Study of Atomic Motions in EuBa$_2$Cu$_3$O$_{7-\delta}$ by Mössbauer and EXAFS Spectroscopies

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We report the results of $^{151}$Eu Mössbauer and Eu K-edge EXAFS measurements on samples of EuBa$_2$Cu$_3$O$_{7-\delta}$. In particular, the ratios between the Eu Debye–Waller factors along the c and ab-plane directions, were obtained from the Mössbauer spectra in the temperature range 10–300 K. From these ratios, we obtained the differences between the corresponding mean square displacements. Moreover the motions of the first four coordination shells of the europium with respect to the latter, for $T = 30–300$ K, were studied by means of EXAFS spectroscopy. Combining the results obtained with the two techniques, we construct a qualitative picture of the collective atomic motions. In particular, we identify a substructure in the unit cell, around the central ion, formed by atoms performing correlate large amplitude anharmonic oscillations.

KEY WORDS: high-$T_c$ superconductivity; atomic motions; Mössbauer; EXAFS.

1. INTRODUCTION

Many of the models that have been proposed in order to establish the nature of high-$T_c$ superconductivity involve unusual vibrational properties of the cuprates [1]. However, despite the large number of experimental and theoretical studies performed on cuprate lattice dynamics, many important questions have not yet been clarified. One of these questions concerns the existence of large anharmonicities in the atomic motions, which is invoked in many experimental and theoretical works on high-$T_c$ superconductivity [2–7]. On the other hand, for the recently discovered superconducting MgB$_2$, a combined ab initio calculation and neutron scattering study has revealed that huge anharmonic oscillations of the boron atoms are strongly coupled to the electron in states near the Fermi surface [8].

In a previous work, we performed a very accurate measure of the mean square displacement (MSD) of the europium in EuBa$_2$Cu$_3$O$_7$ by means of $^{151}$Eu Mössbauer spectroscopy [9]. The Debye–Waller factor was determined as a function of the temperature by using the absolute absorption area method (only by this method low-temperature anharmonicities can be revealed [10]). We found that the Eu MSDs were about four times greater than the values expected for usual harmonic oscillation. Obviously, the Eu compound is not anomalous, i.e., the properties of the RBCO compounds are largely independent of the trivalent R ion (except for R = Pr or La). We then expect that the oscillatory amplitude of the R ion is approximately the same irrespective of R, except small differences due to the different ionic radii and masses.

In Ref. [9] Mössbauer spectra were taken on powder sample with randomly-oriented EBCO grains, so that the MSDs obtained should be the average values of the MSDs in the c and ab-plane directions. Here, a comparison between the MSDs in
these two directions will be performed by measuring the $f_s/f_{ab}$ ratio between the Debye–Waller factors. Moreover, we present EXAFS measurements of the mean square relative displacement (MSRD) of the first atomic coordination shells of the Eu ion. As a consequence, from Mössbauer and EXAFS data, we were able to extract information on single-atom motions and correlations among these motions.

2. MÖSSBAUER EXPERIMENT

In the region of linear absorption, the absorption Mössbauer area $A$ for a single line spectrum is given by $A = f_s a_{is}$, where $a_{is} = m_s f_s s_0$ is the so-called effective thickness, $m_s$ is the mass of the Mössbauer isotope per unit area of the sample, $f_s$ and $f_a$ are the $f$-factors of source and sample, respectively. Lastly, $a$ is a constant that depends on the natural line width $\Gamma_a$ and line hyperfine broadening.

Since the unit cell has quasi-tetragonal symmetry, we will assume the $(a, b)$ MSD of the europium to be isotropic, but different from the MSD in $c$ direction: $(x^2)_{a} \neq (x^2)_{c}$. Under this assumption $f_s$ depends only on the angle $\theta$ between the $y$-ray $k$ vector and the $c$-axis. By posing $(x^2) = (x^2)_{c} \cos^2(\theta) + (x^2)_{a} \sin^2(\theta)$, we can write $f_s(\theta) = f_s x^{\cos(\theta)}$, where $r = f_s/f_{ab}$. Thus, if $p(\theta)$ denotes the distribution function of the grain orientation in the sample, the absorption Mössbauer area is given by

$$A = \int_{0}^{\pi} p(\theta) r^{\cos(\theta)} \sin(\theta) d\theta \tag{1}$$

In order to measure the ratio $r$, the absorption areas of two sample with different grain-orientation distributions $p_1(\theta)$ and $p_2(\theta)$ have to be compared. To do this, we considered the quantity $Z_{12} = (A_1/m_1)/(A_2/m_2)$, which, for Eq. (1), is given by

$$Z_{12} = \frac{\int_{0}^{\pi} p_1(\theta) r^{\cos(\theta)} \sin(\theta) d\theta}{\int_{0}^{\pi} p_2(\theta) r^{\cos(\theta)} \sin(\theta) d\theta} \tag{2}$$

In this equation, the ratio $r$ is implicitly expressed in terms of $Z_{12}$. Therefore, the $r$ value can be obtained from the numerical analysis of Eq. (2), when $p_1(\theta)$, $p_2(\theta)$, and $Z_{12}$ have been determined.

2.1. Mössbauer Samples

Two samples (samples 1 and 2) of oriented single-phase powder of EuBa$_2$Cu$_3$O$_7$ (purity 99.9% and mean grain size 2 $\mu$m) and a sample of randomly-oriented, single-phase powder (sample 3) of EuBa$_2$Cu$_3$O$_7$ were prepared, all in the form of flat disks. The orientation was obtained by means of two different methods: we mixed the powder with epoxy resin and shaped it in a 8-T magnetic field directed along the holder axis. The mixture was kept within the field at a temperature of $-10^\circ$C for about 1 h so as to prevent the glue from hardening during the grain orientation. The temperature was then increased to about 25°C and kept at this value, in the presence of the field, for the time required to make the glue solid (about 0.5 h). Since the magnetic susceptibility of EBCO has the maximum component perpendicular to the $c$-axis [11–14], the grains of EBCO orient themselves with the $c$-axis perpendicular to the field, i.e. parallel to the sample surface.

Another oriented-grain sample, but with the $c$-axis mainly directed perpendicular to the faces, was obtained by exerting a pressure of about 10 MPa on a mixture of powders of EBCO and polythene for 1 day. The micrograins of EBCO have a laminar shape; therefore, the pressure tends to orient the lamellae perpendicularly to the force [13–16].

Finally, a randomly-oriented grain sample was obtained by preparing a mixture of EBCO powder and epoxy resin and letting the glue harden in the absence of orienting forces.

All our samples were made with medium thickness so as to avoid the presence of holes, which would have compromised a correct estimate of the Mössbauer absorption areas. Therefore, correction due to saturation of the spectra is expected to be necessary.

2.2. Mössbauer Results

A detailed description of the determination of the sample masses and orientation degrees is reported elsewhere [17]. Here, we just say that masses were obtained from the absorption measurement of the radiations of 14.4 and 122 keV emitted from a $^{151}$Sm source. Moreover, the orientation distribution functions were obtained by X-ray diffraction. Bragg spectra were collected using the Co$K\alpha$ emission.

Conventional Mössbauer transmission measurements were performed by using a 100 mCi source of $^{151}$Sm in SmF$_3$. For each sample, spectra at the temperatures of 20, 85, 90, 95, 200, and 300 K were collected. Cooling was achieved by means of a Gifford-MacMahon cryogenator [18], and the temperature was stabilized by an ITC4 Oxford Instrument controller. In order to determine the non-Mössbauer background
Fig. 1. Mössbauer spectra of the three samples at T = 20 K and relative fits. Count scales are the same for the three spectra; the baselines are shifted.

fraction \( N_0/N_{\infty} \), PHA spectra were also collected for each sample and for each temperature [17]. If \( A_M \) is the area given back by the fitting procedure of a Mössbauer spectrum, the Mössbauer absorption area \( A \) is given by

\[
A = \frac{(1 - N_0/N_\infty)}{A_M}.
\]

Finally, in order to obtain the \( Z \)-ratios, absorption areas were corrected taking into account saturation effects, according to the procedure described in detail in [17].

Mössbauer spectra at 20 K, together with their fits, are reported as example in Fig. 1, where MG, PX, and RN denote samples with grains oriented by magnetic field, by pressure, and randomly, respectively.

We see that the \( f \)-factor of the \( ^{151}\text{Eu} \) in EBCO is strongly anisotropic. The ratio \( r = \frac{f_c/f_{ab}}{f_{ab}} \) turned out to be practically independent of the temperature and its value is around 0.25, with a statistical error of about 0.05. By denoting with \( \langle x_c^2 \rangle \) and \( \langle x_{ab}^2 \rangle \) the mean square displacements of the europium ion in the \( c \)-direction and in the \( ab \)-planes, respectively, and with \( k \) the wave vector of the 21.6 keV Mössbauer \( \gamma \)-rays, i.e. \( k = 10.93 \, \text{Å}^{-1} \), we have

\[
\langle x_c^2 \rangle - \langle x_{ab}^2 \rangle = -\frac{\ln(r)}{k^2} = (1.2 \pm 0.2) \times 10^{-2} \, \text{Å}^2.
\]

This very large value agrees with a previous Mössbauer result [9] in proving the presence of a low-temperature vibrational anharmonicity of the europium motion. Moreover, the present work shows that this anharmonicity mainly affects the motion along \( c \)-direction.

By assuming for \( \langle x_{ab}^2 \rangle \) the value of 0.003 Å², which was obtained for yttrium in the compound \( \text{YBa}_2\text{Cu}_3\text{O}_{6.0} \) in the temperature range \( T = 45-90 \, \text{K} \) [19], we obtain \( u_c = \sqrt{\langle x_c^2 \rangle} \approx 0.12 \, \text{Å} \). So large a low-temperature oscillation amplitude means that the europium potential has not a parabolic shape along \( c \). Rather, it has to have a flat or wine-bottle-like bottom, whose width is about 0.1 Å.

3. EXAFS EXPERIMENT

As mentioned in the Introduction, EXAFS measurements were performed for investigating the mean square variations of the distances of the atoms from europium; therefore, non-oriented-grain samples could be used. On the other hand, a tetragonal nonsuperconducting sample and an orthorhombic sample were prepared in order to reveal possible differences in the relative motions of the atoms. To be precise, we prepared two samples of \( \text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta} \) single-phase powders mixed with polyethylene, with \( \delta = 1 \) and \( \delta = 0 \) (\( T_c \approx 90 \, \text{K} \)). For each of them, we collected transmission Eu K-edge EXAFS spectra at \( T = 30, 60, 90, 120, 180, 250, \) and 300 K. The measurements were performed at the beam-line GILDA CRG of the European Synchrotron Radiation Facility (ESRF) in Grenoble. We carried out the data analysis by fitting the experimental spectra with the aid of the GNXAS package [20].

The model cluster used for the EXAFS calculations is shown in Fig. 3, which represents the local structure around Eu in EuBCO up to a radial distance \( R_0 \) of 4 Å. The four shells included in the calculations are denoted as Eu—O, Eu—Cu, Eu—Ba, and Eu—Eu(2), in order of (their) increasing distance
Fig. 3. Cluster used in the simulation of the EXAFS spectra. In order of increasing distance from the Eu site, one can see the O shell, the Cu shell, the Ba shell, and the shell of Eu’s lying in the adjacent cells.

from Eu. Actually, the EXAFS Fourier transform (FT) shows further components above 4 Å, but their analysis is much less accurate. Therefore, they have not been considered in fitting the experimental data.

In order to determine the signal shape, only single scattering of the four coordination spheres was considered, as the contributions of the multiple scattering paths (MSPs) were verified to be negligible. This is because a large part of MSPs have lengths much larger than $2R_0$, so that the corresponding signal amplitudes are much smaller than the simple scattering ones. Moreover, the MSPs with lengths shorter than $2R_0$ correspond to double scattering paths with angles different from zero, i.e. with small scattering amplitudes. We assumed the Gaussian approximation of the radial-distribution function. The centers $R$ and the line widths $\sigma$ of its peaks represent the mean values and the standard deviations of the coordination-sphere radii, respectively.

The validity of Gaussian approximation was checked by fitting the spectra including the cumulants $C_3$ and $C_4$. The values obtained for $C_2 (\approx \sigma^2)$ were equal, within the permissible errors, to the ones obtained with the position $C_1 = C_4 = 0$. We accounted for two different subcoordination shells for each neighbor. On the contrary, only one $\sigma^2$ was enough to obtain good fits of the spectra.

Apart from this the coordination spheres were divided in two subspheres with one half of atoms each, but with different $R$’s and the same $\sigma$’s.

The $S_0^2$ parameter accounting for multielectronic excitations was kept free only in the preliminary fits. The values obtained for this parameter showed no dependence on the doping level $\delta$ and temperature. Therefore, in the last fits $S_0^2$ was set at the value of 0.85, i.e., the average of the values obtained in the preliminary fits.

In order to determine the signals corresponding to the various scattering paths, we used the Heding–Lundqvist potential that allows to do an ab initio evaluation of the signal-amplitude decrease due to anelastic scatterings. Therefore, it was not necessary to introduce the photoelectron mean free path as a free parameter.

3.1. EXAFS Results

A typical EXAFS signal with corresponding FT is shown in Fig. 4. We can distinguish three different regions. In the region from 4 to 6 Å$^{-1}$, the small amplitude oscillations are mainly due to scattering from the oxygen atoms of the first coordination shell. In fact the oxygen atom backscattering amplitude has
Atomic Motions in EuBa₂Cu₃O₇₋ₓ

Table I. EXAFS-MSRDs for the Underdoped EBCO

<table>
<thead>
<tr>
<th>T (K)</th>
<th>σ₁²</th>
<th>σ₂²</th>
<th>σ₃²</th>
<th>σ₄²</th>
</tr>
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<tbody>
<tr>
<td>30</td>
<td>4.0 (5)</td>
<td>2.1 (2)</td>
<td>3.0 (6)</td>
<td>2.2 (3)</td>
</tr>
<tr>
<td>60</td>
<td>4.1 (5)</td>
<td>2.2 (2)</td>
<td>3.5 (7)</td>
<td>2.2 (3)</td>
</tr>
<tr>
<td>90</td>
<td>4.4 (5)</td>
<td>2.5 (2)</td>
<td>3.9 (8)</td>
<td>2.4 (3)</td>
</tr>
<tr>
<td>120</td>
<td>4.7 (6)</td>
<td>2.9 (2)</td>
<td>4.1 (9)</td>
<td>3.2 (4)</td>
</tr>
<tr>
<td>180</td>
<td>5.5 (7)</td>
<td>3.7 (3)</td>
<td>4.6 (10)</td>
<td>4.2 (5)</td>
</tr>
<tr>
<td>250</td>
<td>6.7 (9)</td>
<td>4.7 (3)</td>
<td>5.5 (16)</td>
<td>5.1 (6)</td>
</tr>
<tr>
<td>300</td>
<td>8.1 (11)</td>
<td>5.2 (4)</td>
<td>7.4 (19)</td>
<td>6.0 (10)</td>
</tr>
</tbody>
</table>

significant values only in this region, where the contribution of the other shells is negligible. In the central region (6–11 Å⁻¹) the signal is mainly due to scattering from the second-shell copper atoms, though here contributions from barium and europium external shells are present. However the latter contributes to the signal mainly for k larger than 11 Å⁻¹.

The fitting of the signal FT shows that we have a rather good agreement for the first three peaks, which correspond to the considered for coordination shells. The peaks of the barium and europium shells are not spatially resolved because their shell radii, R₁ = 3.7 Å and R₃ = 3.9 Å, respectively, are very close. As R increases, the agreement between FT exp and FT th becomes worse. For instance, the small hump on the right side of the Eu–Ba peak, around r ≈ 4 Å, which is due to single scattering from the fifth and sixth shells, was not included in our model.

As far as the structural parameters are concerned, we found that the average distances between europium and its neighbors do not vary appreciably (less than 0.5% for temperature up to 300 K). The trend of the MSRDs are more interesting. The best fit values are reported, together with their statistical errors, in Tables I and II for the samples with δ ≈ 0 and δ ≈ 1, respectively. It can be seen that they lie in a range which is consistent with normal harmonic vibration (see, e.g., [21], where the σᵢ² values for copper are reported). Moreover, the σᵢ²’s of the first two shells do not depend on the doping. On the contrary, the σᵢ²’s corresponding to the Ba and Eu(2) shells are observed to be somewhat smaller for the overdoped sample.

4. CORRELATIONS AMONG IONIC MOTIONS

As is well known, the EXAFS Debye–Waller factors measure the broadening of the bond distances because of the thermal motions, provided the static disorder is negligible. Denoting by σ₁² and σ₂² the absorber and the backscatterer MSDs along the interatomic distance Rij, respectively, the corresponding σ₂²EXAFS can be written as

$$\sigma_{\text{EXAFS}}^2 = \sigma_1^2 + \sigma_2^2 - 2\rho_{ij}\sigma_1\sigma_2$$

where ρij is the so-called correlation parameter. If ρij ≈ ±1, the motion is highly correlated, in-phase or out-of-phase, respectively. If ρij ≈ 0, the ionic oscillations are uncorrelated. Generally, a decrease of |ρij| is expected as the interatomic distance increases. Furthermore, if the Debye model is a good approximation for the considered solid, ρij is expected to be an increasing function of temperature. This is a consequence of the correlations, as seen by EXAFS, being projected onto the absorber-backscatterer bond distance, thereby being 1D correlations in their very nature [22].

Some qualitative conclusions regarding the correlations among ion motions can be drawn here as follows. Let us consider the ionic radii of Eu³⁺ and O²⁻. We see that the two ions are practically in contact with each other. Consequently, a large positive correlation between the motions of the europium and oxygen ions of the first shell is expected. Moreover, taking into account the tight binding between the oxygen and copper ions in the CuO₂ planes, a large positive correlation is also expected with the copper ions of the second shell [23]. On the other hand, we note that Ba²⁺ ions are not in contact with the inner shells. Nevertheless, the corresponding measured σ² seems to be rather small. Then, in order for these results to be consistent with the large oscillation of the Eu ion along c, as measured by Mössbauer spectroscopy, a large positive correlation between the two ions has to exist. As a side result, we can combine the Mössbauer value for the σ₂²Ba in the

Table II. EXAFS-MSRDs for the Overdoped EBCO

<table>
<thead>
<tr>
<th>T (K)</th>
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</tr>
<tr>
<td>180</td>
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<td>2.8 (9)</td>
<td>3.2 (12)</td>
</tr>
<tr>
<td>250</td>
<td>6.8 (12)</td>
<td>4.8 (3)</td>
<td>4.4 (14)</td>
<td>5.3 (18)</td>
</tr>
<tr>
<td>300</td>
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<td>5.7 (16)</td>
</tr>
</tbody>
</table>

Values of 1.4 and 1.08 Å are reported for O²⁻ and Eu³⁺ ions respectively. They add up to 2.48 Å, when the Eu=O distance is 2.41 Å from our measurements and in good agreement with the crystallographic data. http://www.webelements.com.
(\(\mathbf{a}, \mathbf{b}\)) plane with the \(\sigma^2_{\text{EXAFS}}\) to calculate \(\rho_{\text{Eu-Eu}}\) as a function of temperature. Unlike the normal trend, \(\rho_{\text{Eu-Eu}}\) decreases monotonically from \(\approx 1\) to \(\approx 0.75\) as the temperature increases from 30 to 300 K.

5. CONCLUSIONS

By combining the Mössbauer and EXAFS results we suggest that the ionic motions in EBCO consist of large-amplitude, highly-correlated oscillations with superimposed small-amplitude, weakly-correlated vibrations. The large-amplitude component can be described as follows. Starting from the equilibrium configuration, let us imagine we displace the Eu ion along \(\mathbf{c}\). As a consequence, the oxygen ions will move along the line joining the Eu and O centers (see Fig. 5). But this displacement hardly changes the Eu-O distance, and therefore, it will not be revealed by EXAFS. Hence, the measured \(\sigma^2_{\text{Eu-O}}\) values clearly show that the relative motions of these ions are independent of the doping level. On the contrary, the \(\sigma^2_{\text{Eu-Ba}}\) and \(\sigma^2_{\text{Eu-Eu}}\) values of the overdoped sample are significantly smaller than those of the underdoped one at \(T < T_c\). Such a difference could be due to the coupling phenomenon that takes place at \(T < T_c\) in the superconducting sample. However, in order to clarify this question, further investigations will be necessary. We also note that the observed decrease in \(\rho_{\text{Eu-Eu}}\) as the temperature increases cannot be explained within the framework of phonon theory.

REFERENCES

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