Anomalous oxygen isotope effect on the in-plane FIR conductivity of detwinned YBa$_2$Cu$_{16,18}$O$_{6.9}$.

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Abstract

We observe an anomalous oxygen isotope effect on the a-axis component of the far-infrared electronic response of detwinned YBa$_2$Cu$_{16,18}$O$_{6.9}$. For $^{18}$O a pronounced low-energy electronic mode (LEM) appears around 240 cm$^{-1}$. This a-axis LEM exhibits a clear aging effect, after one year it is shifted to 190 cm$^{-1}$. For $^{16}$O we cannot resolve a corresponding a-axis LEM above 120 cm$^{-1}$. We interpret the LEM in terms of a collective electronic mode that is pinned by ‘isotopic defects’, i.e. by the residual $^{16}$O in the matrix of $^{18}$O.
There is an ongoing debate on whether electron-phonon coupling is at the heart of (at least some of) the unusual electronic properties of the cuprate high-$T_c$ superconductors (HTSC). The fact that the superconducting (SC) transition temperature, $T_c$, exhibits only a very small isotope effect, especially in optimally doped samples with the highest $T_c$ values [1] has led many researchers to neglect electron-phonon coupling. Nevertheless, some recent experiments favor a strong electron-phonon interaction. For example, it has been argued that a kink in the electronic dispersion, as measured by angle-resolved photo-emission (ARPES), arises due to strong electron-phonon interaction [2]. Most notably, it was reported that some electronic properties exhibit a sizeable oxygen isotope effect (OIE). In particular, a very large OIE has been reported for the onset temperature, $T^*$, of the pseudogap phenomenon in underdoped HTSC [3,4] which manifests itself as a suppression of the low-energy spin- and charge excitations already in the normal state (NS). However, the experimental results are still controversial, ranging from only a marginal OIE as seen by nuclear magnetic resonance (NMR) [5,6] to a giant one as obtained by inelastic neutron scattering (INS) utilizing crystal field excitations [3] and by x-ray absorption spectroscopy (XAS) [4]. The significance and the implications of these conflicting results are subject to an ongoing controversial discussion.

The present experiments were motivated by the idea that the huge variation in the OIE may be due to the different time-scales of these techniques, i.e., $10^{-5}$ to $10^{-8}$ s in NMR as compared with $10^{-12}$-$10^{-15}$ in INS and XAS. In that case one might expect that the far-infrared (FIR) electronic response exhibits a sizeable OIE since it involves a time scale of $10^{-12}$-$10^{-14}$ s ($1 \text{ THz} \cong 33 \text{ cm}^{-1}$). So far only few reports exist on the OIE of the IR-electronic response that were obtained on polycrystalline samples or on strongly underdoped twinned crystals [7,8]. These studied do not give a conclusive answer as to the OIE of the FIR electronic response. Accordingly, we performed FIR ellipsometric measurements on detwinned and optimally doped $\text{YBa}_2\text{Cu}_3^{16,18}\text{O}_{6,9}$ crystals with either $^{16}\text{O}$ or $^{18}\text{O}$. To our surprise we find indeed that the a-axis component of the electronic response exhibits sizeable changes upon isotopic substitution. For $^{18}\text{O}$ a pronounced low-energy electronic mode (LEM) occurs around 240 cm$^{-1}$ at 10 K. Moreover, this a-axis LEM exhibits a surprising aging
effect. After one year it has shifted to a lower frequency of $\sim 190 \text{ cm}^{-1}$. In the $^{16}\text{O}$ sample a corresponding LEM is not seen above $120 \text{ cm}^{-1}$. Either it occurs at lower frequency or it is fully absent. We interpret our data in terms of a collective electronic mode that becomes pinned by isotopic defects. The isotopic defects most likely arise due to the few percent of residual $^{16}\text{O}$ in the $^{18}\text{O}$ substituted crystal.

Pairs of flux-grown Y-123 crystals were selected from the same growth batch and annealed in isotopically enriched oxygen under identical conditions to obtain optimally doped crystals (final annealing step for 7 days at $490 \degree \text{C}$ in $\text{O}_2$) [9]. Two pairs were detwinned using a home-built apparatus that allows application of mechanical pressure while the crystal is heated in an enclosed atmosphere of either $^{16}\text{O}_2$ or $^{18}\text{O}_2$ gas. Complete detwinning was confirmed with a polarization microscope and by x-ray diffraction. The sample surfaces were polished to optical grade using diamond paste. The high quality of these surfaces was confirmed by Raman measurements. The crystals exhibit sharp SC transitions at $T_c=92.7\pm0.5 \text{ K}$ for $^{16}\text{O}$ and $92.5\pm0.4 \text{ K}$ for $^{18}\text{O}$ as determined by dc SQUID magnetization.

The ellipsometric measurements were performed at the U4IR beamline at NSLS in Brookhaven, USA and at ANKA in Karlsruhe, Germany [10]. Ellipsometry has the advantage that it measures directly the complex dielectric function without a need for reference measurements or Kramers-Kronig analysis. Details of the techniques are given in [10,11].

Figure 1 displays the spectra for the a-axis component (perpendicular to the CuO chains) of the freshly prepared $^{18}\text{O}$-substituted crystal. Shown are the real parts of (a) the conductivity, $\sigma_{1a}=1/4\pi \cdot \nu \cdot \varepsilon_{2a}$, and (b) the dielectric function, $\varepsilon_{1a}$. The most remarkable feature is a pronounced mode around $240 \text{ cm}^{-1}$ (at $10 \text{ K}$) whose large spectral weight (SW) immediately suggests that it is of electronic origin. The parameters of this low-energy electronic mode (LEM) have been obtained with the function:

$$
\varepsilon(\nu) = \varepsilon_\infty + \frac{S_{\text{LEM}} \cdot \nu^2}{(\nu^2-\nu_{\text{LEM}}^2)} + \frac{\nu_D^2}{\nu^2+i\cdot\nu\cdot\Gamma_{\text{LEM}}} + \sum_{i=1,2} \frac{S_i \cdot \nu^2}{(\nu^2-\nu_i^2)} + i \cdot \nu \cdot \Gamma_i.
$$

The LEM is described by a Lorentz oscillator of strength, $S_{\text{LEM}}$, center frequency, $\nu_{\text{LEM}}$, and width, $\Gamma_{\text{LEM}}$. The remaining part of the electronic response is accounted for by a Drude-term with plasma frequency, $\nu_D = \sqrt{n \cdot e^2 / \pi \cdot m^*}$, carrier density, n, and effective
mass, $m^*$, and by two broad Lorentzians with $\Gamma_{1,2}=\text{const}=1000$ cm$^{-1}$ to reproduce the mid-infrared (MIR) band. For simplicity we did not include the IR active phonons. We obtained $S_{\text{LEM}}=692(8), 596(8)$ and $438(3), \nu_{\text{LEM}}=238.7(0.7), 245(1.5)$ and $285(2.4)$ cm$^{-1}$ and $\Gamma_{\text{LEM}}=134(7), 155(10)$, and $197(6)$ cm$^{-1}$ at 10, 100 and 300 K respectively. The parameters of the Drude-term are $\nu_D=10500(700)$ cm$^{-1}$ (nearly T-independent) and $\Gamma_D=35, 42$ and $98$ cm$^{-1}$ at T=10, 100 and 300 K. The fit functions are shown in the inset of Fig. 1 by the dashed lines. The SW of the LEM amounts to almost 10 % of the total SW of the charge carriers as derived from the unscreened plasma frequency of $\sim 16000$ cm$^{-1}$ (this includes the MIR-band). The a-axis LEM therefore represents a significant fraction of the SW of the charge carriers irrespective of the details of the modelling of the electronic background. The LEM is most pronounced at 10 K but it persists even at room temperature. Notably, its center frequency, $\nu_{\text{LEM}}$, increases as the temperature is raised.

Figure 2a compares the a-axis spectra at 10 K for the $^{18}$O (thick solid line) and the $^{16}$O (thin solid line) samples and highlights the large OIE of the electronic response. Ellipsometric data for a similar $^{16}$O crystal were previously reported [12]. The LEM that dominates the a-axis response for $^{18}$O is probably shifted to much lower frequency for $^{16}$O. Though we cannot exclude the possibility that the LEM is absent for $^{16}$O, we believe that the strong upturn of $\sigma_{1a}(\nu)$ below 250 cm$^{-1}$ is related to a LEM centered around 50-100 cm$^{-1}$ rather than to a Drude peak at zero frequency. A very narrow Drude peak with $\Gamma_D \sim 5 - 30$ cm$^{-1}$ is commonly observed in the microwave spectral range, even at T<<$T_c$ [13], but it cannot account for the broader upturn of $\sigma_{1a}(\nu)$ in the FIR.

The spectra in Figs. 1 and 2 also contain some narrow modes due to IR-active phonons [12]. The apparent red shift of the phonons for $^{18}$O confirms the high degree of isotopic substitution ($\sim 95 \%$). A detailed account of the phonon parameters will be given elsewhere. We only mention the interesting trend concerning the anomalously large SW of the phonons in the vicinity of the LEM. For $^{16}$O we have previously shown that the modes at 190 and 230 cm$^{-1}$, that are located near the upturn of $\sigma_{1a}(\nu, 10 \text{ K})$, acquire an anomalously large SW [12]. For $^{18}$O, where the LEM dominates the electronic response up to 400 cm$^{-1}$, not
only the modes at 180 and 220 cm\(^{-1}\) but also the ones at 275 and 345 cm\(^{-1}\) exhibit an enhanced SW. This signals that the IR-active phonons interact strongly with the LEM but not so much with the remaining part of the electronic background.

After a period of about one year we repeated the ellipsometry measurements on the \(^{18}\)O crystal. Surprisingly, we found that the a-axis LEM had undergone significant changes. As is shown in Fig. 2(b), the center of the LEM has shifted significantly upon aging towards lower frequency. Using eq. (1) we obtain \(S_{\text{LEM}}=920(40), \nu_{\text{LEM}}=185(5)\) cm\(^{-1}\) and \(\Gamma_{\text{LEM}}=120(10)\) cm\(^{-1}\) at 10 K. The Drude-term remains almost unchanged. We repolished and remeasured the crystal and ensured that these changes of the LEM cannot be an artifact due to a poor surface quality. We also reinvestigated the aged \(^{16}\)O crystal (and several others) but did not observe any significant changes of the FIR response. Finally, we repeated the Raman-, x-ray, and SQUID magnetisation measurements on the aged \(^{18}\)O crystal and did not observe any noticeable changes with respect to the freshly prepared state. In particular, the aged \(^{18}\)O crystal was still fully detwinned and (except for the isotopic shift of the phonon modes) similar Raman spectra were obtained for the \(^{16}\)O and \(^{18}\)O crystals.

Finally, Figure 2(c) compares the b-axis spectra of \(\sigma_{1b}(\nu, 10\,\text{K})\) parallel to the 1-d CuO chains for \(^{16}\)O and \(^{18}\)O. In contrast to the a-axis LEM, the b-axis electronic response exhibits no anomalous OIE. A similar b-axis LEM occurs for \(^{16}\)O and \(^{18}\)O, only the narrow peaks due to the IR-active phonons are red shifted for \(^{18}\)O as expected due to the mass change. Using eq. (1) we obtain similar LEM parameters of \(S_{\text{LEM}}=900-1000, \nu_{\text{LEM}}=253-258\) cm\(^{-1}\) and \(\Gamma_{\text{LEM}}=200-240\) cm\(^{-1}\) at 10 K.

The combined set of data, in particular, the observed aging effects suggest that we are not dealing with a true ‘isotope effect’. Instead it appears that defects related to the isotopic replacement are responsible for these marked changes of the FIR electronic response. We analyzed the \(^{18}\)O gas with a mass spectrometer and investigated a pair of \(^{16}\)O and \(^{18}\)O crystals by combined differential thermo-gravimetry and mass-spectrometry analysis. We obtained no evidence for extrinsic impurities that are incorporated during the oxygen exchange for \(^{18}\)O but not for \(^{16}\)O. We also performed a back exchange experiment for twinned Y-123
crystals and found the isotopic effect to be reversible.

Therefore, we consider it most likely that the remaining few percent of $^{16}$O in the $^{18}$O substituted sample act as ‘isotopic defects’ which interact strongly with the electronic excitations. One possibility is that they scatter the free charge carriers within the CuO$_2$ planes and thus lead to localization. Such a scenario was previously used to explain a similar LEM in the a-axis response of Zn-substituted Y-124 [14]. However, strong scattering of the free carriers in the presence of a d-wave order parameter would give rise to a significant reduction of $T_c$ and even more so of the SC condensate density, $n_s$ [15]. Both effects are hardly present in our $^{18}$O crystal with $T_c$=92.5 K and $\lambda_a \approx 1600$-1700 Å as deduced from the zero-frequency limit of $\lambda_a(\nu) = [4 \cdot \pi^2 \cdot \nu^2 \cdot (1 - \varepsilon_1(\nu))]^{-1/2}$ (not shown). A measurable but very small OIE on the magnetic penetration depth was obtained in a previous study [16].

In our opinion the most likely explanation is that the ‘isotopic defects’, i.e. the remaining few percent of $^{16}$O in $^{18}$O, act as pinning centers for a collective electronic mode. A possible candidate is an incommensurate charge density wave (CDW) that involves the flat parts of the Fermi-surface around the so-called ‘hot spots’ close to the X-point of the Brillouin-zone where the nesting condition is most favorable [17]. Corresponding LEM’s frequently occur in low-dimensional materials with a CDW ground state where the phase mode is pinned by lattice defects [18]. In the strong-pinning limit the frequency of the phase mode, $\Omega_o$, is determined by the potential, $V_i$, and concentration, $n_i$, of the pinning centers and by the effective mass $m^*$ of the sliding CDW, $\Omega_o \approx \sqrt{V_i n_i/m^*}$ [18]. In conventional CDW materials $\Omega_o$ is located well below the FIR range. Nevertheless, a pinned CDW in the FIR was recently observed in the ladder-compound Sr$_{14}$Cu$_{24}$O$_{41}$ at 12 cm$^{-1}$ [19] and around 100 cm$^{-1}$ in Ca doped Sr$_6$Ca$_8$Cu$_{24}$O$_{41}$ [20]. Moreover, for the cuprates there exist several reports of a LEM around 100 cm$^{-1}$, especially for samples with defects [14,21–23]. A related model is the stripe (fluctuation) model which assumes that, due to frustration of magnetic exchange, the charges tend to segregate and form quasi one-dimensional hole-rich rivers that are separated by hole-poor stripes where the AF order of the Cu spins is maintained [24]. The existence of a LEM in the FIR has recently been studied theoretically [25] and experimental data on
La$_{2-x}$Sr$_x$CuO$_4$ have been discussed along these lines [26]. The LEM corresponds here to transverse oscillations of the individual stripes. Pinning centers decrease the length of the stripe segments and thereby increase $\nu_{LEM}$ [25].

Unlike defect atoms, the isotopic defects will not affect the static local electronic properties or lattice distortions. Nevertheless, the local difference in the vibrational energy in the vicinity of isotopic defects may well lead to the pinning a collective electronic mode that is coupled to lattice vibrations. Based on theoretical calculations it has even been suggest that an incommensurate CDW becomes stabilized by the lattice vibrations in near optimal doped samples [17]. Accordingly, the higher vibrational energy in the vicinity of $^{16}$O may well give rise to an attractive pinning potential for a CDW or for stripes. An estimate of the pinning potential $V_i$ can be obtained from the red-shift of the highest IR-active phonon mode of $\sim 25$ cm$^{-1} \triangleq 3$ meV. From the purity of the $^{18}$O gas and the shift of the high energy phonon modes in the IR and Raman spectra we deduce a concentration of $^{16}$O ‘isotopic defects’ of about 5 %. Natural oxygen contains only 0.2 % of $^{18}$O. This order of magnitude difference in the concentration of ‘isotopic defects’ thus can account for a three-fold decrease of $\Omega_o$ from $\sim 240$ cm$^{-1}$ for $^{18}$O to $\sim 80$ cm$^{-1}$ for $^{16}$O in agreement with our data. The aging effect of the $^{18}$O crystal can be understood due to a rearrangement (e.g. a clustering) of the $^{16}$O defects within the CuO$_2$ planes. Moreover, the concentration of $^{16}$O defects within the CuO$_2$ planes may have decreased with time due to a gradual exchange of oxygen between the CuO$_2$ planes and the CuO chains whose initial $^{18}$O content likely was somewhat higher.

Based on our present data we cannot easily distinguish between a CDW and the stripe scenario. An important aspect is the anisotropy of the LEM which should be very pronounced for the stripe scenario. The situation is however complicated for Y-123 which in addition contains the one-dimensional CuO chains that are conductive along the $b$-axis direction. It was previously noted that the $b$-axis LEM in Y-123 most likely originates from a CDW within the CuO chains that is pinned by structural defects like oxygen vacancies [12]. The presence of additional strong pinning centers within the CuO chains can indeed explain why the $b$-axis LEM exhibits no significant OIE. Similar experiments of the OIE of
the FIR electronic response in tetragonal systems are in progress in order to the interesting problem of the anisotropy of the OIE of the LEM.

In summary, our ellipsometric data provide compelling evidence for a very unusual oxygen isotope effect on the FIR electronic conductivity along the a-axis. In particular, the observed aging effect suggests that we are not witnessing a true isotope effect but rather the result of ‘isotopic defects’. We suggest that the remaining few percent of $^{16}$O within the $^{18}$O matrix act as pinning centers for a collective electronic mode. Possible candidates are a CDW or stripe fluctuation as suggested in Ref. [24,25]. While we do not arrive at a conclusive answer concerning the nature of the collective mode, our data provide some important insights. First of all, they identify the energy scale that is underlying the OIE on the electronic properties with $\nu_{LEM} \sim 100-250 \text{ cm}^{-1}(\sim 12-30 \text{ meV})$. This resolves previous conflicting data in terms of the energy scales that are probed by the different techniques. Secondly, our data signal that the OIE exhibits a clear aging effect on the time scale of a year. Finally, our new data show that a significant fraction of the electronic spectral weight is contained in a LEM which does not contribute to the SC condensate density. The LEM can be affected in various ways while the impact on the SC state, e.g. on $T_c$ or $n_s$, remains surprisingly small. While this suggests that the LEM may not be of much relevance for the SC pairing interaction, it remains to be seen whether it is closely related to the pseudogap phenomenon which so far has prevented us from obtaining a unique description of the SC state.
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Figure 1: A-axis component of the real part of (a) the conductivity, $\sigma_{1a}(\nu)$, and (b) the dielectric function $\varepsilon_{1a}(\nu)$ of YBa$_2$Cu$_3$O$_{6.9}$ at 300 K (dotted line), 100 K (thin solid line) and 10 K (thick solid line). The insets show the low-frequency range on an enlarged scale. The dashed lines show the fits with the function in eq. (1).

Figure 2: Comparison of $\sigma_1(\nu, 10 \text{ K})$ for the a-axis component of (a) the $^{16}\text{O}$ and the $^{18}\text{O}$ crystals, (b) the $^{18}\text{O}$ crystal in the freshly prepared state and in the aged state ($\sim$1 year), and (c) of the b-axis component parallel to the CuO chains for $^{16}\text{O}$ and the $^{18}\text{O}$.