Determining Hole Locations in High-Temperature Superconductors via Spectral Analysis of Gap Tensor Parameters

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Abstract: The nuclear quadrupole resonance (NQR) method using 63,65Cu isotopes allows for the experimental determination of the total electric field intensity (EFI) on 63,65Cu nuclei in the lattices of high-temperature superconductors (HTSC). Consequently, it is typically not possible to compare the experimental parameters of the electric field gradient (EFG) tensor with those calculated using the point charge model. The emission Mössbauer spectroscopy method with the 67Cu (67Zn) isotope enables us to experimentally determine only the contribution to the total EFG on 67Zn nuclei from the HTSC crystal lattice ions. However, even in this case, there is no quantitative agreement between the calculated and experimental values of the main component of the EFG tensor. This discrepancy is attributed to the lack of reliable data on Sternheimer coefficients and criteria for selecting the lattice charge contrast. Nevertheless, these issues can be resolved if the EFG tensor parameters are determined for two structurally equivalent positions.

1 INTRODUCTION

One of the main problems in high temperature superconductivity (HTSC) physics is determining the localization location of holes, which determine the phenomenon of superconductivity. The most reliable way to identify holes in HTSC lattices is considered to be a comparison of the experimentally determined parameters of the electric field gradient (EFG) tensor with the results of their theoretical calculation. This method is most effective in measuring and calculating the parameters of the gap tensor. All HTSCs, as a rule, contain copper, and the parameters of the gap tensor at copper sites are most sensitive to the charges of atomic centers.

This work is devoted to the consideration of experimental and theoretical results of determining the parameters of the electric field tensor in copper nodes of YBa2Cu3O7-x ceramics. The compound is one of the most typical HTSCs and is distinguished by its relative simplicity of synthesis, high values of the transition temperature to the superconducting state Tc, and the ability to regulate Tc by changing x [1]. It is these features that explain the fact that the overwhelming number of studies on the comparison of calculated and experimental parameters of the EFG tensor relate to YBa2Cu3O7-x.

Calculation of parameters of the gap tensor. The diagonalized gap tensor is described by three components Vxx, Vyy, and Vzz, related by the Laplace equation

$$Vxx+Vyy + Vzz = 0, \quad (1)$$

and a special choice of axes:

$$|Vxx| \le |Vyy| \le |Vzz|. \quad (2)$$

As a result, two independent parameters remain: the main component of the gap tensor eq= Vzz and the asymmetry parameter η=(Vxx-Vyy)/ Vzz.

There are two sources of gap on the nucleus under study: surrounding ions of the crystal lattice eqcr and non-spherical valence electrons of the atom eqval:

$$q = (1-\gamma)\, qcr + (1-R)\, qshaft, \quad (3)$$

where γ, R are the Sternheimer coefficients, taking into account the shielding (anti-shielding) of the gap from ions and valence electrons by the electrons of the inner shells of the atom.

Calculation of the parameters of the gap tensor from ions of the crystal lattice can be carried out within the framework of the point charge model.

For YBa2Cu3O7-x ceramics, such calculations were carried out in [2]-[3]. Table 1 summarizes the most typical results for two models of charge distribution of atomic centers in the lattices YBa2Cu3O7 and YBa2Cu3O6. Let us note, firstly, the satisfactory agreement of the data obtained by different authors, and, secondly, the obvious dependence of the parameters of the gap tensor at copper sites on the charge distribution of atomic centers.

Experimental methods for determining the parameters of the gap tensor. The most complete experimental information on the parameters of the gap tensor can be obtained by nuclear quadrupole resonance (NQR) and Mössbauer spectroscopy methods. These methods are based on the interaction of the quadrupole moment of the nucleus eQ with an inhomogeneous electric field.

Table 1: Parameters of the gap tensor at copper sites for YBa2Cu3O7 and YBa2Cu3O6 (calculation results within the point charge model).

Model	Eq_{qr} (1), e^3	η (1)	Eq_{qr} (2), e^3	η (2)
Y^{3+} Ba_2^{2+} $Cu(1)^{3+}$ $Cu(2)_2^{2+}$ O_7^{2-}	+1,162 +1,165 +1,146 +1,147	0.40 0,40 0,35 0,36	+0,700 +0,701 +0,662 +0,663	0,13 0,12 0,11 0,10
Y^{3+} Ba_2^{2+} $Cu(1)^{+}$ $Cu(2)_2^{3+}$ O_7^{2-}	+0,979 +0,997	0,08 0,02	+0,510 +0,552	0,13 0,16
Y^{3+} Ba_2^{2+} $Cu(1)^{3+}$ $Cu(2)_2^{2+}$ O_6^{2-}	-1,286 -1,256 -1,324 -1,264	0,00 0,00 0,00 0,00	+0,683 +0,668 +0,714 +0,654	0,00 0,00 0,00 0,12
Y^{3+} Ba_2^{2+} $Cu(1)^{3+}$ $Cu(2)_2^{+}$ O_6^{2-}	-1,570 -1,589	0,00 0,00	+0,816 +0,806	0,00 0,00

Nuclear quadrupole resonance. For YBa2Cu3O7-x, nuclear quadrupole resonance can be observed on the isotopes 63Cu and 65Cu. For both isotopes I = 3/2, quadrupole moments Q (63Cu) = - 0.211 b and Q (65Cu) = - 0.195 b [4]. If the copper core is located in the nodes of the crystal lattice and the local symmetry of its environment is lower than cubic.

2 COMPARISON OF RESULTS

When considering the NQR spectra of the 63,65Cu isotopes in YBa2Cu3O7-x, it should be kept in mind that copper occupies two positions, Cu(1) and Cu(2), in the structure of this compound. Furthermore, it should be taken into account that the natural isotopic mixture contains 63Cu and 65Cu.

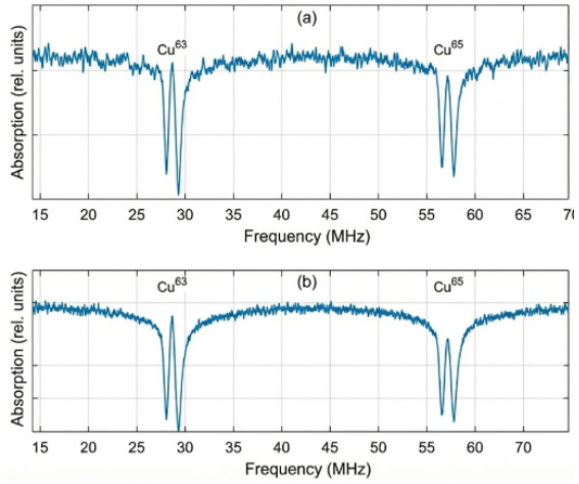

Figure 1: 63.65 NQR spectrum in YBa2Cu3O7 at a)1.7 K and b) 4.2 K.

Therefore, four lines should be expected in the 63.65Cu NQR spectra of YBa2Cu3O-x ceramics: 63Cu (1), 65Cu (1), 63Cu (2) and 65Cu (2), and the intensities of these lines should be determined by the occupancy of the Cu (1), Cu (2) (1:2) and the content of the isotopes 63Cu (~70%) and 65Cu (~30%).

Indeed (see Fig. 1, a), the NQR spectrum of 63.65Cu sample YBa2Cu3O7 consists of two pairs of lines, the positions of which have been determined in a large number of works [5]-[8]: 20.5; 22.05 and 29.2; 31.50 MHz. Based on the values of the quadrupole moments of the 63Cu and 65Cu nuclei, and the content of these isotopes in the natural mixture of isotopes, the less intense lines in these pairs (20.5 and 29.2 MHz) belong to the 63Cu isotope, and the more intense ones (22.05 and 31.50 MHz) - to the 36Cu isotope. In what follows, we will consider only the NQR spectrum of the 63Cu isotope as more intense.

Thus, the NQR spectrum of 63Cu in YBa2Cu3O7 consists of two lines: less intense (22.05 MHz) and more intense (31.50 MHz).

The NQR spectra of 63.65Cu in YBa2Cu3O7 (Fig. 1b) were studied in [9, 10]. Two lines in the 26-30 MHz region refer to the pure quadrupole spectrum on 63.65Cu isotopes for Cu(1) centers, while six lines in the 60-120 MHz region refer to the 63.65Cu NMR

spectrum in an internal magnetic field for Cu centers (2).

Mössbauer spectroscopy. Since there are no Mössbauer isotopes of copper, the study of YBa2Cu3O7 by Mössbauer spectroscopy is possible only using impurity atoms. As a rule, 57Fe is used as impurity atoms: it is assumed that iron replaces Cu(1) and Cu(2) atoms in the structure of HTSC and the parameters of the Mössbauer spectra of 57Fe carry information about the symmetry of the local environment of copper atoms [4]-[6].

The Mössbauer transition in 57Fe occurs between levels with spins 3/2 and 1/2, so that when impurity iron atoms are in an environment whose local symmetry is lower than cubic, the Mössbauer spectrum of 57Fe is split into two components.

We can formulate the following requirements for Mössbauer spectroscopy when used to study copper centers in HTSC [7]-[9]: the probe used must obviously replace copper in the positions of copper atoms: the introduction of an avalet probe into a crystal lattice site should not be accompanied by shell processes, which allows exclude the contribution to the gap from valence electrons. All these conditions are met for Mössbauer emission spectroscopy on the 67Cu (67Zn) isotope. After the beta decay of the parent nucleus 67Cu, the Mössbauer nucleus 67Zn in an excited state is formed in the copper site. The emission of a Mössbauer quantum occurs within a time of ~10-6 s after the formation of a daughter nucleus, which eliminates the possibility of the emergence of compensating centers in the lattice. The daughter zinc atoms have a closed 3d shell (Zn2+, 3d10) and, therefore, for them the contribution to the gap from the unfilled d shell is neglected. The isomeric transition in 67Zn occurs between levels with spins 5 ⁄⁄ 2 and 1 ⁄⁄ 2, and in a crystal field, the local symmetry of which is lower than cubic, three lines of equal intensity appear in the Mössbauer spectrum, and the distance between the lines in the velocity spectrum is determined by the absolute value of e2qQ, the relative location of the three lines is indicated by the sign e2qQ, and the ratio of the distances between the lines allows us to determine the asymmetry parameter η.

Apparently, the authors of [3], [7] were the first to use Mössbaer emission spectroscopy on the 67Cu(67Zn) isotope to determine the parameters of the electric field tensor at the Cu(1) and Cu(2) sites of the YBa2Cu3O7-x lattice.

The spectrum of YBa267Cu3O7 is a superposition of two quadrupole triplets with an intensity ratio of ~ 1:2 (Fig. 2a) [5]. Based on the occupancy of Cu(1) and Cu(2) positions in the YBa2Cu3O7 lattice, the spectrum with lower intensity should be attributed to 67Zn2+ centers at Cu(1) sites, and the spectrum with higher intensity to 67Zn2+ centers at Cu(2) sites. The spectrum of YBa267Cu3O6 is a quadrupole triplet corresponding to a single state of 67Zn2+ centers. Since at T≤420K the Cu(2) sublattice for YBa2Cu3O6 is antiferromagnetically ordered [5], the observed spectrum in Figure 2b should be attributed to 67Zn2+ centers in Cu(1) sites (the spectrum from 67Zn2+ centers in Cu(2) sites is blurred over a large velocity range and does not appear in the experimental spectrum).

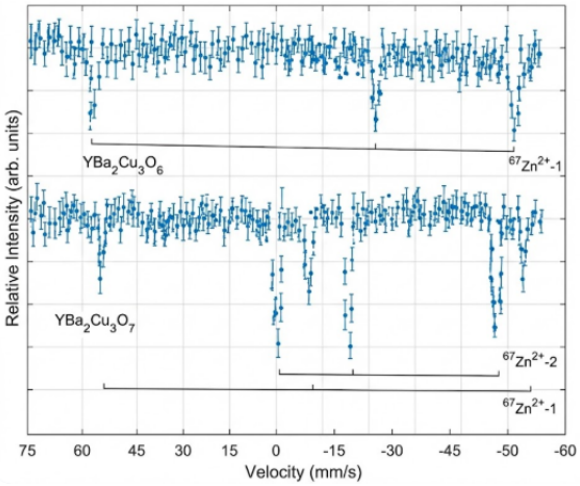

Figure 2: Emission Mössbauer spectra of a) YBa269Cu3O7 and b) YBa267Cu3O6 at 4.2 K.

A comparison of the tabular data shows that for one combination of Y3+, Ba2+, Cu+, Cu2+, Cu3+ and O2- ions in the YBa2Cu3O7 and YBa2Cu3O6 nodes, it is not possible to achieve even an approximate agreement between the calculated and experimental values of the main component of the GAP tensor for copper nodes. The calculated value is always greater than the experimental value (if their signs coincide). One should not think that the observed discrepancy is explained by the complexity of the YBa2Cu3O7-x lattices. The same discrepancy was discovered by the authors of [9] for Cu2O. It is generally accepted that it is an ionic compound with the structural formula Cu2+O2-. The Mössbauer emission spectrum of 67Cu2O is a quadrupole triplet corresponding to 67Zn2+ centers at copper sites (see Table 2). It can be seen that for Cu2O the experimental value eqcr = 0.282 e3 is ~ 4 times higher than eqcr = - 1.092 e3.

Table 2: Parameters of the Mössbauer spectra of 67Cu(67Zn) for YBa2Cu3O7 and YBa2Cu3O6 at 4.2 K.

Connection	Centre	e^2qQ, MHz	H	Eq^e_{qr}, e^3
$YBa_2Cu_3O_7$	$^{67}Zn^{2+}$ (1) $^{67}Zn^{2+}$ (2)	+20,1 ± 0,5 +11,8 ± 0,5	0,95±0,05 ≤0,2	+0,258 +0,151
$YBa_2Cu_3O_6$	$^{67}Zn^{2+}$ (1)	-23,5 ± 0,5	≤0,2	-0,301
Cu_2O	$^{67}Zn^{2+}$	-22,0 ± 0,5	≤0,2	-0,282

However, the authors of [6], [7] noted that the problem of varying the charge contrast and the Sternheimer coefficient can be eliminated for lattices containing several structurally nonequivalent copper atoms. In particular, in the YBa2Cu3O7 lattice there are two structurally nonequivalent positions Cu(1) and Cu(2), and therefore the ratio p = (e2qQ (1))/ (e2qQ (2)) should not depend on the charge contrast of the lattice (it is the same when calculating the HEF at the Cu(1) and Cu(2) sites), nor on the choice of γ (Zn2+) (the Sternheimer coefficient is the same for Zn2+ at the Cu(1) and Cu(2) sites. If we use several natural assumptions about the charges of atomic centers (the charges of Y and Ba atoms are in the ratio 3:2), which corresponds to the ratio of the only valences allowed for them; the charge of Ba ions is equal to the charge of O(1) ions, which corresponds to the electrical neutrality of the Ba – O plane in the YBa2Cu3O7 lattice; and Cu(2) can be in the range from +1 to +3), then the experimental value p = 0.59 ± 0.04 corresponds to the structural formula of the compound YBa2Cu3O7:

U3.14+ + Ba 22.09+ + Cu(1)1.89+ + Cu(2)21.89+ + O(1)22.09- + O(2)21.93- + O(3)21.81- + O(4)1.34-

An essential feature of this formula is that for the O(1), O(2), O(3), O(4) ions the approximate charge ratio is 2:2:2:1. This relationship is the result of hole localization (i.e., decreased valence) at O(4) sites. The existing deviation from the 2:2:2:1 ratio indicates partial hole transfer to the O(2) and O(3) nodes.

Comparison of Mössbauer (67Cu) and NQR (63Cu) spectroscopy data. 63Cu NQR data make it possible to determine the total EFG on 63Cu nuclei, while Mössbauer spectroscopy data on the 67Cu (67Zn) isotope make it possible to determine the contribution to the EFG of the total EFG from crystal lattice ions at copper sites. Obviously, a comparison of the data from the two methods makes it possible, in principle, to estimate the valence contribution to the EFG on 63Cu nuclei.

3 CONCLUSIONS

The main results of this study can be summarized as follows:

1) For the YBa2Cu3O7 lattice in the Cu (1) position, we obtain (1-R) e2qvalQ = 100.1 ± 1.6 MHz, and in the Cu (2) position (1-R) e2qvalQ = 99.4 ± 1.0 MHz. The proximity of valence electron contributions to the total clearance in the Cu (1) and Cu (2) nuclei indicates the similarity of the electronic structures of these centers. The value (1-R) e2qvalQ =100 MHz can also be obtained for the copper centers in the La2CuO4 compound [10], where the copper is clearly divalent Cu2+. Consequently, in YBa2Cu3O7 the Cu(1) and Cu(2) centers are also divalent.
2) The 63.65Cu isotope-based NQR method allows for the experimental determination of the total HEF based on the 63.65Cu nuclei in the HTSC lattices, and consequently, there is usually no possibility of comparing the experimental and calculated (using the point charge model) parameters of the EFG tensor. The method of emission Mössbauer spectroscopy on the 67Cu (67Zn) isotope allows us to experimentally determine the contribution of the total EFG of the crystal lattice ions of the HTSP only in the 67Zn nuclei, however, even in this case, there is no quantitative agreement between the calculated and experimental values of the main component of the EFG tensor. This is explained by the lack of reliable data on the criteria for selecting the lattice charge contrast and the Sternheimer coefficients.

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