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The oxygen isotope effect on the infrared photo-induced absorption spectra of La_2CuO_4

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Abstract. The infrared photo-induced spectra of the isotope-substituted stoichiometric La_2CuO_4 samples were studied at $T = 20$ K. Measured spectra were analyzed within the small polaron hopping theory. A small, but detectable shift of the effective phonon frequency on the substitution ^{16}O to ^{18}O is found for the high-energy surface carrier associated band (∼4000 cm^{-1}) and has a value of $\alpha_O = 0.3 \pm 0.2$. The low-energy band (∼1500 cm^{-1}) originating from the bulk carriers doesn't show any difference within experimental error which is fully in agreement with theory predictions. The isotope shifts of the optically active oxygen-related phonon modes are described well by the harmonic approximation.

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1 Introduction

Investigations of the isotope effect in conventional superconductors revealed the important role of the electron-lattice interaction in the mechanism of the superconductivity [1]. Since the discovery of the high-temperature superconductivity in layered cuprates by Bednorz and Müller [2] a large number of isotope effect studies on T_c and other properties have been performed in this class of the compounds [3], with the main focus being on the oxygen isotope effect (OIE). The isotope effect studies revealed behavior which is more complex than in conventional superconductors. For example, the isotope effect was found to be strongly dependent on the level of doping. In spite of the fact that there are still some discussions regarding the reasons for the OIE on T_c and its magnitude [3] it is now clear that the OIE in cuprates is finite and depends systematically on doping and on the substituted site [4].

Infrared spectroscopy has proven to be a powerful tool for the investigations of the layered cuprates either in normal or superconducting state revealing a variety of elementary excitations [5,6]. Recently, there have been reports on the isotope effect on the infrared spectra of underdoped and optimally doped $YBa_2Cu_3O_{6+y}$, and almost zero [7] and anomalously high [8] OIE values were obtained for the different IR spectral features. While the origin of the spectral features studied in those papers is still a matter of debate, the subject of the present paper is the OIE on the extensively studied and uncontroversial photo-induced absorption (PIA) spectrum of stoichiometric La_2CuO_4 [9–14].

Photoexcitation with light frequency larger than the bandgap creates the charges in the conducting CuO_2 planes [13] resulting in photoinduced changes in the infrared spectrum. As it was revealed with IR spectroscopy, photo-doping is essentially the same as chemical doping, with the hole density corresponding to the heavily-underdoped case [11]. Thus, the PIA spectrum of La_2CuO_4 is qualitatively identical to the mid-IR optical conductivity spectrum of slightly oxygen-doped compound [15,16]. It consists of the wide low-energy (LE) and high-energy (HE) features at ∼1100 cm^{-1} and ∼4000 cm^{-1}, respectively, with the LE intensity being strongly temperature dependent. There is much of the experimental evidence for the polaronic origin of the LE feature, namely: (i) it is strongly pronounced at the temperatures below that of the metal-insulator transition for slightly hole-doped compounds [16,17], so it originates from the localized states; (ii) thermodynamic activation energy found from the Hall effect studies ∼280 cm^{-1} [18] is approximately 4 times less than the lowest electronic excitation observed in doped La_2CuO_{4+y} at ∼1100 cm^{-1} [16],

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being fully in agreement with the small adiabatic polaron theory predictions; (iii) with a temperature increase the spectral weight is transferred from LE band to zero-frequency Drude peak characteristic of free carriers [11,16]. As far as the HE feature is concerned, its origin in doped cuprates is still a matter of a discussion. Results of sample annealing have shown [19] that the HE band in the PIA spectra of La_2CuO_4 originates from the holes localized near the surface paramagnetic Cu^{2+} defects forming a kind of magnetically-stabilized polaron, while the LE feature appears to be intrinsic property of the bulk.

The importance of these observations is connected with the nature of the charge carriers in cuprates. Specifically, it has been shown that the same peak(s) remain visible also in doped (superconducting) phase of the cuprates, although it is masked by additional features in the mid- and far-infrared, particularly the "Drude" peak due to free carriers (see e.g. [20]). From the polaron peak it was inferred that polarons are present also in the doped cuprates [12].

In this paper we present the results of the oxygen isotope effect studies on the IR PIA spectrum in stoichiometric La_2CuO_4. We find that a small but detectable OIE is found on the effective phonon frequency for the mid-IR HE PIA band, while no change in the LE feature exceeding the experimental error is observed. It is shown that these findings are consistent with the proposed polaronic nature of the observed PIA spectrum. Oxygen-related optically active phonon modes show the expected frequency shift.

2 Results and discussion

The polycrystalline samples of La_2CuO_4 were prepared by a solid-state reaction using La_2O_3 and CuO of a minimum purity of 99.99%. The respective amounts of the starting reagents were mixed and then calcinated at 950–1150 °C for 80 h in air, with several intermediate grindings. Phase purity of the sample was checked with X-ray diffractometer (SIEMENS D500). The ^{18}O substituted sample was obtained via the oxygen-isotope exchange, which was performed in a closed apparatus under controlled oxygen $^{18}O_2$ pressure of 1.1 bar, at 800 °C for 15 h and cooled with a rate 100 °C/h. A reference ^{16}O-sample was obtained by annealing in the natural oxygen with the condition same as for the ^{18}O-sample. Oxygen isotope enrichment of the sample was determined from the weight increase of the sample after exchange and in situ during the exchange process using mass spectrometry. This was 84 ± 2% the rest being predominately ^{16}O. The samples after the isotope substitution were found to be slightly oxygen-enriched having $T_N \simeq 260$ K including a very small amount of superconducting inclusions with $T_c \simeq 30$ K and Meissner phase volume fraction of about 4×10^{-4}. After annealing at 600 °C for 2 h in a flow of pure Ar (>99.999%) the samples had $T_N = 325$ K and no detectable diamagnetic inclusions.

For PIA measurements the La_2CuO_4 powder was mixed with KBr at the concentration of 0.1–0.2 wt.% and pressed into homogeneous near-transparent pellets. The pellets were mounted on the cold finger of a continuous flow LHe cryostat equipped with KRS-5 windows. The measurements were performed at $T = 20$ K. For the photoexcitation an Ar^+-ion laser was used, the light with $\lambda = 514.5$ nm (2.41 eV) was guided into the cryostat via an optical fiber. The pump fluence did not exceed 50 mW/cm^2. The spectra in the mid-IR (300–3800 cm^{-1}) and near-IR (3800–10 000 cm^{-1}) were measured with the two different spectrometers (Bomem 102 and Bomem 160) and then the mid-IR and near-IR parts of PIA spectrum were matched to each other. Furthermore, the different sample PIA-spectra were normalized to the integral intensity in the range 800–8000 cm^{-1}.

We took special care of the sample grain size, which was found to have a significant effect on the amplitude and shape of the signal. It is well-known that for the samples prepared in the way we used the grain size should be small. Then the sample extinction would be dominated by the absorption of the incorporated compound. We performed the numerical simulations of the PIA spectra measurements using the code of Mishchenko [21] to solve the general scattering problem in Lorenz-Mie approximation for the homogeneous spherical particles. We used the dielectric constant values $\varepsilon(\mathrm{KBr}) = 2.34$, $\varepsilon(La_2CuO_4) = 5$ and maximum estimated relative photoinduced change in the absorption coefficient $\Delta\alpha = 10^{-3}$ at 4000 cm^{-1}. By means of these calculations we were able to set the maximum allowed grain size of ∼0.3 μm [22]. In this case the registered PIA-signal should reproduce the quantitative peculiarities of the absorption spectrum with the possible slight distortion of the high-frequency part which with our values of the signal to noise ratio will presumably be within the experimental error.

In order to fulfill conditions on grain size the ground samples were dispersed by ultrasound in dry isopropanol and the grains of different sizes were extracted by means of successive sedimentation and further characterized with scanning electron or atomic force microscope. The smallest grain sample according to the obtained histogram had a mean grain size of 0.22 μm and a rather narrow (∼0.1 μm wide) size distribution.

The study of the directly measured PIA dynamics at $T = 20$ K of the HE PIA feature (see below) that dominates the spectrum allowed us to find the upper and obviously overestimated limit of the photo-generated charge carriers. In the case of biparticle recombination the steady-state hole concentration is $n_{p,s} = \sqrt{AI_p/W}$, where A is an efficiency of electron-hole pair creation, I_p is a power flux and W is a biparticle recombination rate. Supposing $A = 1$, with a laser power flux of 10 mW/cm^2 (8×10^{16} photons/cm^{2}s) $W \approx 10^{-17}$ s^{-1} and $n_{p,s} \approx 2.1 \times 10^{20}$ cm^{-3}, or ∼0.038 per Cu. The obtained value is in a good agreement with the calculations of Kim et al. who found the lower limit with the power flux of 100 mW/cm^2 to be ∼0.022 per Cu [11]. Both values correspond to a heavily-underdoped La_2CuO_4. The

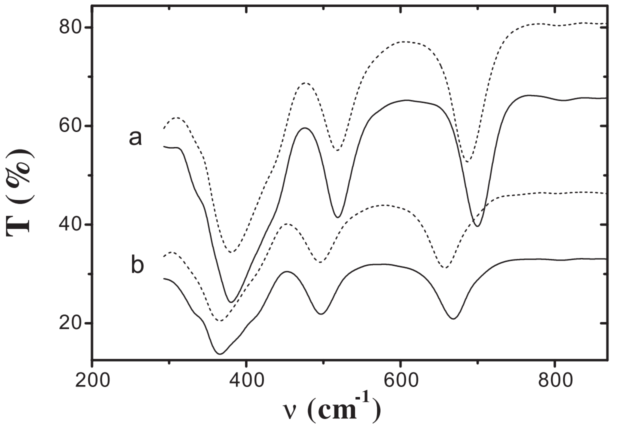

Fig. 1. The transmittance spectrum of La_2CuO_4 samples; a — $La_2Cu^{16}O_4$, b — $La_2Cu^{18}O_4$, solid line — $T = 20$ K, dashed line — $T = 300$ K.

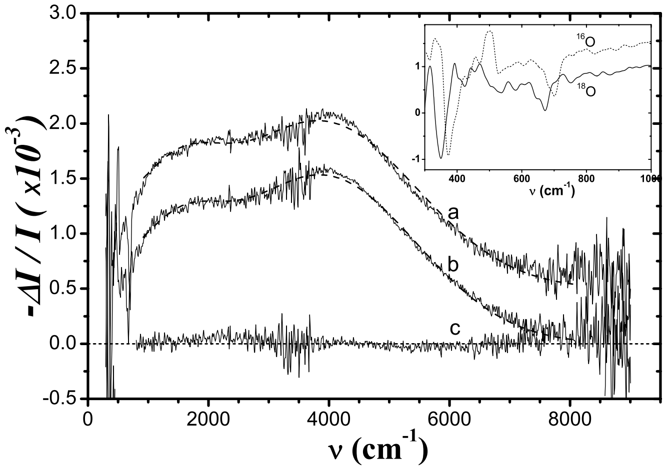

Fig. 2. The normalized PIA spectra of La_2CuO_4 samples; in black: (a) $La_2Cu^{16}O_4$ (shifted); (b) $La_2Cu^{18}O_4$; (c) the difference between (a) and (b). The fits of the spectra using equation (1) are shown by dashed lines. In the inset PIA spectra in the low frequency region are shown in detail.

measurements were performed at $T = 20$ K, well below the insulator-metal transition. So, our experimental conditions of the PIA measurements ensure the polaronic state of the photo-generated charge carriers.

The measured transmission spectra of the $La_2Cu^{16}O_4$ and $La_2Cu^{18}O_4$ samples in the phonon frequency range are presented in Figure 1. The photo-induced absorption spectra are shown in Figure 2 and are characterized quantitatively by the relative change in the transmitted light intensity $-\Delta I/I$ proportional in the limit of weak PIA to the change in the absorption coefficient $\Delta I/I \propto \Delta\alpha$. Possible heating artifacts have been checked and eliminated by a comparison of the transmission spectra measured at different temperatures.

Pronounced changes of both transmission and PIA spectra due to the oxygen isotope substitution are observed in the phonon-frequency region (Fig. 1 and inset of Fig. 2). The phonon absorption line frequencies and the corresponding values characterizing the OIE are shown in Table 1 (signs '+' and '−' near the wavenumbers correspond to photoinduced absorption and bleaching, respectively). In the transmittance spectra, three phonon features are observed, corresponding to in-plane Cu-O bond stretching and bending E_u modes (700/669 cm^{-1} and 383/365 cm^{-1} at 20 K for $^{16}O/^{18}O$ samples, respectively) and out-of-plane oxygen-bending A_{2u} mode (520/497 cm^{-1}) [23–26]. Absorption feature at 383/365 cm^{-1} originates obviously not from a single phonon. In fact, at least two more phonon absorptions have been observed in this spectral region and were assigned to in-plane E_u (400 cm^{-1}) and out-of-plane A_{2u} (340 cm^{-1}) oxygen-bending phonon modes, respectively [23–25]. In the PIA spectra (Fig. 2, inset) two of these modes (700/669 cm^{-1} and 383/365 cm^{-1}) are bleached and two new modes arise as "absorption" (in a good agreement with [9,10,13]). This observation supports the idea that the photo-doping of La_2CuO_4 is very similar to the chemical one as the growth of additional sharp structures in this frequency region has been observed experimentally for $La_{2-x}Sr_xCuO_4$ [27] and La_2CuO_{4+y} [28]. The frequency shifts of all the observed phononic features are described well within the simple harmonic oscillator approximation (compare the data of Table 1 with the calculated for 84% ^{18}O substitution exact value $\alpha_O = 0.464$, where α_O is defined as $\Delta\tilde{\nu}/\tilde{\nu} = -\alpha_O(\Delta m_O/m_O)$). The perfect agreement of the observed frequency shifts of the phonons with the predicted ones shows clearly that the isotope substitution has taken place and its value was estimated well.

Table 1. The frequencies, frequency shifts and oxygen isotope effect on the phonon absorption lines observed in the transmission and photo-induced spectra of La_2CuO_4.

$\tilde{\nu}$, cm^{-1}		T, K	$\Delta\tilde{\nu}$, cm^{-1}	$\delta\tilde{\nu}$, %	α_O
^{16}O	^{18}O				
Transmittance data					
688	657	300	–31	–4.5	0.43
700	669	20	–31	–4.4	0.42
520	497	20, 300	–23	–4.4	0.42
383	365	20, 300	–18	–4.7	0.45
Photo-induced absorption data					
700 (−)	669	20	–30	–4.3	0.42
500 (+)	472	20	–28	–5.6	0.53
456 (+)	435	20	–21	–4.6	0.44
383 (−)	365	20	–20	–5.3	0.45

Turning to the MIR PIA spectra (Fig. 2), we observe a wide feature consisting from two MIR peaks, in agreement with previous works [9,11,12,14]. The two peaks centered at ∼1500 cm^{-1} and ∼4000 cm^{-1} are associated with the bulk and surface carriers, respectively [19]. We see that the shapes of both spectra are almost identical.

It can be easily shown that this observation is consistent with the assignment of the bands to polarons formed by the photo-generated charge carriers. We calculate the expected polaronic PIA spectrum for different isotopic mass using two small-polaron absorption bands of the

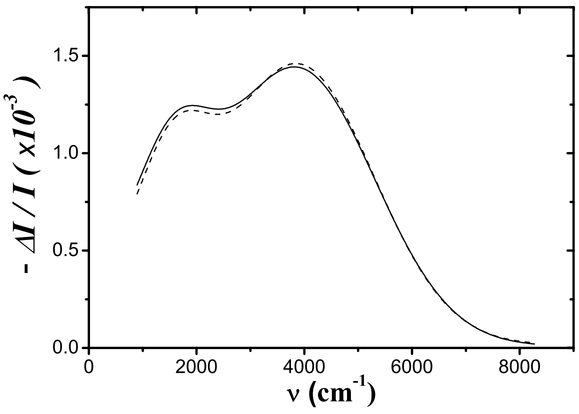

Fig. 3. The fit of the PIA spectrum of $La_2Cu^{16}O_4$ sample with equation (1) (solid line) and predicted by equation (1) spectrum of the oxygen isotope-substituted sample (dashed line).

form [29,30]:

$$\Delta\alpha_i = \frac{A_i}{\omega} \exp\left[-\frac{(2E_{b,i} - \hbar\omega)^2}{\Delta_i^2}\right], \qquad (1)$$

where $\Delta\alpha$ is a photo-induced change of the absorption coefficient, E_b is the polaron binding energy, Δ is expressed as $\Delta = \sqrt{8E_bE_{vib}}$. In the low-temperature limit E_{vib} is just the zero-point vibrational energy $\hbar\omega_{ph}/2$.

In Figure 3, we show the calculated change of the PIA spectrum due to the isotope substitution ^{16}O to ^{18}O. The spectrum calculated for ^{18}O-sample is shown by the dashed line. Using the values of the model parameters obtained from the fit of ^{16}O enriched sample spectrum with equation (1) (find the description of the fitting procedure and parameter values below) and assuming that the effective phonon frequencies $\hbar\omega_{ph,i}$ are defined by the oxygen atom mass, we decrease them by 4.87%: $\hbar\omega_{ph,1} = 484$ cm^{-1} and $\hbar\omega_{ph,2} = 261$ cm^{-1}. The values of $E_{b,i}$ represent the energy position of the polaronic band maxima ($2E_b$). These parameters are not influenced by the isotope substitution and thus remain untouched, while the amplitudes A_i are slightly modified to conserve the integral intensity of PIA spectrum. The resulting difference is indeed subtle and is revealed mainly in the bandwidth values. Moreover, the calculated OIE is the upper limit. The model assumes extreme small polarons in the adiabatic regime, where the phonon frequencies are defined only by the oxygen mass. Departure from this limit can only decrease the OIE, making it even harder to observe.

It was found that the way the spectra are fit was very important. Observed PIA spectra for both $La_2Cu^{16}O_4$ and $La_2Cu^{18}O_4$ samples can be fit with equation (1) remarkably well (Fig. 2). Independent fits of ^{16}O and ^{18}O enriched sample spectra didn't reveal any regular model parameter changes: all three A_i, $\hbar\omega_{ph,i}$ and $E_{b,i}$ differed only slightly. Values of $E_{b,i}$ lied within 20 cm^{-1} which is consistent with the proposed polaronic origin of mid-IR PIA spectra.

Table 2. Parameter values for the fits of photo-induced absorption spectra of oxygen isotope substituted La_2CuO_4 with equation (1).

Parameter	$La_2Cu^{16}O_4$	$La_2Cu^{18}O_4$
A_1, arb.un.	6.31 ± 0.03	6.36 ± 0.03
$E_{b,1}$, cm^{-1}	2211 ± 3[1]	
$\hbar\omega_{ph,1}$, cm^{-1}	509 ± 7	491 ± 6
A_2, arb.un.	1.02 ± 0.03	1.02 ± 0.03
$E_{b,2}$, cm^{-1}	864 ± 6[1]	
$\hbar\omega_{ph,2}$, cm^{-1}	274 ± 12	275 ± 12

[1] These parameters were varied simultaneously for the spectra of $La_2Cu^{16}O_4$ and $La_2Cu^{18}O_4$ samples.

One nevertheless should understand that fitting of the superposition of two wide bands is quite unstable procedure in respect to the small measured signal deviations. Thus, such a deviation can give rise to a slight shift of the band maximum (E_b) and considerable on the scale of predicted effect adjusting of $\hbar\omega_{ph}$. In order to increase the stability of the fitting procedure we've fit simultaneously the spectra of both samples using the same values of $E_{b,i}$ and leaving all the rest parameters varied independently. This approach is physically consistent as regardless of the origin of the PIA bands their maxima should not shift on oxygen isotope substitution. Obtained parameter set is shown in Table 2. As one can see, both LE and HE PIA band intensities as well as $\hbar\omega_{ph,2}$ values are the same within the fit error while $\hbar\omega_{ph,1}$ values are changed by the number exceeding the fit accuracy. The OIE on $\hbar\omega_{ph,1}$ is thus $\alpha_O = 0.3 \pm 0.2$, the value showing that the effective phonon frequency is significantly defined by the oxygen mass.

Another interesting observation is the close value of the effective phonon frequency $\hbar\omega_{ph,1} = 509/491$ cm^{-1} (for HE band) to those of the arising PIA absorption lines. One of those PIA lines thus can originate from the local vibrational mode appearing due to charge localization, which is a well known phenomenon in polaronic materials. Both appearing modes reveal an OIE of $\alpha_O \sim 0.5$ which is within the error bar for α_O obtained from the fit. As far as $\hbar\omega_{ph,2}$ values are concerned, predicted by theory frequency change is ~13 cm^{-1}, which is well within the experimental error.

In conclusion, the oxygen isotope effect on the IR PIA spectrum of the stoichiometric La_2CuO_4 was studied. The measured spectra were analyzed within the small polaron hopping theory for optical conductivity. A small, but detectable shift of the effective phonon frequency on the substitution ^{16}O to ^{18}O was found for the HE PIA band and had a value of $\alpha_O = 0.3 \pm 0.2$; this band originates from the charges localized at the sample surface. The "bulk" polaron LE PIA band doesn't show any difference within experimental error which is fully in agreement with theory predictions. The data and analysis thus show that we cannot dismiss a polaronic origin for the MIR features in cuprates on the basis of the fact that it does not show an OIE.

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