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Theory of internal friction in the high-T_c superconductor YBa$_2$Cu$_3$O$_{7-\delta}$

Du-Ping Yuan† and Chien-Hua Tsai†‡

† Institute of Condensed Matter Physics, Jiao-Tong University, Shanghai 200030, People's Republic of China
‡ Centre of Theoretical Physics, CCAST (World Laboratory), Beijing 100080, People's Republic of China

Abstract. The internal friction in the high-T_c superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ arising from the diffusion of oxygen atoms between the O(1) and O(5) sites under the influence of a periodic mechanical strain is studied microscopically in the linear approximation of the relaxation process. It is analysed for various specific cases in both the tetragonal and the orthorhombic phases as well as in the case of polycrystalline samples.

1. Introduction

Owing to its extraordinarily high critical temperature, the ceramic superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ has excited immense research interest by its discovery at the beginning of 1987 (for review articles, see Wolf and Kresin (1987)). It is now well established that the material undergoes a phase transition from a structure with tetragonal symmetry to a structure with orthorhombic symmetry at about 500 °C (see, e.g., Bell 1988). Superconductivity occurs only in the orthorhombic phase. There are two sets of Cu–O planes in the crystalline structure of YBa$_2$Cu$_3$O$_{7-\delta}$, namely one with barium atoms on both sides of each plane and the other with barium and yttrium atoms separately on the two sides of each plane. In each of the first kind of Cu–O plane the oxygen sites (figure 1) are only partially occupied at a concentration depending upon δ. The structure phase transition is associated with an ordering process of oxygen atoms. In the tetragonal phase the O(1) and O(5) sites (figure 1) have equal occupancies, whereas in the orthorhombic phase the O(1) sites are preferentially occupied forming Cu–O chains along the b axis (see, e.g., Cava *et al* 1987).

Under strained conditions, as illustrated in figure 2, diffusion of oxygen atoms from O(1) to O(5) sites or vice versa will be induced. When a sample is under the action of a time-varying stress generated, for instance, by an acoustic wave, the relaxation process of atomic diffusion causes energy dissipation which attains a maximum at a certain resonanting frequency. Our aim in this article is to study such an effect of internal friction in the superconductor YBa$_2$Cu$_3$O$_{7-\delta}$. We formulate the problem in section 2 and discuss various specific cases in section 3. A theory of linear relaxation processes is presented in the appendix.
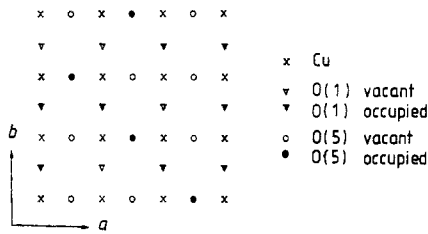
Figure 1. The Cu–O(1), O(5) plane in YBa$_2$Cu$_3$O$_{7-\delta}$.

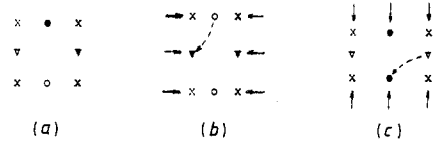Figure 2. Compression-induced hoppings of oxygen atoms between O(1) and O(5) sites.

2. The internal friction in YBa$_2$Cu$_3$O$_{7-\delta}$

We discuss a system which is describable in terms of two independent thermodynamic coordinates x_1 and x_2, with corresponding thermodynamic forces

$$f_i = -\partial\Omega/\partial x_i \qquad i = 1, 2 \tag{1}$$

Ω being the thermodynamic potential. Consider the case in which one of the f-values (say f_1) deviates sinusoidally under external influences at a circular frequency ω from its equilibrium value. Dissipations occur owing to associated irreversible processes inside the system. We assume that the respective relaxation times τ_i, $i = 1, 2$, of f_1 and f_2 towards equilibrium differ by orders of magnitude, such that $\tau_2 \gg \tau_1$. The linear theory of relaxation processes (Cheng 1955) (we refer readers to the appendix, since this paper is difficult to obtain) then implies that the dissipation is given by

$$Q^{-1} = [\omega\tau/(1 + \omega^2\tau^2)](M_{12}M_{21}/M_{11}M_{22}) \tag{2}$$

where ω is the resonating frequency of peak dissipation and the M are the following 'moduli':

$$M_{ij} = -[\partial^2\Omega/(\partial x_i\,\partial x_j)]|_{\text{equilibrium}} \qquad i, j = 1, 2. \tag{3}$$

In the case when f_1 is the mechanical stress, equation (2) gives the internal friction associated with an acoustic wave of frequency ω.

In order to evaluate the internal friction in YBa$_2$Cu$_3$O$_{7-\delta}$ due to diffusion of oxygen atoms between the O(1) and O(5) sites, we need to find the moduli in this case. Let N_1, $\equiv N$ and N_5 denote respectively the number of occupied O(1) and O(5) sites in Cu–O(1), O(5) plane. In terms of the ordering parameter S, they are

$$N_1 \equiv N = cN_{\text{T}}(1 + S)/2 \qquad N_5 = cN_{\text{T}}(1 - S)/2 = cN_{\text{T}} - N \tag{4}$$

where N_{T} is the total number of oxygen sites in a Cu–O(1), O(5) plane, and $c = (1 - \delta)/2$ is the oxygen concentration in this plane. The thermodynamic coordinates in the present case are then the mechanical strain ε and the number N. Since the diffusion of oxygen atoms is much slower than mechanical relaxation, equation (2) is valid.

The problem now is to find the thermodynamic potential Ω of a strained sample. Let P be the nearest-neighbour pairs of oxygen atoms in the Cu–O(1), O(5) plane and w the interaction energy between the two members in each pair, the total energy of the system is, then, when $\varepsilon = 0$,

$$U = U_0 + N\mu_{\text{b}} + (cN_{\text{T}} - N)\mu_{\text{a}} + Pw \tag{5}$$

U_0 being the energy with all O(1) and O(5) sites vacant and μ_{a} and μ_{b} the energies of

interaction of a single O(1) and O(5) atom, respectively, with the lattice while all the other O(1) and O(5) sites vacant. The latter can be obtained by evaluating the following lattice sums over a single two-dimensional Cu lattice in the same plane of the oxygen atom:

$$\mu_a = \sum_{Cu} \left(\frac{\nu}{\gamma_{a-Cu}^m} - \frac{\nu'}{\gamma_{a-Cu}^n} \right)$$

$$\mu_b = \sum_{Cu} \left(\frac{\nu}{\gamma_{b-Cu}^m} - \frac{\nu'}{\gamma_{a-Cu}^n} \right) \tag{6}$$

where, as usual, $m \simeq 12$ and $n \simeq 6$, and we take into account only interactions within a single Cu–O(1), O(5) plane, since YBa$_2$Cu$_3$O$_{7-\delta}$ has a layered structure with weak inter-layer coupling. When the sample is under strain, there is an additional energy

$$\Delta U = Y\varepsilon^2/2 + N(\Delta\mu_b - \Delta\mu_a) + cN\,\Delta\mu_a \tag{7}$$

with Y the appropriate elastic modulus and $\Delta\mu_a$ and $\Delta\mu_b$ the accompanying changes in μ_a and μ_b, respectively, when $\varepsilon = 0$. The thermodynamic potential is thus given by

$$\Omega = -k_B T \ln g + U + \Delta U \tag{8}$$

where, in the quasi-chemical approximation (Toshinosuke and Yotaka 1955),

$$g = [(N_T/2)!(N_T/2)!P_0!(4N - P_0)!(4cN_T - 4N - P_0)!(2N_T - 4cN_T + P_0)!]$$

$$\times [N!(N_T/2 - N)!(cN_T - N)!(N_T/2 - cN_T + N)!P!$$

$$\times (4N - P)!(4cN_T - 4N - P)!(2N_T - 4cN_T + P)!]^{-1} \tag{9}$$

with $P_0 = 8N(cN_T - N)/N_T$. The paring parameter P introduced in equation (5) is fixed by requiring Ω to attain a minimum value $\partial\Omega/\partial P|_{P=\bar{P}} = 0$, implying that

$$\bar{P} = 4c^2(1 - S^2)N_T/[\xi + 2c(1 - \xi) - \eta] \tag{10}$$

$$\xi = \exp(w/k_B T) \tag{11}$$

$$\eta = \{[\xi + 2c(1 - \xi)] - 4c^2(1 - \xi)(1 - S^2)\}^{1/2}. \tag{12}$$

Equation (10) constitutes, in fact, an implicit equation defining $\bar{P}$. The effect of the strain on $\bar{P}$ is also implicitly implied. We have therefore,

$$\Omega(c, N_T, N, \varepsilon, T) = -k_B T \ln g(c, N_T, N, \bar{P}) + N\mu_b(\varepsilon = 0) + (cN_T - N)\mu_a(\varepsilon = 0)$$

$$+ N(\Delta\mu_b - \Delta\mu_a) + cN_T\,\Delta\mu_b + \bar{P}w + Y\varepsilon^2/2. \tag{13}$$

Let ε_a, ε_b and ε_c be the dilatations along the crystal axes a, b and c, respectively, and ψ the deviation from $\pi/2$ of the angle between the crystal axes under shear; one has, for example, in the strained state

$$\mu_b(\varepsilon = 0) = \sum_{\gamma,s = -\infty}^{\infty} \{\nu[r^2a^2 + (s + \tfrac{1}{2})^2b^2]^{-m/2} - \nu[r^2a^2 + (s + \tfrac{1}{2})^2b^2]^{-n/2}\}$$

$$- \sum_{\gamma,s = -\infty}^{\infty} \{m\nu[r^2a^2 + (s + \tfrac{1}{2})^2b^2]^{-(m+2)/2} - n\nu'[r^2a^2 + (s + \tfrac{1}{2})^2b^2]^{-(n+2)/2}\}$$

$$\times [r^2a^2\varepsilon_a + (s + \tfrac{1}{2})^2b^2\varepsilon_b + r(s + \tfrac{1}{2})ab\psi]$$

so that

$$\Delta\mu_b - \Delta\mu_a = \sum_{\gamma,s=-\infty}^{\infty} \{(A_{\gamma s} - A'_{\gamma s})[(r + \tfrac{1}{2})^2 a^2 \varepsilon_a + s^2 b^2 \varepsilon_b + (r + \tfrac{1}{2})sab\psi]$$

$$- (B_{\gamma s} - B'_{\gamma s})[r^2 a^2 \varepsilon_a + (s + \tfrac{1}{2})^2 b^2 \varepsilon_b + r(s + \tfrac{1}{2})ab\psi]\} \qquad (14)$$

where

$$A_{\gamma s} = m\nu[(r + \tfrac{1}{2})^2 a^2 + s^2 b^2]^{-(m+2)/2} \qquad B_{\gamma s} = m\nu[r^2 a^2 + (s + \tfrac{1}{2})^2 b^2]^{-(m+2)/2}$$

$$A'_{\gamma s} = n\nu'[(r + \tfrac{1}{2})^2 a^2 + s^2 b^2]^{-(n+2)/2} \qquad B'_{\gamma s} = n\nu'[r^2 a^2 + (s + \tfrac{1}{2})^2 b^2]^{-(n+2)/2}.$$

$$(15)$$

We are thus provided with everything necessary to evaluate the internal friction.

Basically, to determine the oxygen site energies μ_a and μ_b, one needs to resort to band calculations. Once μ_a and μ_b have been found as functions of parameters of the two-dimensional Cu lattice, $\Delta\mu_b - \Delta\mu_a$ results immediately by direct differentiation. Here we adopt, however, an alternative phenomenological description by considering μ_a and μ_b to result from an equivalent lattice sum of interactions between an O atom and the Cu atoms, the latter being described by means of Lenard–Jones-like potentials as in equation (6).

3. Discussion of specific cases

Since our relevant thermodynamic coordinates are ε and N, the 'moduli' which we need are

$$M_{\varepsilon\varepsilon} = -\partial^2\Omega/\partial\varepsilon^2 \qquad M_{\varepsilon N} = M_{N\varepsilon} = -\partial^2\Omega/(\partial\varepsilon\,\partial N) \qquad M_{NN} = -\partial^2\Omega/\partial N^2. \qquad (16)$$

It follows immediately that

$$M_{\varepsilon\varepsilon} = -Y \qquad (17)$$

$$M_{NN} = -(4k_B T/N_T)[3(cS^2 + c - 1)/c(1 - S^2)][(1 - c^2) - c^2 S^2] + F_1 + F_2 + F_3$$

$$+ F_4\{w/k_B T - \ln[4c^2(1 - S^2) - 4c\zeta + 2\zeta]/[4c^2(1 - S^2) - 4c\zeta + \zeta^2]\}]$$

$$(18)$$

where

$$F_1 = 16S^2[(1 - 2c)\zeta + 4c^2(1 - S^2)][2c^2(1 - \xi)(1 - S^2)$$

$$- \zeta\eta]^2/(1 - S^2)[(1 - 2c)\zeta + 2c^2(1 - S^2)]\zeta^3\eta^2$$

$$F_2 = 2[\zeta^2\eta - 8c^3 S(1 - S^2)(1 - \xi) + 4cS\zeta\eta]^2/c(1 + S)[\zeta - 2c(1 - S)]\zeta^3\eta^2 \qquad (18')$$

$$F_3 = 2[\zeta^2\eta + 8c^3 S(1 - S^2)(1 - \xi) - 4cS\zeta\eta]^2/c(1 - S)[\zeta - 2c(1 + S)]\zeta^3\eta^2$$

$$F_4 = (8/\zeta^3\eta^3)[2c^2(1 - \xi)(1 - S^2)\zeta\eta^2 - \zeta^2\eta^3 + 8c^4(1 - \xi)^2 S^2(1 - S^2)(2\eta - \zeta)]$$

with

$$\zeta = \xi + 2c(1 - \xi) - \eta. \qquad (19)$$

For the evaluation of $M_{\varepsilon N}$, we need to discuss separately the specific cases.

3.1. Orthorhombic phase

Consider first the case of a sample in the orthorhombic phase. The O(1) and O(5) sites are unequally occupied, so that $S \neq 0$.

When the acoustic stress is a tension along the a axis,

$$\varepsilon_a = \varepsilon \qquad \varepsilon_b = [(C_{13}C_{23} - C_{12}C_{33})/(C_{22}C_{33} - C_{23}^2)]\varepsilon$$

$$\varepsilon_c = [(C_{12}C_{23} - C_{13}C_{22})/(C_{22}C_{33} - C_{23}^2)]\varepsilon \qquad \psi = 0 \tag{20}$$

$C_{\alpha\beta}$, $\alpha, \beta = 1, \ldots, 6$ being the components of the elastic modulus tensor. Accordingly,

$$M_{\varepsilon\varepsilon} = -C_{11} - (2C_{12}C_{23}C_{13} - C_{12}^2C_{33} - C_{13}^2C_{22})/(C_{22}C_{33} - C_{23}^2)$$

$$M_{\varepsilon N} = -\frac{C_{13}C_{23} - C_{12}C_{33}}{C_{22}C_{33} - C_{23}^2}\, b^2 \sum_{\gamma,s}[(A_{\gamma s} - A'_{\gamma s})s^2 - (B_{\gamma s} - B'_{\gamma s})(s + \tfrac{1}{2})^2] \tag{21}$$

$$- a^2 \sum_{\gamma,s}[(A_{\gamma s} - A'_{\gamma s})(r + \tfrac{1}{2})^2 - (B_{\gamma s} - B'_{\gamma s})r^2]. \tag{22}$$

We remark that, since ε is assumed to originate only from the acoustic wave, the indirect contribution to $M_{\varepsilon N}$ through the implicit dependence of $\bar{P}$ on ε vanishes when we evaluate

$$M_{\varepsilon N} = -[\partial^2 \Omega/(\partial \varepsilon\, \partial N)]|_{\text{equilibrium}}.$$

When the acoustic stress is a tension along the b axis,

$$\varepsilon_a = [(C_{13}C_{23} - C_{12}C_{33})/(C_{11}C_{33} - C_{13}^2)]\varepsilon \qquad \varepsilon_b = \varepsilon$$

$$\varepsilon_c = [(C_{12}C_{13} - C_{11}C_{23})/(C_{11}C_{33} - C_{13}^2)]\varepsilon \qquad \psi = 0. \tag{23}$$

In this case,

$$M_{\varepsilon\varepsilon} = -C_{22} - (2C_{12}C_{13}C_{23} - C_{12}^2C_{33} - C_{11}C_{23}^2)/(C_{11}C_{33} - C_{13}^2) \tag{24}$$

$$M_{\varepsilon N} = -b^2 \sum_{\gamma,s}[(A_{\gamma s} - A'_{\gamma s})s^2 - (B_{\gamma s} - B'_{\gamma s})(s + \tfrac{1}{2})^2]$$

$$- \frac{C_{13}C_{33} - C_{12}C_{33}}{C_{11}C_{33} - C_{13}^2}\, a^2 \sum_{\gamma,s}[(A_{\gamma s} - A'_{\gamma s})(r + \tfrac{1}{2})^2 - (B_{\gamma s} - B'_{\gamma s})r^2]. \tag{25}$$

When the acoustic stress is a tension along the c axis,

$$\varepsilon_a = [(C_{12}C_{23} - C_{13}C_{22})/(C_{11}C_{22} - C_{12}^2)]\varepsilon$$

$$\varepsilon_b = [(C_{12}C_{13} - C_{11}C_{23})/(C_{11}C_{22} - C_{12}^2)]\varepsilon \qquad \varepsilon_c = \varepsilon \qquad \psi = 0 \tag{26}$$

and

$$M_{\varepsilon\varepsilon} = -C_{33} - (2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2)/(C_{11}C_{22} - C_{12}^2) \tag{27}$$

$$M_{\varepsilon N} = -\frac{C_{12}C_{13} - C_{11}C_{23}}{C_{11}C_{22} - C_{12}^2}\, b^2 \sum_{\gamma,s}[(A_{\gamma s} - A'_{\gamma s})s^2 - (B_{\gamma s} - B'_{\gamma s})(s + \tfrac{1}{2})^2]$$

$$- \frac{C_{12}C_{23} - C_{13}C_{22}}{C_{11}C_{22} - C_{12}^2}\, a^2 \sum_{\gamma,s}[(A_{\gamma s} - A'_{\gamma s})(r + \tfrac{1}{2})^2 - (B_{\gamma s} - B'_{\gamma s})r^2]. \tag{28}$$

When the stress is a shear in the ac or bc plane,

$$\varepsilon_a = \varepsilon_b = \varepsilon_c = 0 \qquad \psi = \varepsilon_{ac}\ \text{or}\ \varepsilon_{bc}. \tag{29}$$

Hence

$$M_{\varepsilon\varepsilon}\,(\psi = \varepsilon_{ac}) = -C_{55} \qquad \text{or}\ M_{\varepsilon\varepsilon}(\psi = \varepsilon_{bc}) = -C_{44} \tag{30}$$

and, in either case,

$$M_{\varepsilon N} = -ab \sum_{\gamma,s} [(A_{\gamma s} - A'_{\gamma s})(r + \tfrac{1}{2})s - (B_{\gamma s} - B'_{\gamma s})(s + \tfrac{1}{2})r]. \tag{31}$$

When the stress is a shear in the *ab* plane, $M_{\varepsilon N} = 0$, where the change in *w* has been included in the appropriate elastic modulus.

3.2. Tetragonal phase

Next, in a case of a sample in the tetragonal phase, the O(1) and O(5) sites are equally occupied, so that $S = 0$. Furthermore, in the tetragonal phase,

$$a = b \qquad C_{11} = C_{22} \qquad C_{13} = C_{23}. \tag{32}$$

It follows that $A_{\gamma s} = B_{\gamma s}$, $A'_{\gamma s} = B'_{\gamma s}$. Equation (18) reduces to

$$M_{NN} = -(4k_B T/N_T)[\![(8/\zeta^2 \eta)[2c^2(1 - \xi) - \zeta\eta]\{w/k_B T$$
$$+ \ln(4c^2 - 4c\zeta + 2\zeta)/(4c^2 - 4c\zeta + \zeta^2)]\} + 4\zeta/c(\zeta - 2c) - 3/c(1 - c)]\!]. \tag{33}$$

When the stress is a tension along either the *a* or the *b* axis, we have

$$M_{\varepsilon\varepsilon} = -C_{11} - (2C_{12}C_{13}^2 - C_{12}^2 C_{33} - C_{13}^2 C_{11})/(C_{11}C_{23} - C_{13}^2) \tag{34}$$

$$M_{\varepsilon N} = -\frac{C_{11}C_{33} + C_{12}C_{33} - 2C_{13}^2}{C_{11}C_{33} - C_{13}^2} a^2 \sum_{\gamma,s} (A_{\gamma s} - A'_{\gamma s})[r^2 - (s + \tfrac{1}{2})^2]. \tag{35}$$

From equations (28) and (31), we conclude that, when the stress is either a tension along the *c* axis or a shear in the *ac* or *bc* plane, $M_{\varepsilon N} = 0$, and no internal friction exists. This, of course, is trivial physically.

3.3. Polycrystalline sample

Let us now discuss lastly the case of a polycrystalline sample. In this case we need to average over crystal orientations. When a single microcrystal experiences a stress in the direction which forms a polar angle θ with the *c* axis and an azimuthal angle φ with the *a* axis,

$$\varepsilon_a = (D_{11} \sin \theta \cos \varphi + D_{12} \sin \theta \sin \varphi + D_{13} \cos \theta)\sigma$$
$$\varepsilon_b = (D_{21} \sin \theta \cos \varphi + D_{22} \sin \theta \sin \varphi + D_{23} \cos \theta)\sigma$$
$$\varepsilon_c = (D_{31} \sin \theta \cos \varphi + D_{32} \sin \theta \sin \varphi + D_{33} \cos \theta)\sigma$$
$$\varepsilon_{bc} = \kappa_{bc}D_{44}(\sin \theta \sin \varphi + \cos \theta)\sigma \tag{36}$$
$$\varepsilon_{ca} = \kappa_{ac}D_{55}(\sin \theta \cos \varphi + \cos \theta)\sigma$$
$$\varepsilon_{ab} = \kappa_{ab}D_{66} \sin \theta(\cos \varphi + \sin \varphi)\sigma$$

where $(D_{\alpha\beta}) = (C_{\alpha\beta})^{-1}$ and the κ-values are constants that measure the degree of transmitting σ into shearing stresses. They depend upon the surface conditions of the microcrystal. In this case, one does not have a single principal strain ε, and we need to change our choice of variables to σ and *N*. The thermodynamic potential is accordingly considered as $\Omega = \Omega(c, N_T, N, \sigma, T)$ with σ replacing ε. It can be verified by following the formalism in the appendix that this change in variable does not affect the basic formula, equation (2), where we now understand that $x_1 = \sigma$ and $x_2 = N$.

The elastic energy of the system under the action of the stress is

$$W = \tfrac{1}{2} \hat{\Sigma} \hat{D}^T \hat{\Sigma}^T \tag{37}$$

where $\hat{\Sigma}$ is the one-row matrix

$$\hat{\Sigma} = (\varepsilon_a, \varepsilon_b, \varepsilon_c, \varepsilon_{bc}, \varepsilon_{ca}, \varepsilon_{ab}) \tag{38}$$

$\hat{D}$ denotes the matrix of tensor D and the superscript T implies the transposed matrix. Thus

$$M_{\sigma\sigma} = -(\partial^2 \Omega / \partial \sigma^2)|_{\sigma=0} = -\hat{A}\,\hat{D}\,\hat{A}^T \tag{39}$$

where

$$\hat{A} = [\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta, \kappa(\sin\theta\sin\varphi + \cos\theta),$$

$$\kappa(\sin\theta\cos\varphi + \cos\theta), \kappa\sin\theta\,(\sin\varphi + \cos\varphi)]. \tag{40}$$

Substitution of equation (37) with $\psi = \varepsilon_{bc} + \varepsilon_{ac}$ in equation (14) yields $\Delta\mu_b - \Delta\mu_a$ as a function of σ, so that

$$M_{\sigma N} = -[\Delta\mu_b(\sigma) - \Delta\mu_a(\sigma)]/\sigma. \tag{41}$$

Finally, an average over the angles θ and φ gives us the internal friction of a polycrystalline sample:

$$Q^{-1} = \frac{\omega\tau}{1 + \omega^2\tau^2} \frac{1}{4\pi M_{NN}} \int_0^\pi \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\varphi \, \frac{M_{\sigma N}^2(\theta, \varphi)}{M_{\sigma\sigma}(\theta\varphi)}. \tag{42}$$

We remark that, in the case of polycrystalline samples, the internal friction discussed here is, quite possibly, mixed and being masked by friction due to other causes such as grain boundaries.

It is interesting to see, by the above analysis, that the internal friction due to diffusion of oxygen atoms between O(1) and O(5) sites depends strongly upon the crystal phase of the sample and the nature of the strain impelled in the material by the acoustic wave, in particular, in the case of single-crystal samples. One would certainly like to see a comparison with measurements. A number of experimental studies do exist (Esquinazi *et al* 1988, Izbizky *et al* 1988, Cannelli *et al* 1988, Mizubayashi *et al* 1988, Duran *et al* 1988). However, there is still a lack of measurements on well defined single crystals. On the other hand, owing to lack of knowledge of material parameters, for instance, the elastic modulus tensor, the parameters ν, ν', m, n in equation (6), and the pair interaction energy w introduced in equation (5), we are still unable to produce concrete theoretical curves which can be checked by experiments. Therefore, we have provided in this article only formal results and regretfully can only wait to see what an evaluation and comparison with measurements shows as soon as possible in the future.

Appendix. Linear theory of relaxation processes (Cheng 1955)

Consider a system whose equilibrium states are describable in terms of a collection of thermodynamic coordinates x_α, $\alpha = 1, \ldots, n$. We need to study the relaxation of the corresponding conjugate forces

$$f_\alpha = -\partial\Omega/\partial x_\alpha \qquad \alpha = 1, \ldots, n \tag{A1}$$

following variations in x_α. A continuous change in x_α can be considered as a series of discontinuous sudden jumps at successive time instants. Hence we need first to describe the relaxation of f_α following a sudden jump in x_α from x_α^i to $x_\alpha^f = x_\alpha^i + \Delta x_\alpha$.

The response of the f_α-values consists of two parts: an instantaneous change from f_α^i to f_α^s

$$f_\alpha^s - f_\alpha^i = \sum_\beta M_{\alpha\beta}^I \, \Delta x_\beta \tag{A2}$$

followed by a relaxation towards a final equilibrium state specified by (x_α^f, f_α^f):

$$f_\alpha^f = -(\partial\Omega/\partial x_\alpha)_{x_\alpha = x_\alpha^f}. \tag{A3}$$

The latter variation in f_α is determined by the relaxation equations

$$\frac{\mathrm{d}}{\mathrm{d}t}(f_\alpha - f_\alpha^f) = \frac{\mathrm{d}}{\mathrm{d}t}(\Delta f_\alpha) = \sum_\beta T_{\alpha\beta} \, \Delta f_\beta \tag{A4}$$

$T_{\alpha\beta}$ being the elements of the inverse relaxation time matrix.

Starting from the initial equilibrium state (x_α^i, f_α^i), the final state (x_α^f, f_α^f) can certainly be reached through an alternative quasi-static process; hence

$$f_\alpha^f - f_\alpha^i = \sum_\beta M_{\alpha\beta}^s \, \Delta x_\beta \tag{A5}$$

where

$$M_{\alpha\beta}^s = \partial f_\alpha/\partial x_\beta = -\partial^2\Omega/(\partial x_\alpha \, \partial x_\beta). \tag{A6}$$

Combining equations (A2) and (A5), we have

$$\Delta f_\alpha^0 \equiv f_\alpha^s - f_\alpha^f = \sum_\beta (M_{\alpha\beta}^I - M_{\alpha\beta}^s) \, \Delta x_\beta = \sum_\beta m_{\alpha\beta} \, \Delta x_\beta. \tag{A7}$$

Δf_α^0 (or f_α^s) defines the initial value of Δf_α (or f_α) at the beginning of the relaxation process:

$$\Delta f_\alpha = \Delta f_\alpha^0 \qquad (\text{or } f_\alpha = f_\alpha^s) \qquad \text{at } t = 0. \tag{A8}$$

The problem now is reduced to finding the solution of equation (A4) under the initial condition (A8). A particular solution of equation (A4) is obviously of the form

$$\Delta f_\alpha = C_\alpha \exp(-t/\tau).$$

Substitution into equation (A4) yields

$$\sum_\beta (T_{\alpha\beta} + \tau^{-1}\delta_{\alpha\beta})C_\beta = 0. \tag{A9}$$

The relaxation times are given by the roots of

$$\det|T_{\alpha\beta} + \tau^{-1}\delta_{\alpha\beta}| = 0. \tag{A10}$$

There are, in general, n different relaxation times, τ_ν, $\nu = 1, \ldots, n$. For each τ_ν, the

corresponding coefficients C_β which will, hereafter, be denoted as $C_{\beta\nu}$, are fixed by equation (A9) to within an arbitrary common multiplier. The latter can be chosen, for instance, as $C_{1\nu}$, so that

$$C_{\beta\nu} = C_{1\nu}D_{\beta\nu} \qquad D_{1\nu} = 1. \tag{A11}$$

The general solution to equation (A4) is then

$$\Delta f_\alpha = \sum_\beta C_{\alpha\beta} \exp\left(-\frac{t}{\tau_\beta}\right) = \sum_\beta C_{1\beta}D_{\alpha\beta} \exp\left(-\frac{t}{\tau_\beta}\right).$$

The n integration constants C are in turn determined by the initial conditions (A8), (A7).

$$\Delta f_\alpha^0 = \sum_\beta C_{1\beta}D_{\alpha\beta} = \sum_\beta m_{\alpha\beta}\,\Delta x_\beta.$$

Multiplying by $(D^{-1})_{\nu\alpha}$ and summing over α, it follows that

$$C_{1\nu} = \sum_\beta C_{1\beta}\delta_{\nu\beta} = \sum_{\alpha\beta} D_{\nu\alpha}^{-1}m_{\alpha\beta}\,\Delta x_\beta.$$

Therefore, the general solution to equation (A4) with the initial condition incorporated

$$\Delta f_\alpha = f_\alpha - f_\alpha^f = \sum_{\beta\delta} D_{\alpha\beta} \exp\left(-\frac{t}{\tau_\beta}\right) D_{\beta\nu}^{-1}m_{\nu\delta}\,\Delta x_\delta$$

$$f_\alpha = f_\alpha^i + \sum_\delta \left(M_{\alpha\delta}^s + \sum_{\beta\nu} D_{\alpha\beta} \exp\left(-\frac{t}{\tau_\beta}\right) D_{\beta\nu}^{-1}m_{\nu\delta}\right)\Delta x_\delta \tag{A12}$$

where in the second line we have used the relation (A5).

It is now apparent that, for continuously time-varying values of $x_\alpha(t)$,

$$f_\alpha = f_\alpha^i + \sum_\delta M_{\alpha\delta}^s x_\delta(t) + \sum_{\beta\nu\delta} D_{\alpha\beta} \int_0^t \exp\left(-\frac{(t-t')}{\tau_\beta}\right) D_{\beta\nu}^{-1}m_{\nu\delta}\frac{\mathrm{d}x_\delta(t')}{\mathrm{d}t'}\,\mathrm{d}t'. \tag{A13}$$

Multiplying both sides by $D_{\sigma\alpha}^{-1}$, summing over α, differentiating the resulting equation with respect to t and eliminating the integral term between (A13) and the derived equation, we have

$$\frac{\mathrm{d}f_\alpha}{\mathrm{d}t} - \sum_\beta T_{\alpha\beta}(f_\beta - f_\beta^i) = \sum_\beta M_{\alpha\beta}^l\frac{\mathrm{d}x_\beta}{\mathrm{d}t} - \sum_{\beta\nu} T_{\alpha\beta}M_{\beta\nu}^s x_\nu(t). \tag{A14}$$

This is, in fact, equation (A13) in differential form.

In a number of important cases ($|T_{\alpha\beta}| \ll |T_{\alpha\alpha}|$ when $\alpha \neq \beta$), $T_{\alpha\beta}$ can then be approximated by

$$T_{\alpha\beta} = -\tau_\alpha^{-1}\delta\alpha\beta \tag{A15}$$

and equation (A14) reduces, in this case, to

$$\frac{\mathrm{d}f_\alpha}{\mathrm{d}t} + \tau_\alpha^{-1}(f_\alpha - f_\alpha^i) = \sum_\beta M_{\alpha\beta}^l\frac{\mathrm{d}x_\beta}{\mathrm{d}t} + \tau_\alpha^{-1}\sum_\beta M_{\alpha\beta}^s x_\beta(t). \tag{A16}$$

In our problem of internal friction arising from diffusion of oxygen atoms between O(1) and O(5) sites, we take as the thermodynamic coordinates the acoustic strain and

the occupation number N of O(1) sites. The corresponding conjugate forces are the stress and the relevant chemical potential. Since in static equilibrium $\sigma^i = 0$,

$$
\begin{aligned}
\mathrm{d}\sigma/\mathrm{d}t + \tau_1^{-1}\sigma &= M_{\varepsilon\varepsilon}^I \, \mathrm{d}\varepsilon/\mathrm{d}t + M_{\varepsilon N}^I \, \mathrm{d}N/\mathrm{d}t + \tau_1^{-1}(M_{\varepsilon\varepsilon}^s\varepsilon + M_{NN}^sN) \\
\mathrm{d}\mu/\mathrm{d}t + \tau_2^{-1}(\mu - \mu^i) &= M_{N\varepsilon}^I \, \mathrm{d}\varepsilon/\mathrm{d}t + M_{NN}^I \, \mathrm{d}N/\mathrm{d}t + \tau_2^{-1}(M_{N\varepsilon}^s\varepsilon + M_{NN}^sN).
\end{aligned}
\tag{A17}
$$

Since the O(1) and O(5) sites are always in chemical equilibrium, $\mathrm{d}\mu/\mathrm{d}t = 0$, $\mu = \mu^i$. Furthermore, $\Delta\varepsilon$ will not cause instantaneous change in N, so that $(\partial N/\partial\varepsilon)_I = 0$, and

$$
\Delta\mu = (\partial\mu/\partial\varepsilon)_I \, \Delta\varepsilon + (\partial\mu/\partial N)_I(\partial N/\partial\varepsilon)_I\Delta\varepsilon = 0
$$

implying that

$$
(\partial\mu/\partial\varepsilon)_I = M_{N\varepsilon}^I = 0.
$$

Lastly, pure mechanical relaxation in σ is a much faster process than the relaxation through atomic diffusion, so that $\tau_1 \ll \tau_2$ or $\tau_1 \to 0$ in equation (A17). With all the above considerations,

$$
\sigma = M_{\varepsilon\varepsilon}^s\varepsilon + M_{\varepsilon N}^sN \qquad M_{NN}^I \, \mathrm{d}N/\mathrm{d}t + \tau_2^{-1}(M_{N\varepsilon}^s\varepsilon + M_{NN}N) = 0.
\tag{A18}
$$

In the case of a sinusoidal variation,

$$
\varepsilon = \varepsilon_0 \exp(-\mathrm{i}\omega t) \qquad N = N_0 \exp(-\mathrm{i}\omega t).
$$

We have from the second equation of (A18) that

$$
N = [\omega\tau/(1 + \omega^2\tau^2)](-\mathrm{i} - 1/\omega\tau)\varepsilon \qquad \tau = \tau_2 M_{NN}^I/M_{NN}^s.
$$

Substitution into the first equation of (A18) yields

$$
\sigma = \{M_{\varepsilon\varepsilon}^s - [1/(1 + \omega^2\tau^2)](M_{\varepsilon N}^s M_{N\varepsilon}/M_{NN}^s)\} - \mathrm{i}[\omega\tau/(1 + \omega^2\tau^2)](M_{N\varepsilon}^s M_{\varepsilon N}^s/M_{NN}^s).
$$

The internal friction is then

$$
Q^{-1} = [1 - \lambda/(1 + \omega^2\tau^2)]^{-1}[\lambda\omega\tau/(1 + \omega^2\tau^2)] \qquad \lambda = M_{\varepsilon N}M_{N\varepsilon}/M_{\varepsilon\varepsilon}M_{NN}.
\tag{A19}
$$

In most cases $Q^{-1} \ll 1$, so that (A19) can be simplified into

$$
Q^{-1} = [\omega\tau/(1 + \omega^2\tau^2)](M_{\varepsilon N}M_{N\varepsilon}/M_{\varepsilon\varepsilon}M_{NN}).
\tag{A20}
$$

In equations (A19) and (A20), τ^{-1} is the experimental resonance frequency. Since only $M_{\alpha\beta}^s$ appear explicitly in these equations, We have deleted the subscript s. The moduli $M_{\alpha\beta}$ are equilibrium thermodynamic quantities defined by equation (A6).

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