)

where C_{IJ} and C_{IJK} are the SOECs and TOECs in Voigt's notation.

Putting $\rho_0 v^2 = Z$, the determinantal equation (28) can be expanded to give the cubic equation

$$
Z^3 - AZ^2 + BZ - C = 0 \tag{33}
$$

where

$$
\begin{aligned}
A &= \sum_i D_{ii} \\
B &= \begin{vmatrix} D_{xx} & D_{xy} \\ D_{xy} & D_{yy} \end{vmatrix} + \begin{vmatrix} D_{yy} & D_{yz} \\ D_{yz} & D_{zz} \end{vmatrix} + \begin{vmatrix} D_{zz} & D_{xz} \\ D_{xz} & D_{xx} \end{vmatrix} \\
C &= \begin{vmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{xy} & D_{yy} & D_{yz} \\ D_{xz} & D_{yz} & D_{zz} \end{vmatrix}.
\end{aligned}
$$

(34)

The coefficients A, B and C are functions of ε' and ε''. In the unstrained state, i.e. when ε' and ε'' are zero, their values are $\overline{A}$, $\overline{B}$ and $\overline{C}$ and the roots of the equation are $\overline{Z}_1$, $\overline{Z}_2$ and $\overline{Z}_3$. Differentiating equation (33) with respect to ε' and using the definition

$$
\gamma_j'(\theta, \phi) = -\frac{1}{2}\frac{\partial \log Z_j}{\partial \varepsilon'},
$$

we have

$$
\gamma_j'(\theta, \phi) = \frac{-1}{2\overline{Z}_j}\left[\frac{\overline{Z}_j^2\left(\frac{\partial A}{\partial \varepsilon'}\right)_0 - \overline{Z}_j\left(\frac{\partial B}{\partial \varepsilon'}\right)_0 + \left(\frac{\partial C}{\partial \varepsilon'}\right)_0}{3\overline{Z}_j^2 - 2\overline{A}\,\overline{Z}_j + \overline{B}}\right]. \tag{35}
$$

Similarly, differentiating equation (33), with respect to ε'' and using

$$
\gamma_j''(\theta, \phi) = -\frac{1}{2}\frac{\partial \log Z_j}{\partial \varepsilon''},
$$

we have

$$\gamma_j''(\theta, \phi) = \frac{-1}{2\overline{Z}_j} \left[\frac{\overline{Z}_j^2 \left(\frac{\partial A}{\partial \varepsilon''}\right)_0 - \overline{Z}_j \left(\frac{\partial B}{\partial \varepsilon''}\right)_0 + \left(\frac{\partial C}{\partial \varepsilon''}\right)_0}{3\overline{Z}_j^2 - 2\overline{A}\overline{Z}_j + \overline{B}} \right]. \tag{36}$$

The derivatives of A, B and C are to be evaluated at equilibrium configuration. The low temperature limits of the effective Grüneisen functions can be calculated using the individual GPs of the acoustic modes. In tetragonal crystals, the acoustic wave velocities and the GPs are assumed to be depend only on θ and not on the azimuth ϕ, where (θ, ϕ) gives the direction of wave propagation [10]. At very low temperatures where only acoustic modes of long wavelength are predominant the low temperature limits of the Grüneisen function are calculated using

$$\overline{\gamma}_\perp(0) = \left(\int \sum_{j=1}^3 \gamma_j'(\theta) v_j^{-3}(\theta) \, d\Omega \right) \left(\int \sum_{j=1}^3 v_j^{-3}(\theta) \, d\Omega \right)^{-1}$$
$$\overline{\gamma}_{||}(0) = \left(\int \sum_{j=1}^3 \gamma_j''(\theta) v_j^{-3}(\theta) \, d\Omega \right) \left(\int \sum_{j=1}^3 v_j^{-3}(\theta) \, d\Omega \right)^{-1}. \tag{37}$$

Here, $v_j(\theta)$ is the velocity of the long wavelength acoustic modes of polarization index j and Ω is the solid angle. The low temperature limits $\overline{\gamma}_\perp(0)$ and $\overline{\gamma}_{||}(0)$ in equations (37) are evaluated using the GPs of the acoustic modes by numerical integration. Since the solid angle of the cone of semi-vertical angle θ is proportional to $\sin\theta$, the values $\gamma_j' Z_j^{-\frac{3}{2}}$, $\gamma_j'' Z_j^{-\frac{3}{2}}$ and $Z_j^{-\frac{3}{2}}$ at any angle θ are multiplied by $\sin\theta$ and the sum $\sum \gamma_j' Z_j^{-\frac{3}{2}} \sin\theta$ over all θ values is taken to be proportional to $\int \gamma_j' Z_j^{-\frac{3}{2}} \, d\Omega$.

The lattice thermal expansion coefficients at various temperatures can be expressed in terms of the effective Grüneisen functions $\overline{\gamma}_\perp(0)$ and $\overline{\gamma}_{||}(0)$ as follows:

$$V\alpha_\perp = [(S_{11} + S_{12})\overline{\gamma}_\perp(0) + S_{13}\overline{\gamma}_{||}(0)]C_v = \gamma_\perp^{\text{Br}} C_v \chi_{\text{iso}}$$
$$V\alpha_{||} = [2S_{13}\overline{\gamma}_\perp(0) + S_{33}\overline{\gamma}_{||}(0)]C_v = \gamma_{||}^{\text{Br}} C_v \chi_{\text{iso}}. \tag{38}$$

Here, S_{ij} are the elastic compliance coefficients, V is the molar volume, χ_{iso} is the isothermal compressibility and C_v is the specific heat at constant volume. From equation (38), we may calculate the Brugger gammas $\gamma_\perp^{\text{Br}}$ and $\gamma_{||}^{\text{Br}}$ as

$$\gamma_\perp^{\text{Br}} = [(S_{11} + S_{12})\overline{\gamma}_\perp(T) + S_{13}\overline{\gamma}_{||}(T)]\chi_{\text{iso}}^{-1}$$

and

$$\gamma_{||}^{\text{Br}} = [2S_{13}\overline{\gamma}_\perp(T) + S_{33}\overline{\gamma}_{||}(T)]\chi_{\text{iso}}^{-1} \tag{39}$$

where T is the temperature.

At low temperatures, equations (39) yield

$$\gamma_\perp^{\text{Br}}(0) = [(S_{11} + S_{12})\overline{\gamma}_\perp(0) + S_{13}\overline{\gamma}_{||}(0)]\chi_{\text{iso}}^{-1}$$

and

$$\gamma_{||}^{\text{Br}}(0) = [2S_{13}\overline{\gamma}_\perp(0) + S_{33}\overline{\gamma}_{||}(0)]\chi_{\text{iso}}^{-1}. \tag{40}$$

The low temperature limit of the volume Grüneisen function (γ_L) is then obtained by

$$\gamma_L = 2\gamma_\perp^{\text{Br}}(0) + \gamma_{||}^{\text{Br}}(0). \tag{41}$$

2.3. Procedure to obtain the second- and third-order elastic constants

Elastic constants of all orders can be obtained as algebraic functions of potential parameters. Higher-order elastic constants will depend on higher-order coordinate derivative of the potential.

Consider a crystal of large but finite volume V. The crystal is assumed to be free of any forces or stresses in the initial state. So

$$\phi_j(L\mu) = 0$$

for every atom μ in the cell L. The potential energy ϕ of the crystal is expanded in powers of atomic displacements $u_j(L\mu)$ using Taylor series as

$$\phi = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \cdots \tag{42}$$

where ϕ_0 is the static potential energy of the crystal and

$$\phi_1 = \sum_{L\mu} \sum_i \phi_i(L\mu) u_i(L\mu) \tag{43}$$

$$\phi_2 = \frac{1}{2!} \sum_{L\mu} \sum_{L'\mu'} \sum_{ij} \phi_{ji}(L\mu, L'\mu') u_i(L\mu) u_j(L'\mu') \tag{44}$$

and

$$\phi_3 = \frac{1}{3!} \sum_{L\mu} \sum_{L'\mu'} \sum_{L''\mu''} \sum_{ijk} \phi_{ijk}(L\mu, L'\mu', L''\mu'') u_i(L\mu) u_j(L'\mu') u_k(L''\mu''). \tag{45}$$

Here i, j, k refers to Cartesian components.

$$\phi_{ijk}(L\mu, L'\mu', L''\mu'') = [\partial^3\phi/\partial u_i(L\mu)\partial u_j(L'\mu')\partial u_k(L''\mu'')]_0. \tag{46}$$

where L, L', L'' stand for cell indices and μ, μ', μ'' stand for basis indices. The subscript zero in equation (46) means that the derivatives are to be evaluated in the equilibrium configuration. ϕ_{ijk} are both translationally and rotationally invariant [11].

Since ϕ_1 vanishes at equilibrium conditions [9], the contribution to the potential energy per unit cell is approximated only from ϕ_2 and ϕ_3, which are second- and third-order terms respectively. Therefore,

$$\phi = \phi_0 + \phi_2 + \phi_3. \tag{47}$$

In a homogeneous deformation

$$u_j(L\mu) = \sum_p \epsilon_{jp} R_p(L\mu) + w_i(\mu) \tag{48}$$

$\epsilon_{js} = (\partial R'_j/\partial R_s - \delta_{js})$ is the deformation parameter and $w_j(\mu)$ is the jth component of the internal displacement of the sublattice μ. Here R_j is the jth component of the position vector of the atom $(L\mu)$ in the unstrained state and R'_j is the corresponding vector component in the strained state. In order to express the strain energy in a form invariant with respect to rigid rotation the proper parameters to use are [12]

$$\eta_{ij} = \frac{1}{2}\left(\epsilon_{ij} + \epsilon_{ji} + \sum_p \epsilon_{pi}\epsilon_{pj}\right) \tag{49}$$

$$\overline{w}_j(\mu) = w_j(\mu) + \sum_p \epsilon_{pj} w_p(\mu). \tag{50}$$

Let a two-body interaction be considered. The scalar quantity that can be created from $R(L\mu, L'\mu')$ is $R(L\mu, L'\mu') \cdot R(L\mu, L'\mu')$. This quantity is obviously invariant towards a rigid rotation and translation of the lattice. Now if atoms suffer displacements $u(L\mu)$ and

$u(L'\mu')$ from their equilibrium positions, the interatomic vector changes to $R'(L\mu, L'\mu') = R(L\mu, L'\mu') + u(L'\mu') - u(L\mu)$. The two-body potential between this pair of atoms can be written in powers of $|R'(L\mu, L'\mu')|^2 - |R(L\mu, L'\mu')|^2$. Therefore, after substituting equations (43) and (44) in (47) and using the above, equation (47) can be written as

$$\phi = \phi_0 + k_2[R'(L\mu, L'\mu') \cdot R'(L\mu, L'\mu') - R(L\mu, L'\mu') \cdot R(L\mu, L'\mu')]^2$$
$$+ k_3[R'(L\mu, L'\mu') \cdot R'(L\mu, L'\mu') - R(L\mu, L'\mu') \cdot R(L\mu, L'\mu')]^3 \quad (51)$$

where

$$k_2 = \frac{1}{2!} \sum_{L\mu} \sum_{L'\mu'} \sum_{ij} \phi_{ij}(L\mu, L'\mu') \quad (52)$$

$$k_3 = \frac{1}{3!} \sum_{L\mu} \sum_{L'\mu'} \sum_{L''\mu''} \sum_{ijk} \phi_{ijk}(L\mu, L'\mu', L''\mu''). \quad (53)$$

After substituting equation (50) in (48) and neglecting fourth and higher powers we can write the strain energy density $\phi = (1/V_z)(\phi - \phi_0)$ from equation (51) as

$$\phi = \frac{1}{V_z} \left\{ 4k_2 \left[\sum_{L\mu} \sum_{L'\mu'} \sum_{ijkl} R_i(L\mu, L'\mu') R_j(L\mu, L'\mu') R_k(L\mu, L'\mu') R_l(L\mu, L'\mu') \eta_{ij} \eta_{kl} \right. \right.$$

$$+ \sum_{ij} \overline{w}_i(\mu) w_j(\mu) R_i(L\mu, L'\mu') R_j(L\mu, L'\mu')$$

$$+ 2 \sum_{ijk} R_i(L\mu, L'\mu') R_j(L\mu, L'\mu') R_k(L\mu, L'\mu') \overline{w}_k(\mu) \eta_{ij}$$

$$+ \sum_{ijk} R_i(L\mu, L'\mu') R_j(L\mu, L'\mu') \overline{w}_k^2(\mu) \eta_{ij}$$

$$\left. + \sum_{ik} R_i(L\mu, L'\mu') \overline{w}_i(\mu) \overline{w}_k^2(\mu) \right]$$

$$+ 8k_3 \sum_{L\mu} \sum_{L'\mu'} \sum_{ijklmn} \left[R_i(L\mu, L'\mu') R_j(L\mu, L'\mu') R_k(L\mu, L'\mu') \right.$$

$$\times R_l(L\mu, L'\mu') R_m(L\mu, L'\mu') R_n(L\mu, L'\mu') \eta_{ij} \eta_{kl} \eta_{mn}$$

$$+ \sum_{ijk} R_i(L\mu, L'\mu') R_j(L\mu, L'\mu') R_k(L\mu, L'\mu') \overline{w}_i(\mu) \overline{w}_j(\mu) \overline{w}_k(\mu)$$

$$+ 3 \sum_{ijkl} R_i(L\mu, L'\mu') R_j(L\mu, L'\mu') R_k(L\mu, L'\mu') R_l(L\mu, L'\mu')$$

$$\times \overline{w}_i(\mu) \overline{w}_j(\mu) \eta_{kl} + 3 \sum_{ijklm} R_i(L\mu, L'\mu') R_j(L\mu, L'\mu') R_k(L\mu, L'\mu')$$

$$\left. \left. \times R_l(L\mu, L'\mu') R_m(L\mu, L'\mu') \overline{w}_m(\mu) \eta_{ij} \eta_{kl} \right] \right\} \quad (54)$$

where V_z is the volume of the unit cell.

The interlattice displacements $\overline{w}_j(\mu)$ are obtained as a power series in the strains from the condition that the strain energy is a minimum with respect to these displacements. For elastic constants up to third order these displacements need to be known only to the first order in strains [11].

So the components $\overline{w}_j(\mu)$ in the above equation are obtained by imposing the condition that

$$\frac{\partial \phi}{\partial \overline{w}_j(\mu)} = 0. \quad (55)$$

Table 1. The SOECs and TOECs of $Bi_2Sr_2CaCu_2O_8$ (in 10^{11} Pa).

$C_{11} = 1.18$	$C_{44} = 0.29$	$C_{111} = -8.12$	$C_{133} = -3.87$	$C_{344} = -4.37$
$C_{12} = 0.40$	$C_{66} = 0.37$	$C_{112} = -5.26$	$C_{144} = -1.49$	$C_{366} = -1.36$
$C_{13} = 0.26$		$C_{113} = -3.91$	$C_{155} = -4.04$	$C_{456} = -1.38$
$C_{33} = 0.76$		$C_{123} = -1.52$	$C_{166} = -5.11$	$C_{333} = -21.79$

This leads to the equation

$$\overline{w}_j(\mu) = -4k_2 \sum_{ikl} \eta_{il} D_{ikl} M_{jk}^{-1} \tag{56}$$

where M_{jk}^{-1} is the inverse of the 3×3 matrix

$$M_{jk} = \begin{bmatrix} M_{xx} & M_{xy} & M_{xz} \\ M_{yx} & M_{yy} & M_{yz} \\ M_{zx} & M_{zy} & M_{zz} \end{bmatrix} = 4k_2 \sum_{L\mu} \sum_{L'\mu'} \sum_{jk} R_j(L\mu, L'\mu') R_k(L\mu, L'\mu') \tag{57}$$

and the matrix

$$D_{ikl} = \sum_{L\mu} \sum_{L'\mu'} \sum_{ikl} R_i(L\mu, L'\mu') R_k(L\mu, L'\mu') R_l(L\mu, L'\mu'). \tag{58}$$

Substituting $\overline{w}_j(\mu)$ from equation (56) in (54), the lattice sums are taken by making use of the position co-ordinates of nine nearest neighbours of each atom in the unit cell of the Bi 2212 system. Comparing the strain energy density thus obtained from equation (54) with the lattice energy density derived from equation (17) we get the expressions for the SOECs and TOECs of the Bi 2212 system. The SOECs and TOECs thus obtained for Bi 2212 are presented in table 1.

3. Results and discussion

We have used the deformation theory for the evaluation of the SOECs and TOECs. The strain energy density ϕ is estimated by taking into account the interactions of nine nearest neighbours of each atom in the unit cell of $Bi_2Sr_2CaCu_2O_8$. The energy density ϕ thus obtained is compared with the strain-dependent lattice energy derived from the continuum model approximation to get the SOECs and TOECs. The evaluated SOECs and TOECs of $Bi_2Sr_2CaCu_2O_8$ given in table 1 are used to obtain the Grüneisen functions $\gamma_j'(\theta)$ and $\gamma_j''(\theta)$ to the acoustic modes using equations (35) and (36). The results of GPs for the corresponding elastic wave velocities at different angles θ for $Bi_2Sr_2CaCu_2O_8$ are shown in figures 1 and 2.

The low temperature limits $\overline{\gamma}_\perp(0)$ and $\overline{\gamma}_{||}(0)$ are obtained from equations (37) by a numerical integration procedure using the data given in figures 1 and 2. The results of $\overline{\gamma}_\perp(0)$ and $\overline{\gamma}_{||}(0)$ thus obtained for $Bi_2Sr_2CaCu_2O_8$ are given in table 2. The values of S_{ij} and χ_{iso} along with the values of $\overline{\gamma}_\perp(0)$ and $\overline{\gamma}_{||}(0)$ given in table 2 are substituted in equation (40) to calculate the Brugger gammas $\gamma_\perp^{Br}(0)$ and $\gamma_{||}^{Br}(0)$. The values thus obtained for $\gamma_\perp^{Br}(0)$ and $\gamma_{||}^{Br}(0)$ are presented in table 2. The low temperature volume lattice thermal expansion γ_L for $Bi_2Sr_2CaCu_2O_8$ is obtained from equation (41) by substituting the values of $\gamma_\perp^{Br}(0)$ and $\gamma_{||}^{Br}(0)$ from table 2. The value of γ_L thus obtained is given in table 2.

The anisotropy of the longitudinal acoustic branch γ_3'' is most pronounced and it attains a maximum value of 13.6 along the crystal axis and a minimum of 1.33 at $\theta = 0$ to the crystal axis of $Bi_2Sr_2CaCu_2O_8$. The transverse acoustic mode γ_1' attains negative values from $\theta = 25°$ to $55°$. The transverse acoustic branch γ_2' exhibits less anisotropy as the values ranges from 3.52 at angle $\theta = 0$ to 4.38 at angle $\theta = 90°$. The longitudinal acoustic branch γ_3' assumes a
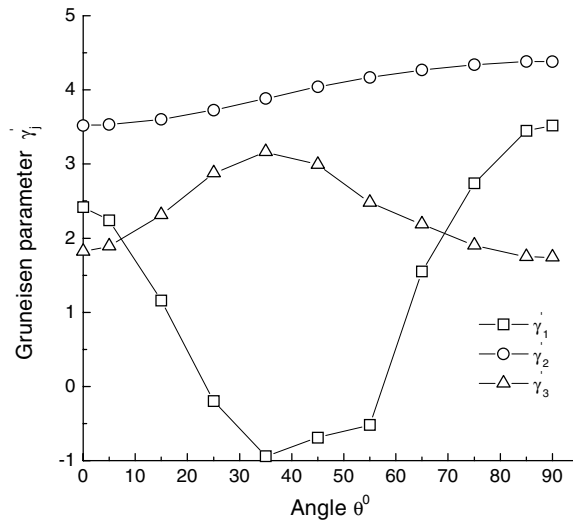
Figure 1. Variation of the generalized GPs γ_j' as a function of angle θ to the c-axis of the $Bi_2Sr_2CaCu_2O_8$ system.
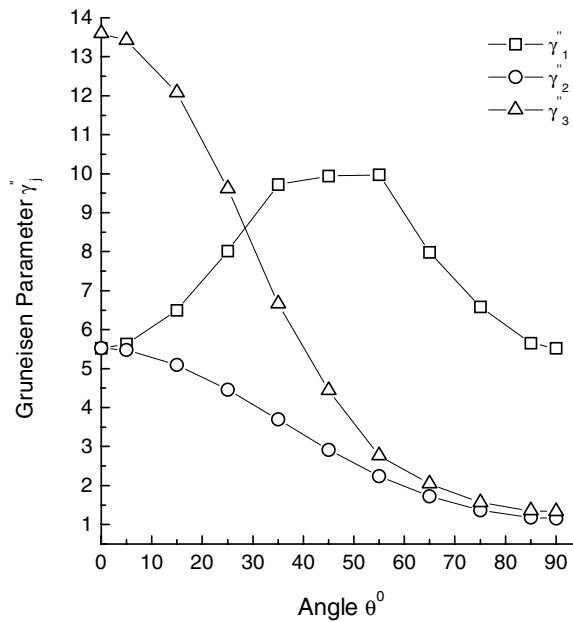
Figure 2. Variation of the generalized GPs γ_j'' as a function of angle θ to the c-axis of the $Bi_2Sr_2CaCu_2O_8$ system.

maximum value 3.16 at $\theta = 35°$ and a minimum of 1.74 at $\theta = 90°$. The transverse acoustic mode γ_1'' has a maximum value 9.97 at $\theta = 55°$ and a minimum of 5.52 both at angle $\theta = 90°$ and $0°$. However, the acoustic mode γ_2'' attains a maximum value of 5.52 at $\theta = 0°$ and steadily decreases to a minimum of 1.16 at $\theta = 90°$ to the c-axis of $Bi_2Sr_2CaCu_2O_8$.

Table 2. The values of the Grüneisen functions $\overline{\gamma}_{\perp}(0)$, $\overline{\gamma}_{\parallel}(0)$, $\gamma_{\perp}^{\mathrm{Br}}(0)$, $\gamma_{\parallel}^{\mathrm{Br}}(0)$ and γ_L for $Bi_2Sr_2CaCu_2O_8$.

				γ_L		
$\overline{\gamma}_{\perp}(0)$	$\overline{\gamma}_{\parallel}(0)$	$\gamma_{\perp}^{\mathrm{Br}}(0)$	$\gamma_{\parallel}^{\mathrm{Br}}(0)$	Present work	Saunders et al [13]	White [14]
2.68	5.5	0.22	3.76	4.2	2.5	2.3

Saunders et al [13] have determined the acoustic mode GPs, from the measured pressure derivatives of elastic constants for $Bi_2Sr_2CaCu_2O_8$ at 290 K, as a function of wave propagation direction. They observed that the vibrational anharmonicity of longitudinal mode propagated along the c-axis is much higher than other mode gammas. This result is consistent with our observation regarding the acoustic mode γ_j''. Saunders et al [13] also calculated the mean acoustic mode GP γ of $Bi_2Sr_2CaCu_2O_8$ by summing over the long wavelength acoustic mode GPs with the same weight for each mode and the value of γ is given in table 2. White [14] estimated the low temperature thermal GP γ, using the equation $\gamma = \beta B^S V / C_p$, where β is the volume thermal expansion coefficient, B^S is the bulk modulus, V is the volume and C_p is the specific heat. The value of γ obtained by White [14] is 2.3 and is also given in table 2. The value of low temperature lattice thermal expansion $\gamma_L = 4.2$ obtained in the present study is higher than the γ values of Saunders et al [13] and White [14]. White [14] did not include the correction for change of bulk modulus B^S or of molar volume V with temperature while calculating γ. This may be the reason for the deviation of his result with the γ_L value obtained in the present study. Wang et al [3] have shown that values of the mean acoustic mode GP γ of ceramic superconducting compounds, determined by ultrasonic measurements, have a linear relationship with the porosity of the samples. This could be a reason for the lower value of $\gamma = 2.5$ obtained by Saunders et al [13] where the porosity correction is not included. For polycrystalline high temperature superconductors, the values of the mean acoustic mode Grüneisen γ are spread over a wide range from 1.5 to 23.7 [13, 15–20]. Hence the value for $\gamma_L = 4.2$ for $Bi_2Sr_2CaCu_2O_8$ obtained in the present study is reasonable.

The GP plays a significant role in studies of contributions of the lattice vibrations to both the superconducting and normal properties of superconductors [3], since it is a measure of vibrational anharmonicity. The values of the low temperature thermal expansion γ_L obtained in the present work for $Bi_2Sr_2CaCu_2O_8$ are found to be greater than those for metals [21,22] as well as for non-metallic compounds [23,24]. However, in fullerenes C_{60}, there are reports [25,26] of a GP value of 9. In certain derivatives of the Bi 2212 system, the effective longitudinal γ varies from 10.3 to 13.9 and the effective shear mode GP assumes a value of 9.4 [27]. The anisotropy of the cuprate superconductors comes mainly from the larger compressibility along the c-axis than that in the ab-plane. The low temperature volume lattice thermal expansion obtained in the present work for $Bi_2Sr_2CaCu_2O_8$ is positive. So we expect volume lattice thermal expansion to be positive down to absolute zero in this compound. At low temperatures, the acoustic wave velocities in high-T_c superconductors increase their value due to the freezing out of optical phonons. This can be a reason for the higher value of the low temperature Grüneisen gammas in $Bi_2Sr_2CaCu_2O_8$.

4. Conclusions

The mode GPs of $Bi_2Sr_2CaCu_2O_8$ for different acoustic wave propagation directions have been calculated. This data give evidence for thermal expansion anisotropy of the material for various acoustic modes. γ_j'', which refers to the change in frequencies due to a uniform

longitudinal strain along the c-axis of Bi 2212 is found to be more anisotropic than γ'_j, which refers to the change in frequencies due to a uniform areal strain perpendicular to the c-axis. Thus the vibrational anharmonicity along the c-axis is more pronounced than that along the ab-plane in $Bi_2Sr_2CaCu_2O_8$, which has been established in various elasticity studies of high-T_c superconductors [28, 29].

The low temperature limit of GPs $\overline{\gamma}_{||}(0)$ along the c-axis is found to be greater than $\overline{\gamma}_\perp(0)$ perpendicular to c-axis. Here it could be concluded that the discrepancy in the vibrational anharmonicity in the CuO_2-plane of $Bi_2Sr_2CaCu_2O_8$ and that along the c-axis persists even at low temperatures.

The low temperature limit of the lattice thermal expansion γ_L is calculated from mode Grüneisen gammas. γ_L is found to have a value $= 4.2$ for $Bi_2Sr_2CaCu_2O_8$. The low temperature limit γ_L is positive and therefore we expect the volume lattice thermal expansion to be positive down to 0 K. At low temperatures, the acoustic wave velocities in high-T_c superconductors increase their value due to the freezing out of optical phonons. This can be a reason for the rather high value of the low temperature limit of Grüneisen gammas in $Bi_2Sr_2CaCu_2O_8$. A study remains to examine any relationship between the size and sign of mode GPs and superconductivity in $Bi_2Sr_2CaCu_2O_8$.

References

[1] Liu H J, Wang Q, Saunders G A, Almond D P, Chapman B and Kitahama K 1995 *Phys. Rev.* B **51** 9167
[2] Hirata T 1998 *Phys. Status Solidi* b **209** 17
[3] Wang Q, Saunders G A, Almond D P, Cankurtaran M and Goretta K C 1995 *Phys. Rev.* B **52** 3711
[4] Hirata T 1999 *Physica* B **263–4** 822
[5] See for a review Schilling J S and Klotz S 1992 *Physical Properties of High Temperature Superconductors* vol 3, ed D M Ginsberg (Singapore: World Scientific)
[6] Jayachandran K P and Menon C S 1999 *J. Phys. Chem. Solids* **60** 267
[7] Jayachandran K P and Menon C S *Phys. Rev.* B submitted
[8] Thurston R N and Brugger K 1964 *Phys. Rev.* A **133** 1604
[9] Murnaghan F D 1951 *Finite Deformation of an Elastic Solid* (New York: Wiley)
[10] Jayachandran K P and Menon C S 1996 *J. Solid State Chem.* **123** 267
[11] Srinivasan R 1966 *Phys. Rev.* **144** 620
[12] Born M and Huang K 1962 *Dynamical Theory of Crystal Lattices* (New York: Oxford University Press)
[13] Saunders G A, Chang Fanggao, Jiaqiang Li, Wang Q, Cankurtaran M, Lambson E F, Ford P J and Almond D P 1994 *Phys. Rev.* B **49** 9862
[14] White G K 1993 *Studies of High Temperature Superconductors* vol 9, ed Anant Narlikar (New York: Science)
[15] Chang Fanggao, Cankurtaran M, Saunders G A, Al-Kheffaji A, Almond D P, Ford P J and Ladds D A 1991 *Phys. Rev.* B **43** 5526
[16] Al-Kheffaji A, Cankurtaran M, Saunders G A, Almond D P, Lambson E F and Draper R C J 1989 *Phil. Mag.* B **59** 487
[17] Cankurtaran M, Saunders G A, Goretta K C and Poeppel R B 1992 *Phys. Rev.* B **46** 1157
[18] Cankurtaran M and Saunders G A 1992 *Supercond. Sci. Technol.* **5** 210
[19] Cankurtaran M, Saunders G A, Balachandran U, Poeppel R B and Goretta K C 1993 *Supercond. Sci. Technol.* **6** 75
[20] Chang Fanggao, Cankurtaran M, Saunders G A, Al-Kheffaji A, Almond D P and Ford P J 1991 *Supercond. Sci. Technol.* **4** 13
[21] Ramji Rao R and Menon C S 1973 *Phys. Rev.* B **7** 644
[22] Menon C S and Ramji Rao R 1973 *J. Phys. Chem. Solids* **34** 77
[23] White G K 1984 *Thermal Expansion* vol 8, ed T A Hahn (New York: Plenum)
[24] White G K and Collins J G 1973 *Proc. R. Soc.* A **333** 237
[25] Girifalco L A 1995 *Phys. Rev.* B **52** 9910
[26] White M A, Meingast, David W I F and Matsuo T 1995 *Solid State Commun.* **94** 481
[27] Dominec J, Plechacek V, Vasek P and Laermans C 1994 *J. Alloys Comp.* **211/212** 273
[28] For see a review Dominec J 1993 *Supercond. Sci. Technol.* **6** 153
[29] Xiang T and Hardy W N 2000 *Phys. Rev.* B **63** 024506