Isotope effect and bond-stretching phonon anomaly in high-Tc cuprates

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Abstract

We analyse a model where the anomalies of the bond-stretching LO phonon mode are caused by the coupling to electron dynamic response in the form of a damped oscillator and explore the possibility to reconstruct the spectrum of the latter from the phonon measurements. Preliminary estimates point to its location in the mid infrared region and we show how the required additional information can be extracted from the oxygen isotope effect on the phonon spectrum. The model predicts a significant measurable deviation from the "standard value" of the isotope effect even if the phonon frequency is far below the electron excitation spectrum, provided the latter is strongly incoherent. In this regime, which corresponds to the "mid infrared scenario", the phonon linewidth becomes a sensitive and informative probe of the isotope effect.

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I. INTRODUCTION

One of the reasons the lattice degrees of freedom of cuprate superconductors remain an intensively debated topic on both experimental and theoretical sides is the existence of strong anomalies in some of the phonon spectrum branches and their possible relation to electronic properties \[1, 2, 3, 4\]. In particular, the high frequency, about 80 meV, in-plane bond-stretching LO (BS or the "half-breathing") mode shows large damping, typically several meV, and dispersion dip of about 20% for momenta \(q_x, q_y\) around 0.25 r.l.u. The line broadening and softening increase with hole doping and are sensitive to temperature close to \(T_c\) (see \[5\] for a review; the superconductivity induced anomalies have been discussed in \[6\] for Raman active phonons). The first measurements of the Cu-O BS mode only reported a cosine-like dispersion, which can be understood in terms of conventional calculations. Subsequent measurements, however, pointed to anomalous behavior related to charge inhomogeneities and different interpretations have been given. McQueeney and co-workers \[7\] reported a dynamic doubling of the unit cell in the \(Cu-O\) bond direction and discontinuous phonon dispersion. This has been related to charge stripes with a slower dynamics than the BS phonon frequency and formation of a second phonon mode with a lower frequency. In contrast, Pintschovius and Braden \[8\] have found a smooth BS mode dispersion with an anomalously large slope and broadening around \(q = (0.25, 0, 0)\). Reznik and co-workers \[9\] have studied \(La_{2-x}Ba_xCuO_4\) for \(x \sim 1/8\), where quasistatic stripes exist, and have assigned the observed strong enhancement of the phonon broadening to the sharp softening. D’Astuto et al. \[10\] have carried out high precision X-ray scattering experiments on \(La_{2-x}Sr_xCuO_{4+\delta}\) and concluded that this phonon broadening is caused by intrinsic damping and not to an apparent one due to steep dispersion.

In an earlier paper \[11\], based on a semi-phenomenological model, we have suggested that the anomalously strong softening and broadening of the half-breathing mode could be related to the other anomaly observed in the mid-infrared region of the optical conductivity spectra (MIR) in high-Tc cuprates \[12\]. Apart from making this connection, the way our model addresses the problem of the phonon anomaly is opposite to other approaches: phonon properties are taken as an experimental input which then serves to determine certain properties of the electron excitations. It explains that the measurements taken so far are insufficient and motivates new experiments. Namely, to bridge the existing gap it is
important to know the effect of oxygen isotope substitution upon the phonon spectrum. In what follows we describe the details of this approach which can be directly applied to the analysis of such experiments as well as to test the consistency of the model. We also calculate the expected values of the measurable parameters depending on the frequency of the electronic oscillator which spans the range between MIR and near resonance frequencies. As the BS phonon mode couples to electron density excitation only at $q \neq 0$, it could give a unique opportunity to access the finite momentum evolution of the MIR excitation. On the other side, the present work could stimulate further theoretical investigation of the isotope effect within microscopic models, as for instance on the mechanism of dynamical stripe fluctuations [13]. An interesting possibility is implied by the analysis of site-selective isotope substitution on Raman active phonons [14] when, in contrast to total substitution, a significant change of coupling occurs due to modification of phonon eigenvectors.

II. THE MODEL

Description of the phonon softening relies on the Dyson equation for Green’s function (GF):

$$D(q, \omega) = \frac{2\omega_0}{\omega^2 - \omega_0^2 (1 + \lambda \sin^2(q_x) P(q, \omega))}$$  \hspace{1cm} (1)

where $\lambda$ is the dimensionless coupling constant and $P(q, \omega)$ electron density response function [15]. It is assumed that the part of this response which is relevant for the phonon softening can be considered in the form of a damped oscillator [11]

$$P(q, \omega) = \frac{\eta_q}{\omega^2 - \Omega_q^2 + i\Gamma_q\omega}.$$  \hspace{1cm} (2)

The oscillator is parametrised by the full-width at half-maximum (FWHM) $\Gamma_q$, frequency $\Omega_q$ and oscillator strength $\eta_q$ which have to be determined by analyzing the data on the anomalous BS phonon branch. The experimentally determined values of the linewidth $\tilde{\gamma}_q$ and frequency $\tilde{\omega}_q$ are used to define the standard form of the renormalized phonon GF

$$D^{-1}(q, \omega) \sim \omega^2 - \tilde{\omega}_q^2 + i\tilde{\gamma}_q\tilde{\omega}_q.$$  \hspace{1cm} (3)

In our model the phonon GF is found by solving for the complex poles of (1) $\omega = \omega_q - i\gamma_q$:

$$\omega_0^2 - \omega_q^2 + \gamma_q^2 = \frac{\xi_q\omega_0^2 (\Omega_q^2 - \Gamma_q\gamma_q - \omega_q^2 + \gamma_q^2)}{(\Omega_q^2 - \Gamma_q\gamma_q - \omega_q^2 + \gamma_q^2)^2 + ((\Gamma_q - 2\gamma_q)\omega_q)^2},$$  \hspace{1cm} (4)
\[ 2\gamma_q = \frac{\xi_q \omega_0^2 (\Gamma_q - 2\gamma_q)}{(\Omega_q^2 - \Gamma_q \gamma_q - \omega_0^2 + \gamma_q^2)^2 + ((\Gamma_q - 2\gamma_q) \omega_q)^2}. \]  

Thus, we have the correspondence \( \tilde{\omega}_q = \sqrt{\omega_0^2 - 4\gamma_q^2} \) and \( \tilde{\gamma}_q \tilde{\omega}_q = 2\omega_q \gamma_q \), where the phonon linewidth measured in experiments, \( \tilde{\gamma}_q \), is roughly twice as large as the quantity we use in the calculations, \( \gamma_q \). Still these two equations are insufficient to determine the three parameters of the model, \( \Gamma_q, \Omega_q \) and \( \xi_q = \lambda \eta_q \sin^2 (q_x) \), and we further discuss additional input that could be obtained by varying the frequency of the phonon mode, i.e., by oxygen isotope substitution \( O^{16} \rightarrow O^{18} \).

In fact, there exists a detailed information about the isotope effect (IE) on electronic properties of cuprates, e.g. on \( T_c \) \[16\] and ARPES \[17\], but there have apparently been no attempts to consider the effect such substitution has on the phonon spectra. It is known that the high energy phonon modes, and in particular the one considered here, are dominated by oscillations of oxygen ions. Therefore such experiments should contain important information about both lattice and electronic excitations. The mass dependence of the phonon dispersion has been studied for other materials. For instance in \[18\], where suppressed boron IE on \( T_c \) of the \( MgB_2 \) is related to giant anharmonicity and nonlinear electron-phonon coupling \[19\]. In cuprates anharmonicity could be relevant for apical oxygen \[20\], but for the in plane modes the harmonic approximation was shown to be accurate \[21\] and is therefore adopted for the present model. Moreover, as discussed in \[22\], the width of the half-breathing phonon in cuprates is mainly due to the electron–phonon coupling. In more conventional materials, like \( \alpha - Sn \) \[23\] or \( Ge \) \[24\], the isotopic frequency shifts show a dependence inversely proportional to the square root of the mass and a linewidth inversely proportional to the mass. The error of such measurements is within a fraction of \( cm^{-1} \), the isotopic effect on the linewidth is of the order of a few \( cm^{-1} \) and is due to anharmonicity and isotopic disorder. Since in cuprates the linewidth of the anomalous phonon is an order of magnitude larger, one might expect that also the IE should be enhanced respectively. However, it will be shown below that the answer is not so straightforward.

The quantity \( \xi_q \) in (3) contains the coupling constant, the structure factor of the BS phonon and the spectral weight of the response function (2). It can be trivially eliminated to obtain the first equation of the required set:

\[ \frac{2\gamma_q}{\Gamma_q} = \frac{\omega_0^2 - \omega_q^2 + 3\gamma_q^2}{\Omega_q^2 - (2\omega_q^2 - 2\gamma_q^2 - \omega_0^2)}. \]  

(4)
Eq. (4) gives a simple approximate relation between softening and linewidth, generally a relatively small quantity: \( \gamma_q \sim C_q (\omega_q - \omega_q). \) It is useful when analyzing phonon spectra and making analytic estimates below. The other two equations can be obtained from (3) by calculating the isotope coefficients (IC) according to their usual definitions

\[
\alpha_q = -\frac{d \ln \omega_q}{d \ln M}, \quad \beta_q = -\frac{d \ln \gamma_q}{d \ln M}.
\]

We then get simple but somehow lengthy expressions for the two momentum dependent quantities (below the momentum index is omitted for brevity) that have to be obtained from the proposed experiments:

\[
a = \alpha - 0.5, \quad b = \beta - 1; \quad a = \frac{v_2 u_{12} + v_1 u_{22}}{u_{21} u_{12} + u_{22} u_{11}}, \quad b = \frac{v_2 u_{11} - v_1 u_{21}}{u_{21} u_{12} + u_{22} u_{11}};
\]

where

\[
u_{11} = \frac{(1 - g^2/2 + gy - x^2 - y^2) (4xy)^2}{(g - 2y)^2 (\psi^2 - x^2 + y^2)^2 + (2xy)^2},
\]

\[
u_{12} = \left(1 + \frac{2y}{g - 2y} - \frac{(2y)^3 (1 - gy + x^2 + y^2)}{(g - 2y) ((\psi^2 - x^2 + y^2)^2 + (2xy)^2)}\right),
\]

\[
u_1 = \frac{2y}{(g - 2y)} - \frac{8 (yx)^2 (1 - g^2/2 + gy - x^2 - y^2)}{(g - 2y)^2 ((\psi^2 - x^2 + y^2)^2 + (2xy)^2)} - \frac{(2y)^3 (1 - gy + x^2 + y^2)}{(g - 2y) ((\psi^2 - x^2 + y^2)^2 + (2xy)^2)},
\]

\[
u_{21} = - (2x^2) \left(1 - \frac{2y}{g - 2y}\right) \frac{(1 - g^2/2 + gy - x^2 - y^2)}{(g - 2y) ((\psi^2 - x^2 + y^2)^2 + (2xy)^2)} + \frac{(2y)^2 (2 (1 + gy - x^2 - y^2) - g^2)}{(g - 2y) ((\psi^2 - x^2 + y^2)^2 + (2xy)^2)},
\]

\[
u_{22} = \frac{(2y)^2}{(\psi^2 - x^2 + y^2)} - \frac{(2y)^3 (1 - gy + x^2 + y^2)}{(g - 2y) ((\psi^2 - x^2 + y^2)^2 + (2xy)^2)},
\]

\[
u_2 = \frac{(2y)^3 (1 - gy + x^2 + y^2)}{(g - 2y) ((\psi^2 - x^2 + y^2)^2 + (2xy)^2)} - \frac{3y^2}{(g - 2y) \psi^2 - x^2 + y^2} + \frac{(2y)^2 \psi^2 - x^2 + y^2}{(g - 2y) (\psi^2 - x^2 + y^2)^2 + (2xy)^2} - \frac{1}{2y x^2}.
\]

All the quantities above have been scaled with \( \Omega_q \) (Eq. (4) can be scaled in the same way):

\[
x_q = \frac{\omega_q}{\Omega_q}, \quad y_q = \frac{\gamma_q}{\Omega_q}, \quad \psi_q = \frac{\omega_q}{\Omega_q}, \quad g_q = \frac{\Gamma_q}{\Omega_q}.
\]

The coefficients \( a_q \) and \( b_q \) define the deviations from the reference values which are observed in many materials where such IE has been measured. It is easy to see from (3) that for a large energy separation between the phonon and electron excitations (\( \Omega_q \gg \omega_q \)) one obtains
\( \alpha_q^0 = 0.5 \) and \( \beta_q^0 = 1 \) given that \( \omega_0 \sim M^{-1/2} \): these are the "standard" values for the isotope coefficients (IC). To be mentioned that there is also a purely phononic source of the "normal" value \( \beta_q \), since the linewidth of a phonon in isotopically pure perfect crystal is caused by anharmonicity, which scales as \( \gamma \sim M^{-1} \) at low temperature.

When the energy of electronic excitation approaches the phonon frequency one could expect these deviations should grow in absolute value, and we indeed find this trend in the present model. However, there is a qualitative difference between the linewidth IC \( b_q \) and the dispersion IC, \( a_q \). To clarify this point we show the explicit solution approximated by the first few relevant terms when \( \Omega_q \) and \( \Gamma_q \) are the largest parameters in the problem (actual calculations below were carried out for the complete equations). Consequently, the linewidth \( \gamma_q \) and the two coefficients are small and one can obtain an analytic estimate:

\[
a \simeq y \left( 2g^{-1}x^2 + g + 2g(y/x)^2 - y/x^2 - g^{-1} \right),
\]

\[
b \simeq 2yg \left( 1 - g^{-2} \right) + 2x^2 \left( 1 - g^2/2 \right),
\]

where we have again dropped the \( q \)-index. We see that \( a_q \) vanishes with phonon coupling constant \( \xi_q \) (or with the linewidth \( y_q \), see Eq. (3)), while the coefficient \( b_q \) remains finite and depends on the energy separation between the two coupled excitations. Of course, when \( \xi_q \to 0 \), one cannot measure the mass shift of \( \gamma_q \), instead this relation indicates that for a vanishing linewidth one should expect a saturation of the respective IC at a finite value determined by the ratios like \( x_q \) and \( g_q \), while the dispersion IC is at its "standard" value. Below we will see that there is another important property of the \( b_q \) coefficient, that it can take relatively large values even when the two interacting excitations are far from resonance. Here we note that the sign of the linewidth-derived IC depends on the ratio between \( \Omega_q \) and \( \Gamma_q \).

The set of three equations ((4) and (5) or the approximation (4) and (8)) on the two parameters, \( \Gamma_q \) and \( \Omega_q \), is overcomplete. It therefore gives a possibility to check also the consistency of the model when the respective data become available. We now solve these equations for \( a_q \) and \( b_q \) with \( x_q \) and \( y_q \) as independent variables to demonstrate the correlation between the two sets, but bearing in mind that \( \omega_q \) and \( \gamma_q \) are in fact intrinsically connected through a microscopic mechanism of electron-phonon interaction and it is the IC which are measured in experiments to localize the "physical" point in \((x_q, y_q)\). We use the data obtained from inelastic neutron and X-ray scattering for some representative values of the momentum...
transfer $q$ in $La_{1.85}Sr_{0.15}CuO_4$ (e.g. [2, 3]) and calculate these coefficients together with the corresponding ratio $g_q$ for several assumed values of the electronic frequency $\Omega_q$. At the $\Gamma$-point the frequency of the BS phonon is $\omega_0 = 85.5 \text{ meV}$. For momentum 1) $q_1 = (0.25, 0, 0)$ we have $\tilde{\omega}_{q_1} = 73 \text{ meV}$ and $\tilde{\gamma}_{q_1} = 13 \text{ meV}$; 2) for $q_2 = (0.22, 0, 0)$ we have $\tilde{\omega}_{q_2} = 78 \text{ meV}$ and $\tilde{\gamma}_{q_2} = 9 \text{ meV}$; and 3) for $q_3 = (0.2, 0, 0)$ respectively $\tilde{\omega}_{q_3} = 81 \text{ meV}$ and $\tilde{\gamma}_{q_3} = 6.5 \text{ meV}$. The results are shown in the table.

| $q$ (rlu) | assumed $\Omega$ (meV) | $b$  | $a$  | $g$  |
|-----------|------------------------|------|------|------|
| 0.25      | 400                    | -0.074 | 0.03 | 2.4  |
| 0.25      | 300                    | -0.025 | 0.025 | 1.78 |
| 0.25      | 150                    | 0.33   | -0.017 | 0.79 |
| 0.25      | 100                    | 0.48   | -0.18  | 0.36 |
| 0.22      | 400                    | -0.15  | 0.0278 | 2.7  |
| 0.22      | 300                    | -0.095 | 0.021 | 1.97 |
| 0.22      | 100                    | 1.7    | -0.09  | 0.36 |
| 0.22      | 150                    | 0.37   | -0.002 | 0.82 |
| 0.2       | 300                    | -0.21  | 0.018 | 2.3  |
| 0.2       | 150                    | 0.29   | 0.009 | 0.9  |

The main trends are also illustrated by the Figs. 1 and 2. As mentioned above, not all the values in the $(x, y)$ plane are physically relevant and we have restricted the interval to the neighborhood of the data used in the table. The dispersion IC is relatively small: it

![FIG. 1: Linewidth isotope coefficient $b_q$ calculated for $\Omega_q = 400$ meV in a broader range of $x (= \omega_q/\Omega_q)$ and $y (= \gamma_q/\Omega_q)$.](image)
varies within a few percents around the "standard" value $\alpha = 0.5$ even when $\Omega_q$ is close to
the phonon frequency. Maximum of $a_q$ is reached at $q = 0.25$, the momentum corresponding
to the largest softening and damping. In contrast, the IE on the phonon linewidth ($b_q$) can
be large even when the phonon and electron energy scales are rather distant (20% and
more for the "MIR scenario"), provided the electron excitation is overdamped ($g > 1$). In
this case $b_q$ is negative and $a_q$ is positive. With "standard" $\beta_q = 1$ this means a decrease
below $\beta_q = 0.8$: as mentioned in relation to Eq.(8) this coefficient tends to be negative
when $\Gamma_q > \Omega_q$ and positive otherwise. Interestingly, that the sign of $a_q$ seems to have an

![Graph](image)

FIG. 2: Linewidth to frequency ratio $\Gamma_q/\Omega_q$ of the electronic oscillator (2) associated to the calculation in Fig. 1.

opposite tendency. For a given frequency $\Omega_q$ the largest values of the IC $b_q$ are achieved in
the region with maximal slope of $\omega (\gamma)$ and not where softening (linewidth) has reached
its highest value. This is because unlike $a_q$, which mainly depends on the value of linewidth
(proportional to softening), $b_q$ also strongly depends on the frequency ratio $\omega_q/\Omega_q$.

From the above analysis it can be concluded that both isotope coefficients of the half-
breathing phonon mode contain a reach and complementary information on the electron
excitation responsible for the phonon anomalies. This information can be used to extract
the momentum resolved dynamical electron density response function after a detailed exper-
imental data on the isotope coefficients become available. The response function is expected
to be strongly inhomogeneous and anisotropic following the strong momentum dependence
of the BS phonon softening. In our model it is fully described by the three momentum de-
pendent parameters of the damped oscillator (2). If the value of $b_q$ is found to be negative (or
$\beta_q < 1$), that would be a strong indication in favor of the "MIR scenario" and would allow to
study the finite momentum counterpart of the anomaly known from optical experiments by using the BS phonon as a probe. The accuracy of neutron and X-ray scattering experiments is sufficient to quantify the oxygen isotope effect, although it is "usually" weak. We have, however, shown that for high-Tc cuprates the IE effect on the linewidth of the BS phonon mode can be large and is highly sensitive to the parameters of the electron spectrum.

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