Parameters of the electric-field gradient tensor at the copper sites in $YBa_2Cu_3O_{7-y}$. Problems of comparison of calculated and experimental values

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Mössbauer emission spectroscopy of the $^{67}Cu(^{67}Zn)$ and $^{123}Ba(^{133}Cs)$ isotopes was used to determine the parameters of the electric-field gradient (EFG) tensor of the $^{67}Zn^{2+}$ centers at the Cu(1) and Cu(2) positions and of the $^{133}Cs^{+}$ centers at the Ba positions in the lattices of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$. A disagreement between the experimental values of the principal component of the EFG tensor with those calculated using the model of point charges prevented identification of charges carried by the lattice atoms. However, a comparison of the experimental and calculated values of $p = q_{cr}(1)/q_{cr}(2)$ [$q_{cr}(1)$ and $q_{cr}(2)$ are the principal components of the EFG tensor at the Cu(1) and Cu(2) sites, respectively] for $YBa_2Cu_3O_7$ makes it possible to determine the relative charges of the atoms and to identify the most probable structural formula of this compound.

1. INTRODUCTION

Determination of the parameters of the electric-field gradient (EFG) tensor is currently one of the most reliable methods for establishing the distribution of the charges between the lattice sites in high-temperature superconductors. The distribution of these charges can in turn be interpreted in terms of the valence state and electron structure of the atoms at the lattice sites.

The diagonalized EFG tensor is described by three components V_{xx}, V_{vv}, and V_{zz} linked by the Laplace equation ($V_{xx} + V_{yy} + V_{zz} = 0$) and a special selection of the axes ($|V_{xx}| \leqslant |V_{yy}| \leqslant |V_{zz}|$). This leaves two independent parameters: the principal component of the EFG tensor $eq = V_{zz}$ and an asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, which together with the quadrupole nuclear moment eQ describes completely the quadrupole interaction. In the point-charge approximation the parameters of the EFG tensor of any crystal lattice site can be calculated from

$$V_{zz} = eq_{cr} = \sum_i e_i^* \frac{3\cos^2\theta_i - 1}{r_i^3}, \tag{1}$$

$$\eta = \frac{1}{V_{zz}} \sum_i e_i^* \frac{3\sin^2\theta_i \cos^2\varphi_i}{r_i^3}. \tag{2}$$

Here, r_i, θ_i, φ_i are the polar coordinates of a charge e_i^*.

The fullest information on the EFG tensor parameters can be obtained by the methods of nuclear quadrupole resonance (NQR), perturbed angular correlation (PAC), and Mössbauer spectroscopy. The experimental results are summarized in the form of the values of the asymmetry parameter and the quadrupole interaction constant e^2qQ. In the case of $YBa_2Cu_3O_{7-x}$ these data apply either directly to the copper centers (NQR of the $^{63,65}Cu$ isotopes)[1] or to impurity atoms at the copper sites [Mössbauer effect in the $^{57}Fe(^{57}Co)$ (Ref. 2) and ^{119}Sn (Ref. 3) isotopes; PAC of the $^{111}Cd(^{111}In, ^{111}Ag)$ isotope (Refs. 4 and 5)]. However, all these methods suffer from significant shortcomings. On the one hand, interpretation of the data on the impurity atoms[2–5] meets with the problem of identification of their positions in the lattice (see, for example, Ref. 6) and with the problem of compensation of the excess charge of the heterovalent impurity (see, for example, Ref. 7). On the other hand, the experimental values of e^2qQ obtained from NQR of the $^{63,65}Cu$ isotopes cannot be compared with the results of theoretical calculations of the value of eq_{cr} because of indeterminacy of the contribution of the valence electrons eq_{val} to the total EFG eq at a given nucleus.[1,8] In fact, we have in general

$$q = (1-\gamma)q_{cr} + (1-R)q_{val}, \tag{3}$$

where γ and R are the Sternheimer coefficients; in the case of the atomic centers with a partly filled d shell (Cu^{2+}, Cu^{3+}) it is usual to find that $|q_{val}| > |q_{cr}|$ and these quantities may differ also in respect of the sign (see, for example, Ref. 9). Naturally, we can calculate q_{val} from first principles (see, for example, Ref. 10), but at present the reliability of such calculations is in doubt.[9]

Obviously, in order to obtain reliable experimental information on the value of eq_{cr} at the lattice sites in $YBa_2Cu_3O_{7-x}$, we have to satisfy the following conditions: a probe employed for this purpose should replace copper at the copper atom positions; introduction of a heterovalent probe at a crystal lattice site should not be accompanied by the formation of compensating centers; the probe should have a closed d shell, because this makes it possible to eliminate q_{val} and to find eq_{cr} from the expression

$$q = (1-\gamma)q_{cr}. \tag{4}$$

All these conditions are satisfied by Mössbauer emission spectroscopy of the $^{67}Cu(^{67}Zn)$ isotope. Beta decay of the parent nucleus ^{67}Cu at a lattice site creates a Mössbauer ^{67}Zn nucleus in an excited state. The emission of a Mössbauer photon occurs within $\sim 10^{-5}$ s from the formation of a daughter nucleus, which excludes the possibility of the appearance of compensating centers in the lattice. The zinc daughter atoms have a closed d shell (Zn^{2+}, $3d^{10}$), so their contribution to the total EFG due to the partly filled d shell is negligible. Naturally, even in the case of the Zn^{2+} ions we can expect, in principle, a valence contribution to the EFG because of the partial covalence of the chemical binding, which is typical of zinc compounds. However, according to

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Ref. 11, at least in the case of oxides of zinc the valence contribution to the EFG is negligible and practically the whole of the EFG at the zinc nuclei is created by the crystal lattice atoms and it is found that $\gamma(\mathrm{Zn}^{2+}) = -12.2$ (Ref. 12). Finally, the nuclear parameters of the ^{67}Zn isotope are such that Mössbauer spectroscopy makes it possible to determine the sign of e^2qQ, its absolute value, and also the value of η. All this provides an opportunity to compare the experimental and calculated EFG tensor parameters at the copper sites in the $\mathrm{YBa_2Cu_3O_{7-x}}$ lattice.

Similar conditions for the determination of the EFG tensor apply also to Mössbauer emission spectroscopy of the ^{133}Ba(^{133}Cs) isotope: the capture of an electron by the ^{133}Ba nucleus produces a Mössbauer ^{133}Cs nucleus and the daughter cesium atoms in their chemical compounds have a closed d shell (Cs^+, $5d^{10}$) and are characterized by $\gamma(\mathrm{Cs}^+) = -121.3$ (Ref. 13). The Mössbauer photons are emitted in 10^{-9} s after the formation of the ^{133}Cs nucleus and this avoids the problem of the appearance of the centers that compensate the difference between the charges of the parent (Ba^{2+}) and daughter (Cs^+) atoms. Although, as shown below, Mössbauer spectroscopy of the ^{133}Ba(^{133}Cs) isotope is not as informative as Mössbauer spectroscopy of ^{67}Cu(^{67}Zn), simultaneous experimental determination of the EFG tensor parameters at positions in two cation (copper, barium) sublattices makes it possible to draw more reliable conclusions when the calculated and experimental values are compared. Our preliminary results were published earlier.[14,15]

2. EXPERIMENTAL RESULTS

We investigated ceramic samples of $\mathrm{YBa_2Cu_3O_7}$ and $\mathrm{YBa_2Cu_3O_6}$. They were prepared by the usual ceramic technology using either the ^{67}Cu or the ^{133}Ba isotope. The ^{67}Cu isotope was generated by the reaction $^{67}\mathrm{Zn}(n,\ p)^{67}\mathrm{Cu}$ when ^{67}ZnO was irradiated with fast reactor neutrons and this was followed by chromatographic separation of the carrier-free compound $^{67}\mathrm{CuCl_2}$. The ^{133}Ba isotope was generated by the reaction $^{132}\mathrm{Ba}(n,\ \gamma)^{133}\mathrm{Ba}$ involving irradiation of ^{132}BaO with thermal reactor neutrons. Control $\mathrm{YBa_2Cu_3O_7}$ samples were characterized by $T_c \sim 85$ K and the rhombohedral structure, whereas control $\mathrm{YBa_2Cu_3O_6}$ samples failed to exhibit the transition to the superconducting state right down to 4.2 K and had the tetragonal structure. The Mössbauer spectra were recorded at 4.2 K using the following absorbers: ^{67}ZnS (1000 mg/cm^2) for ^{67}Cu(^{67}Zn) and ^{133}CsCl (400 mg/cm^2) for ^{133}Ba(^{133}Cs). Typical spectra are reproduced in Figs. 1 and 2.

The spectrum of $\mathrm{YBa_2}{}^{67}\mathrm{CuO_7}$ represents a superposition of two quadrupole triplets with the intensity ratio ~1:2 (Fig. 1a). Using the populations of the positions Cu(1) and Cu(2) in the $\mathrm{YBa_2Cu_3O_7}$ lattice, we attributed the spectrum with the lower intensity to the $^{67}\mathrm{Zn}^{2+}$ centers at the Cu(1) sites and the spectrum with the high intensity to the $^{67}\mathrm{Zn}^{2+}$ centers at the Cu(2) sites. The spectrum of $\mathrm{YBa_2}{}^{67}\mathrm{Cu_3O_6}$ was found to be a quadrupole triplet corresponding to a single state of the $^{67}\mathrm{Zn}^{2+}$ centers (Fig. 1b). Since at temperatures $T<290$ K the Cu(2) sublattice in

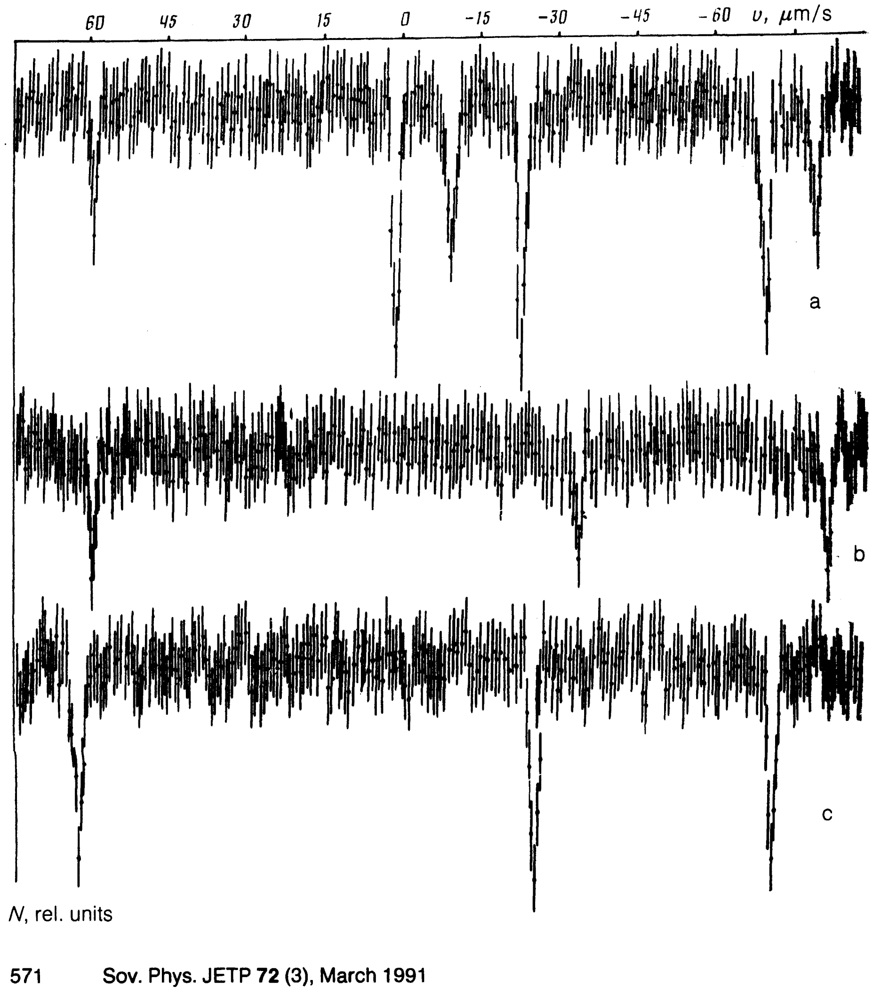

FIG. 1. Mössbauer spectra of $\mathrm{YBa_2}{}^{67}\mathrm{Cu_3O_7}$ (a), $\mathrm{YBa_2}{}^{67}\mathrm{Cu_3O_6}$ (b), and $^{67}\mathrm{Cu_2O}$ (c).

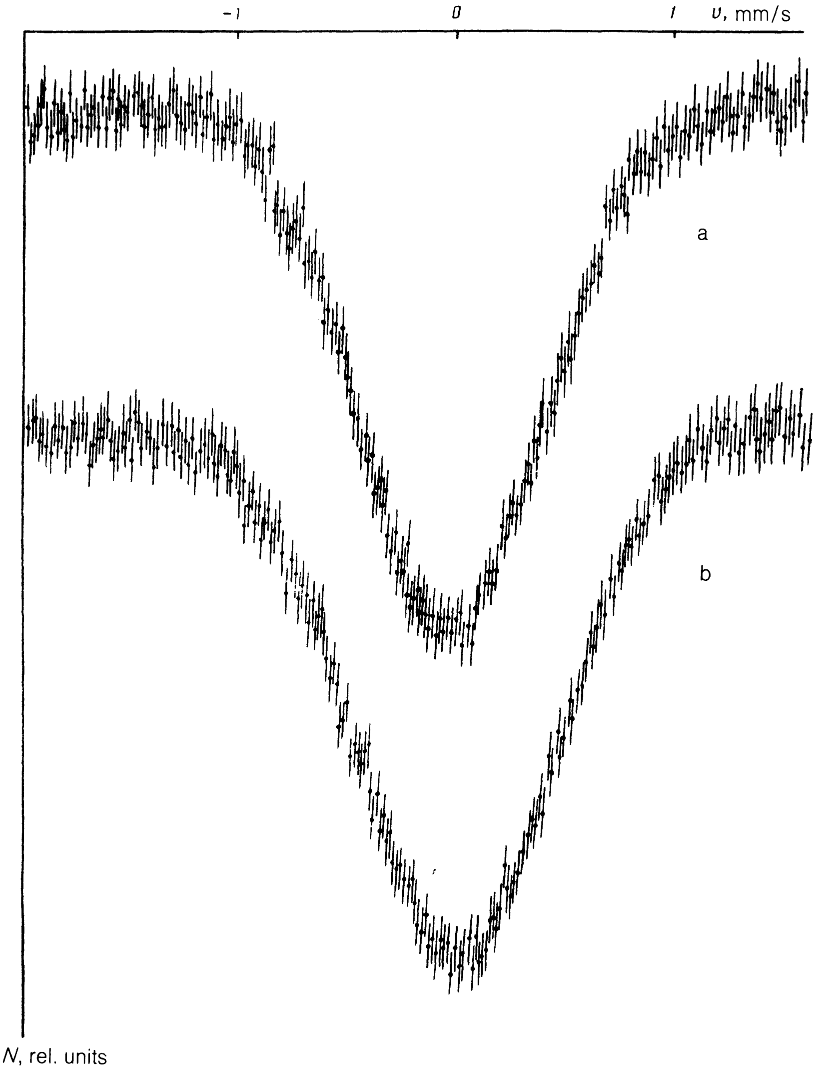

FIG. 2. Mössbauer spectra of $Y^{133}Ba_2Cu_3O_7$ (a) and $Y^{133}Ba_2Cu_3O_6$ (b).

$YBa_2Cu_3O_6$ was antiferromagnetically ordered,[16] the observed spectrum of $YBa_2{}^{67}Cu_3O_6$ should be attributed to the $^{67}Zn^{2+}$ centers at the Cu(1) sites [spectrum of the $^{67}Zn^{2+}$ centers at the Cu(2) sites was smeared out over a wide range of velocities and did not appear in the experimental spectrum]. This was allowed for in an analysis of the experimental Mössbauer spectra of $^{67}Cu(^{67}Zn)$ which gave the results collected in Table I. In the conversion of the quadrupole interaction constant e^2qQ to the experimental value of eq^e_{cr} in accordance with Eq. (4) we used the values $\gamma(Zn^{2+}) = -12.2$ and $Q(^{67}Zn) = 0.17$ b (Ref. 17).

The spectra of $Y^{133}Ba_2Cu_3O_7$ and $Y^{133}Ba_2Cu_3O_6$ (Fig. 2) represented single somewhat broadened lines [the instrumental width of the spectral line $\Gamma = (0.90 \pm 0.02)$ mm/s was assumed to be equal to the width of the experimental spectrum of the ^{133}BaO source with the ^{133}CsCl absorber]. These spectra should be attributed to the $^{133}Cs^+$ centers at the barium sites and the broadening of the spectral line should be attributed to an unresolved quadrupole splitting. Conversion of e^2qQ to eq^e_{cr} in accordance with Eq. (4) was made using the values $\gamma(Cs^+) = -121.3$ and $Q(^{133}Cs) = -0.003$ b (for the ground state) and $Q(^{133}Cs) = -0.22$ b (for the excited state).[13] It is clear from Table I that Mössbauer spectroscopy of the $Ba(^{133}Cs)$ isotope in $YBa_2Cu_3O_{7-x}$ made it possible to determine only the absolute value of eq^e_{cr} at the barium sites, whereas the Mössbauer spectroscopic data for $^{67}Cu(^{67}Zn)$ made it possible to determine additionally the sign of eq^e_{cr} and the value of η at the copper sites.

3. DISCUSSION OF RESULTS

The EFG tensor parameters obtained by us for the Mössbauer spectra of the $^{67}Cu(^{67}Zn)$ isotope can be interpreted in two ways. On the one hand, the daughter zinc atom experiences the same crystal EFG eq_{cr} as the substituted copper atom. Consequently, comparing the results of the influence of eq_{cr} on the zinc and copper atoms, i.e., the values of e^2qQ for ^{67}Zn [representing the Mössbauer spectroscopy data on $(e^2qQ)_{^{67}Zn}$] and for ^{63}Cu [NQR data, $(e^2qQ)_{^{63}Cu}$], we can obtain information on the electron structure of the replaced copper atom. On the other hand, the crystal EFG at the copper sites is created by the surrounding ions and, consequently, the values of eq^e_{cr} and η for ^{67}Zn can be used to obtain information on the distribution of the charges between the $YBa_2Cu_3O_{7-x}$ lattice sites.

The former type of interpretation was proposed by us in a preliminary paper.[15] We analyzed the ratio $(e^2qQ)_{^{67}Zn}/(e^2qQ)_{^{63}Cu}$, where $(e^2qQ)_{^{63}Cu}$ was known from the NQR investigations.[1,8] It was found that this ratio for

TABLE I. Parameters of the Mössbauer spectra of ^{67}Cu(^{67}Zn) and ^{133}Ba(^{133}Cs).

Compound	Center	e^2qQ, MHz	η	eq^e_{cr}, $e/\text{Å}^3$	Center	$\lvert e^2qQ \rvert$, MHz	eq^e_{cr}, $e/\text{Å}^3$
$YBa_2Cu_3O_7$	^{67}Zn(1)$^{2+}$	+20,1	0,95	+0,258	^{133}Cs$^+$	45	0,048
	^{67}Zn(2)$^{2+}$	+11,8	⩽0,2	0,151			
$YBa_2Cu_3O_6$	^{67}Zn(1)$^{2+}$	−23,5	⩽0,2	−0,301	^{133}Cs$^+$	65	0,069
Cu_2O	^{67}Zn^{2+}	−22,0	⩽0,2				
Погрешности		±0,5	±0,05	±0,006		±5	±0,005

the Cu(1) position in $YBa_2Cu_3O_7$ is equal to 0.53, which is practically identical with the ratio

$$\frac{[1-\gamma(Zn^{2+})]Q(^{67}Zn)}{[1-\gamma(Cu^{+})]Q(^{63}Cu)}=0,59$$

for equal values of η [it was assumed that $\gamma(Cu^+) = -17$ (Ref. 18) and $Q(^{63}Cu) = -0.211$ b (Ref. 19)]. Hence, we concluded that copper at the Cu(1) position was in the Cu$^+$ state. In the case of Cu(2) the above ratio was found to be 0.19, indicating a major contribution of the valence electrons to the EFG at the ^{63}Cu nuclei, i.e., that the 3*d* shell of these ions is only partly filled. It should be pointed out that the generally accepted values $\gamma(Cu^+) = -17$, $Q(^{63}Cu) = -211$ b, and $Q(^{67}Zn) = 0.17$ b used by us were questioned in Refs. 9 and 20 and, therefore, our conclusion about the location of Cu$^+$ at the Cu(1) site should be reviewed (see Sec. 3.4).

3.1. Calculations of the crystal EFG tensor

We shall adopt the second approach to the interpretation of the Mössbauer spectra of ^{67}Cu(^{67}Zn) (see also Ref. 14). We shall do this by calculating the components of the crystal EFG tensor for all the cation sites in the $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ lattices and represent the results as the sums of the contributions of the individual sublattices:

$$V_{\alpha\alpha}=\sum_k e_k^{*}\sum_i \frac{1}{r_{ki}^3}\left(3\frac{\alpha_{ki}^2}{r_{ki}^2}-1\right)=\sum_k e_k^{*}U_{\alpha\alpha k}, \tag{5}$$

$$V_{\alpha\beta}=\sum_k e_k^{*}\sum_i \frac{3\alpha_{ki}\beta_{ki}}{r_{ki}^5}=\sum_k e_k^{*}U_{\alpha\beta k}, \tag{6}$$

where k is the index in the summation between the sublattices [$k = 1$ for Y, $k = 2$ for Ba, $k = 3$ for Cu(1), $k = 4$ for Cu(2), $k = 5$ for O(1), $k = 6$ for O(2), $k = 7$ for O(3), and $k = 8$ for O(4)], and i is the index of summation over the sublattice sites; α and β are the Cartesian coordinates.

The $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ lattices consist of eight and seven sublattices, respectively, and their structural formulas allowing for the inequivalent positions can be written in the form $YBa_2Cu(1)Cu(2)_2O(1)_2O(2)_2O(3)_2O(4)$ and $YBa_2Cu(1)Cu(2)_2O(1)_2O(2)_2O(3)_2$. The positions of the atoms in the unit cell are described by the following coordinates: (0.5, 0.5, 0.5) for Y; (0.5, 0.5, 0.1881) and (0.5, 0.5, −0.1881) for Ba; (0, 0, 0) for Cu(1); (0, 0, 0.3574) and (0, 0, −0.3574) for Cu(2); (0, 0, 0.1573) and (0, 0, −0.1573) for O(1); (0, 0.5, 0.3782) and (0, 0.5, −0.3782) for O(2); (0.5, 0, 0.3782) and (0.5, 0, −0.3782) for O(3); (0, 0.5, 0) for O(4) (Ref. 21). The unit cell parameters of the rhombohedral phase are: *a*) 3.817, $b = 3.883$, $c = 11,683$ Å; for the tetragonal phase these parameters are $a = b = 3.869$, $c = 11.723$ Å (Ref. 21). The lattice sums U_Φ and $U_{\alpha\beta}$ were calculated on a computer and the summation was carried out within spheres of 30 Å radius.

The results of calculations of the lattice sums are given in Table II. The lattice sum tensors U_k of the individual substrates (and, consequently, the combined EFG tensor) are diagonal in terms of the crystallographic axes and this applies to all the cation sublattices in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$. Therefore, in Table II, we used not U_{xxk}, U_{yyk}, and U_{zzk}, but U_{aak}, U_{bbk}, and U_{cck}. There is a satisfactory agreement between our data and the published fragmentary results of calculations of the total EFG carried out using the point charge model.[9,22-24] A special feature of our calculations is that the contribution of each sublattice to the EFG is obtained separately and it is possible to vary the charges e_k^* when comparing the calculated and experimental EFG tensor parameters.

A correct comparison requires a simultaneous analysis of the relationships

$$\sum_k e_k^{*}U_{zzk}=eq^e_{cr}, \tag{7}$$

$$\sum_k e_k^{*}(U_{xxk}-U_{yyk}-\eta U_{zzk})=0, \tag{8}$$

which are obtained from Eqs. (1) and (2) for both copper positions. The relationships (7) and (8) differ from Eqs. (5) and (6) because they require such a selection of the axes that $|V_{zz}|\geqslant|V_{yy}|\geqslant|V_{xx}|$. Since the orientation of the principal axes of the tensors U_k relative to the crystallographic axes is different for different sublattices (Table II), it follows that the orientation of the principal axes of the total EFG tensor depends on the ratio of the effective charges e_k^* in the sublattices. Therefore, we cannot know *a priori* which crystallographic directions should be regarded as the *z*, *x*, and *y* axes of the EFG tensor. We can select the principal axes bearing in mind that the EFG at a site is governed primarily by the immediate environment of the site. Figure 3 shows the immediate environments of Cu(1) and Cu(2) in $YBa_2Cu_3O_7$, whereas Fig. 4 shows the qualitative dependences of the diagonal components of the EFG tensor on the ratio of the charges O(1) and O(2).

Bearing in mind that in the case of Cu(1) we have $eq^e_{cr} > 0$ and $\eta \sim 1$ (it follows from the condition $\eta = 1$ that one of the diagonal components of the EFG tensor vanishes), we can identify two ranges of the possible values of e_8^*/e_5^* for $YBa_2Cu_3O_7$ and these are shown shaded in Fig. 4. For

TABLE II. Contributions made to the EFG by various sublattices (in units of $e/\text{Å}^3$) at the cation sites in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$.

Site	EFG component	Sublattice							
		Y	Ba	Cu(1)	Cu(2)	O(1)	O(2)	O(3)	O(4)
					$YBa_2Cu_3O_7$				
Cu(1)	U_{aa}	−0,023	0,000	+0,057	−0,051	−0,286	−0,049	−0,045	−0,202
	U_{bb}	−0,024	−0,004	+0,052	−0,051	−0,290	−0,046	−0,050	+0,556
	U_{cc}	+0,047	+0,004	−0,109	+0,102	+0,576	+0,095	+0,095	−0,354
Cu(2)	U_{aa}	+0,025	−0,015	−0,026	+0,025	−0,087	−0,230	+0,548	−0,025
	U_{bb}	+0,028	−0,012	−0,025	+0,021	−0,089	+0,522	−0,246	−0,022
	U_{cc}	−0,053	+0,027	+0,051	−0,046	+0,176	−0,292	−0,302	+0,047
Ba	U_{aa}	−0,028	+0,032	0,000	−0,015	+0,084	−0,002	−0,074	+0,021
	U_{bb}	−0,028	+0,027	+0,002	−0,012	+0,093	−0,076	−0,001	−0,052
	U_{cc}	+0,056	−0,059	−0,002	+0,027	−0,177	+0,078	+0,075	+0,031
Y	U_{aa}	+0,057	−0,057	−0,023	+0,049	−0,044	+0,284	−0,190	−0,024
	U_{bb}	+0,052	−0,057	−0,024	+0,056	−0,044	−0,200	+0,281	−0,024
	U_{cc}	−0,109	+0,114	+0,047	−0,105	+0,088	−0,084	−0,091	+0,048
					$YBa_2Cu_3O_6$				
Cu(1)	U_{aa}	−0,023	+0,004	+0,054	−0,050	−0,274	−0,049	−0,045	
	U_{bb}	−0,023	+0,004	+0,054	−0,050	−0,274	−0,045	−0,049	–
	U_{cc}	+0,046	−0,008	−0,108	+0,100	+0,548	+0,094	+0,094	
Cu(2)	U_{aa}	+0,025	−0,014	−0,025	+0,023	−0,089	−0,233	+0,523	
	U_{bb}	+0,025	−0,014	−0,025	+0,023	−0,089	+0,523	−0,233	–
	U_{cc}	−0,050	+0,028	+0,050	−0,046	+0,178	−0,290	−0,290	
Ba	U_{aa}	−0,028	+0,029	+0,002	−0,014	+0,089	−0,004	−0,072	
	U_{bb}	−0,028	+0,029	+0,002	−0,014	+0,089	−0,072	−0,004	–
	U_{cc}	+0,056	−0,058	−0,004	+0,028	−0,178	+0,076	+0,076	
Y	U_{aa}	+0,054	−0,055	−0,023	+0,050	−0,044	+0,279	−0,193	
	U_{bb}	+0,054	−0,055	−0,023	+0,050	−0,044	−0,193	+0,279	–
	U_{cc}	−0,108	+0,110	+0,046	−0,100	+0,088	−0,086	−0,086	

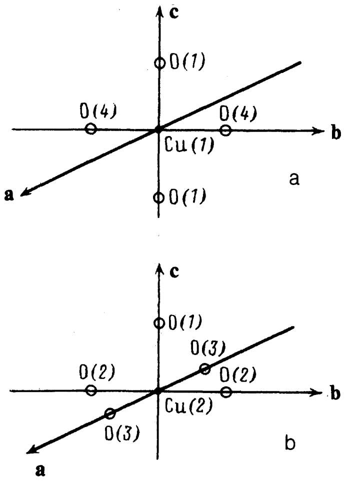

FIG. 3. Immediate environment of Cu(1) and Cu(2) in $YBa_2Cu_3O_7$.

both regions the principal component of the EFG tensor is V_{aa}, so that Eq. (7) for both regions is of the form

$$\sum_k e_k^* U_{aak}(1) = eq^e_{cr}. \tag{9}$$

In the region A we have $|V_{cc}| > |V_{bb}|$ and Eq. (8) becomes

$$\sum_k e_k^*[U_{bbk}(1) - U_{cck}(1) - \eta(1)U_{aak}(1)] = 0. \tag{10}$$

In the region B, where $|V_{bb}| > |V_{cc}|$ and Eq. (8) transforms to

$$\sum_k e_k^*[U_{cck}(1) - U_{bbk}(1) - \eta(1)U_{aak}(1)] = 0 \tag{11}$$

[the quantities $U_{aak}(1)$, $U_{bbk}(1)$, $U_{cck}(1)$, $eq^e_{cr}(1)$ and $\eta(1)$ apply to the Cu(1) positions].

Since Cu(2) is at the center of the base an almost-square perimeter (Fig. 3b), it follows that when the charges in the sublattices O(2) and O(3) do not differ too greatly, the EFG tensor axis z is always oriented along the crystallographic axis c:

$$\sum_k e_k^* U_{cck}(2) = eq^e_{cr}\ (2). \tag{12}$$

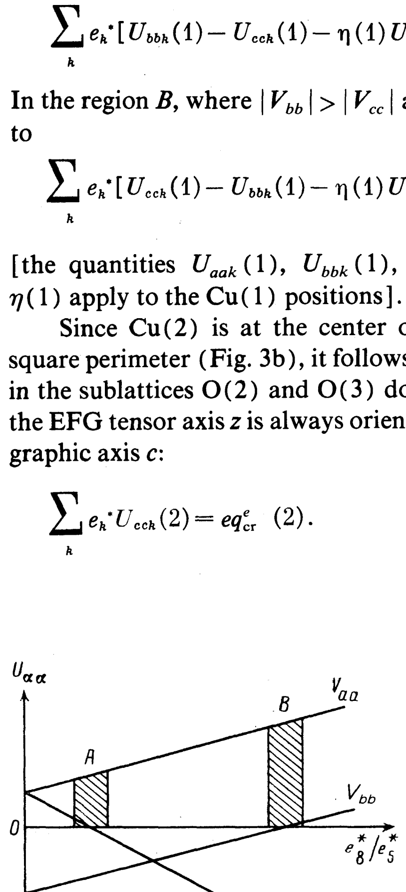

FIG. 4. Qualitative dependences of the diagonal components of the EFG tensor at the Cu(1) sites in the $YBa_2Cu_3O_7$ lattice on the ratio of the O(1) and O(4) charges.

The low values of η for the Cu(2) position imply similarity of the values of V_{aa} and V_{bb}, and the difference between them can be of either sign, so that Eq. (8) becomes either

$$\sum_k e_k^*[U_{aak}(2) - U_{bbk}(2) - \eta(2)U_{cck}(2)] = 0, \tag{13}$$

or

$$\sum_k e_k^*[U_{bbk}(2) - U_{aak}(2) - \eta(2)U_{cck}(2)] = 0 \tag{14}$$

[the quantities $U_{aak}(2)$, $U_{bbk}(2)$, $U_{cck}(2)$, $eq^e_{cr}(2)$, and $\eta(2)$ apply to the Cu(2) position].

The four equations (9), (10) [or (11)], (12), (13) [or (14)] relating eight unknowns $e_1^* - e_8^*$ must be supplemented by an equation describing the electrical neutrality of the lattice

$$e_1^* + 2e_2^* + e_3^* + 2e_4^* + 2e_5^* + 2e_6^* + 2e_7^* + e_8^* = 0 \tag{15}$$

and also by three additional equations that give the relationships between the individual values of e_k^*, which will be discussed later in Sec. 3.3.

3.2. Determination of the absolute charges of the lattice ions

The absolute values of e_k^* can be found from Eq. (9) [or from Eq. (12)] because these two equations have zero free terms and can give only the relative values of the charges. No combination of the Y^{3+}, Ba^{2+}, Cu^+, Cu^{2+}, Cu^{3+}, and O^{2-} ions at the lattice sites in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ can ensure even an approximate agreement between the calculated value of $V_{zz} = eq_{cr}$ and the experimental value eq^e_{cr} at the copper sites. The calculated value is always greater than the experimental one when η and the sign of the principal component of the EFG tensor are the same. Since the valences of copper and oxygen in $YBa_2Cu_3O_7$ cannot yet be regarded as fully established, we carried out a comparison for $YBa_2Cu_3O_6$ whose structural formula

$$Y^{3+}Ba^{2+}Cu(1)^{+}Cu(2)_2^{2+}O_6^{2-} \tag{16}$$

has been accepted practically without questioning. The calculations for the Cu(1) position gave $V_{zz} = 1.253\ e/\text{Å}^3$ and $\eta = 0$, whereas the experimental values were $eq^e_{cr} = -0.301 \pm 0.006\ e/\text{Å}^3$ and $\eta \leqslant 0.2$, i.e., the ratio was $|V_{zz}|/|eq^e_{cr}| \sim 4.2$. A quantitative agreement between the calculated and experimental values of the principal component of the EFG tensor is not obtained either for the barium sites: $|eq^e_{cr}| = 0.069 \pm 0.006\ e/\text{Å}^3$, whereas the calculated value is $V_{zz} = +0.158\ e/\text{Å}^3$.

We cannot assume that this discrepancy is due to the complexity of the $YBa_2Cu_3O_{7-x}$ lattices. A similar discrepancy is obtained also for the copper oxide Cu_2O. It is generally accepted that this is an ionic compound with the structural formula $Cu_2^+O^{2-}$ (Ref. 9). The Mössbauer emission spectrum of $^{67}Cu_2O$ recorded by us is shown in Fig. 1c. It is a quadrupole triplet, corresponding to an equidistant position of the daughter $^{67}Zn^{2+}$ ions at the copper site. It should be noted that the immediate environment of copper in Cu_2O and Cu(1) in $YBa_2Cu_3O_6$ is similar and the parameters of the Mössbauer spectra of $^{67}Cu(^{67}Zn)$ in Cu_2O and $YBa_2Cu_3O_6$ are also similar, confirming our interpretation of the Mössbauer spectrum of $YBa_2{}^{67}Cu_3O_6$, which is attributed to the $^{67}Zn^{2+}$ centers at the Cu(1) sites (Table I). In calculations of the EFG tensor at the copper sites in Cu_2O we assumed the following coordinates of the atoms in a unit cell: Cu (1/4, 1/4, 1/4), (3/4, 3/4, 1/4), (1/4, 3/4, 3/4), (3/4, 1/4, 3/4); O (0, 0, 0), (1/2, 1/2, 1/2); here, $a = b = c = 4.27$ Å (Ref. 25). The EFG tensor expressed in terms of the crystallographic axes is off-diagonal and the z axis of the diagonalized tensor has the [111] direction. Calculations give $V_{zz} = -1.092\ e/\text{Å}^3$ for $\eta = 0$, which is in agreement with the experimental value of the asymmetry parameter and with the sign of the principal component of the EFG tensor, but exactly as in the case of $YBa_2Cu_3O_6$, the absolute value of V_{zz} is almost four times as high as the experimental value $eq^e_{cr} = -0.280 \pm 0.006\ e/\text{Å}^3$.

Since, as pointed out already, the reason for the discrepancy between the calculated and experimental values of eq_{cr} at the lattice sites is not the valence contribution to the total EFG (see Ref. 11), there are two ways of ensuring agreement between the calculated and experimental values of e^2qQ and eq^e_{cr}: a revision of the generally accepted values of the Sternheimer coefficients when converting the experimental value of e^2qQ to eq^e_{cr} and a reduction by the same factor of the charges e^*_k of all the lattice ions in the calculation of V_{zz}, i.e., a reduction in the charge contrast of the lattice.

The authors of Ref. 9 interpreted the NQR spectra of the ^{63}Cu isotope in Cu_2O and, instead of the generally accepted value $\gamma(Cu^+) = -17$ (Ref. 18), they used $\gamma(Cu^+) = -5.48$. The use of this fitting procedure in the case of our data on ^{67}Zn in Cu_2O gives not $\gamma(Zn^{2+}) = -12.2$, but $\gamma(Zn^{2+}) = -2.41$. If the latter value is applied to the data on ^{67}Zn in $YBa_2Cu_3O_6$, it is found that $eq^e_{cr} = -1.167 \pm 0.006\ e/\text{Å}^3$, which is quite close to the calculated value $V_{zz} = 1.253\ e/\text{Å}^3$.

The ability to use in the EFG calculations the ion charges smaller than those expected formally could be explained on the basis of general considerations, but it is not clear what reduction in the charges is permissible. Attempts to apply this approach to ^{67}Zn in the simple lattice of Cu_2O gives the effective charge $+0.3e$ for copper and $-0.6e$ for oxygen, which are unlikely to be correct for this ionic compound.

On the whole, this ambiguity of the interpretation means that we cannot determine the absolute values of the charges of the lattice atoms from the quantities eq^e_{cr}.

3.3. System of equations for the effective charges of ions and its solution

The problem of variation of the charge contrast and of the Sternheimer coefficients can be avoided in the case of the lattices that contain only structurally inequivalent copper atoms. In particular, the $YBa_2Cu_3O_7$ lattice has two such structurally inequivalent positions Cu(1) and Cu(2) and, therefore, the ratio $p = (e^2qQ)_{Zn(1)}/(e^2qQ)_{Zn(2)}$ should be independent of the charge contrast of the lattice [it is the same for the calculation of the EFG at the Cu(1) and Cu(2) sites] or of the selection of the Sternheimer coefficients [they should be similar for Zn^{2+} at the Cu(1) and Cu(2) positions]. Consequently, Eqs. (9) and (12) should be replaced with

$$\sum_k e_k^*[U_{cck}(2) - pU_{aak}(1)] = 0, \tag{17}$$

which is obtained by dividing Eq. (12) by Eq. (9), and which contains the experimentally determined parameter $p = 0.59 \pm 0.04$, independent of the Sternheimer coefficient and of the quadrupole moment of the nucleus.

We have considered above four linear equations (10) [or (11)], (13) [or (14)], (15), and (17), and at first sight the number of these equations is insufficient to obtain even a qualitative solution of the problem. However, the structure of Eqs. (10), (11), (13), (14), and (17) is such that the coefficients in front of the charges of the oxygen ions (e^*_5–e^*_8) are at least an order of magnitude greater than the coefficients in front of the cation charges (e^*_1–e^*_4). This reflects the simple fact that the EFG tensor at the copper sites is governed primarily by the charges of the ions in the immediate environment, i.e., by the oxygen ions. The four equations mentioned above determine the charges of the oxygen ions (e^*_5–e^*_8), apart from small corrections that depend on the cation charges (e^*_1–e^*_4).

The number of independent experimental parameters is insufficient to determine the cation charge. However, we can make a number of natural assumptions about the cation charge bearing in mind that the uncertainty introduced by such assumptions can cause only small variations in the oxygen charge. We shall impose the following conditions on the cation charge.

1) The charges of the Y and Ba ions are in the ratio 3:2, which corresponds to the only valences allowed for these ions:

$$2e_1^* - 3e_2^* = 0. \tag{18}$$

2) The charge of the Ba ion is equal to the charge of the O(1) ion, which corresponds to an electrical neutrality of the Ba–O plane in the $YBa_2Cu_3O_7$ lattice:

$$e_2^* + e_5^* = 0. \tag{19}$$

3) Finally, we shall vary the ratio S of the charge of the Cu(1) ion to the charge of Cu(2) within the range from 1:3 to 3:1 since the valences could vary from +1 to +3:

$$e_3^* - Se_4^* = 0. \tag{20}$$

Equations (18), (19), and (20), together with the four equations discussed above form a homogeneous system of seven equations for eight charges. Such a system can give only the relative charges e^*_k with one of them as unity. The solutions can be physical by supplementing the system with an equation that gives the total charge of the oxygen ions as a sum of their valences:

$$2e_2^* + 2e_6^* + 2e_7^* + e_8^* = Q_v. \tag{21}$$

The quantity Q_v should be taken as equal to $-14e$, if we assume standard valences for all the oxygen atoms, or $-13e$, if we assume the existence of a hole localized at an oxygen ion.[26]

When solving this system of equations we varied Q_v and S, as mentioned above, as well as the parameters p and η for Cu(1) and Cu(2) within the errors in their determination (Table I). The results obtained are collected in Table III.

TABLE III. Effective charges (in units of the electron charge) of ions at the lattice sites in $YBa_2Cu_3O_7$.

Region in Fig. 4.	Q_v	S	Y	Ba	Cu(1)	Cu(2)
A	$-13e$	1 : 3	3,09±0,10	2,06±0,06	3,47±0,13	1,16±0,05
		1 : 1	3,14±0,08	2,09±0,05	1,89±0,06	1,89±0,06
		3 : 1	3,18±0,07	2,12±0,05	0,80±0,02	2,40±0,07
	$-14e$	1 : 3	3,33±0,11	2,22±0,06	3,75±0,14	1,25±0,06
		1 : 1	3,38±0,09	2,25±0,05	2,04±0,06	2,04±0,06
		3 : 1	3,42±0,08	2,28±0,06	0,86±0,02	2,58±0,08
B	$-13e$	1 : 3	2,26±0,06	1,51±0,04	1,11±0,02	3,32±0,06
		1 : 1	2,04±0,05	1,36±0,04	2,75±0,10	2,75±0,10
		3 : 1	1,69±0,08	1,13±0,05	5,44±0,17	1,81±0,06
	Q_v	S	O(1)	O(2)	O(3)	O(4)
A	$-13e$	1 : 3	−2,06±0,06	−1,89±0,10	−1,78±0,10	−1,54±0,05
		1 : 1	−2,09±0,05	−1,93±0,07	−1,81±0,07	−1,34±0,04
		3 : 1	−2,12±0,05	−1,95±0,07	−1,84±0,07	−1,20±0,04
	$-14e$	1 : 3	−2,22±0,06	−2,04±0,11	−1,92±0,10	−1,66±0,06
		1 : 1	−2,25±0,05	−2,08±0,08	−1,95±0,08	−1,44±0,04
		3 : 1	−2,28±0,06	−2,10±0,08	−1,98±0,08	−1,29±0,04
B	$-13e$	1 : 3	−1,51±0,04	−1,93±0,17	−1,83±0,17	−2,48±0,06
		1 : 1	−1,36±0,04	−1,89±0,21	−1,79±0,20	−2,92±0,05
		3 : 1	−1,13±0,05	−1,83±0,24	−1,74±0,24	−3,62±0,07

There are two sets of values of e_k^* which satisfy the experimental values of p and η, as already mentioned in connection with selection of Eqs. (10) and (11) and as shown in Fig. 4. They correspond to different orientations of the principal axes of the EFG tensor at the Cu(1) sites relative to the crystallographic axes. However, it is clear from Table III that the solutions corresponding to the region B in Fig. 4 can hardly be physically meaningful, because they require far too high charges of O(4) and of at least one of the copper ions. In contrast, the solution corresponding to the region A gives reasonable results for all the lattice sites in $YBa_2Cu_3O_7$.

An important feature of the solution for the region A is that in the case of the O(1), O(2), O(3), and O(4) ions there is an approximate ratio of the charges 2:2:2:1. This ratio can clearly be interpreted as the result of localization of a hole (i.e., a reduction in the valence) at the O(4) sites. The deviations from the 2:2:2:1 ratio, namely a larger charge at O(4) and a smaller at O(2) and O(3), indicate a partial transfer of this hole to the O(2) and O(3) sites. Hence, we can conclude that the correct total charge of the oxygen ions is $Q_v = -13e$. This is formally manifested by the fact that the charges of the oxygen ions and the yttrium and barium ions are closer to integers if $Q_v = -13e$ than if $Q_v = -14e$.

3.4. Determination of the valence state of copper

It is clear from Table III that the likely charges of all the ions in the $YBa_2Cu_3O_7$ lattice can be selected for an arbitrary ratio of the charges of the copper ions Cu(1) and Cu(2). This means that direct determination of the charges and from them the valence states of Cu(1) and Cu(2) cannot be made on the basis of the tensor parameters at the Cu(1) and Cu(2) sites. However, the valence state of copper can be found by comparing the valences of all the cations with the valence of oxygen. Since the total valence of oxygen Q_v is 13 and the valences of yttrium and barium are 3 and 2, respectively, the net valence of three copper atoms should be 6. The only possible combination of the valences is that in which the copper is divalent at the Cu(1) and Cu(2) sites. Consequently, the structural formula $YBa_2Cu_3O_7$ can be written in the form

$$Y^{3,14+}\,Ba_2^{2,09+}Cu(1)^{1,89+}\,Cu(2)_2^{1,89+}O(1)_2^{2,09-}O(2)_2^{1,93-}O(3)_2^{1,81-}O(4)^{1,34-}. \tag{22}$$

The structural formula (22) is in agreement with the experimental NQR criterion for the ^{63}Cu isotope ($e^2qQ>0$ at both copper sites).[1] The same structural formula and the NQR data for ^{63}Cu (Refs. 1 and 8) can be used to estimate the contribution of the valence electrons to the total EFG at the ^{63}Cu nuclei. In the case of the Cu(1) position a calculation gives $eq_{cr} = 0.982 \pm 0.025\ e/Å^3$ ($\eta = 0.92$) or $e^2q_{cr}(1-\gamma)Q = 61.9 \pm 1.6$ MHz [on the assumption that $\gamma(Cu^{2+}) = -7.59$ (Ref. 27) and $Q(^{63}Cu) = -0.211$ b], since the experimental value is $e^2qQ = 38.2$ MHz (Refs. 1 and 8). Consequently, in the case of the Cu(1) centers the contribution of the valence electrons to the total EFG amounts to $e^2q_{val}(1-R)Q = 100.1 \pm 1.6$ MHz. A similar calculation for the Cu(2) site [$eq_{cr} = 0.581 \pm 0.015\ e/Å^3$, $\eta = 0.0$, $e^2q_{cr}(1-\gamma)Q = -36.6 \pm 1.0$ MHz] gives $e^2q_{val}(1-R)Q = 99.4 \pm 1.0$ MHz (when the experimental value $e^2qQ = 62.8$ MHz is used from Refs. 1 and 8). The similarity of the contribution of the valence electrons to the total EFG at the ^{63}Cu nuclei located at the Cu(1) and Cu(2) sites is evidence of similarity of the electron structures of these centers. The value $e^2q_{val}(1-R)Q = 100$ MHz was obtained also for the copper centers in La_2CuO_4 (Ref. 9), where copper is known to be divalent: Cu^{2+}. Clearly, the Cu(1) and Cu(2) centers in $YBa_2Cu_3O_7$ are also divalent.

We are now faced with the natural question is it possible to compare the calculated and experimental parameters of the EFG tensor using

$$F = \frac{(e^2qQ)_{YBa_2Cu_3O_7}}{(e^2qQ)_{YBa_2Cu_3O_6}}$$

for the relevant centers, since in compounds with similar compositions and structures we can expect similar values of the Sternheimer coefficient of these centers and a similar contrast of the lattices? For example, in the case of the $^{67}Zn^{2+}$ (1) centers in the model described by Eqs. (16) and (22) the calculated ratio is $F = 0.78 \pm 0.02$, whereas the experimental value is $F^e = 0.86 \pm 0.04$. The corresponding values for the ^{133}Cs centers are $F = 0.92 \pm 0.02$ and $F^e = 0.69 \pm 0.13$. Although F and F^e are similar for the centers in question, they do not agree within the limits of the experimental error. It therefore follows that the simple model of the compound $YBa_2Cu_3O_6$ described by Eq. (16) does not represent the true effective charges of the ions.

4. CONCLUSIONS

The method of Mössbauer emission spectroscopy was applied to the $^{67}Cu(^{67}Zn)$ and $^{133}Ba(^{133}Cs)$ isotopes to determine the EFG tensor parameters at the copper and barium sites of the compounds $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$. The experimental results were compared with the results of calculations of the EFG tensor parameters carried out using the model of point charges. The quantitative agreement between the calculated and experimental values of the principal component of the EFG tensor was not achieved, which was attributed to the absence of reliable data on the Sternheimer coefficients for the Zn^{2+} and Cs^+ centers and the inaccuracies of the model used in the calculations. It was found that these problems can be eliminated if the parameters of the EFG tensor are determined for the two structurally inequivalent positions of the copper atoms (in the case of $YBa_2Cu_3O_7$). The most probable structural formula was obtained for the latter compound and it corresponds to the divalent state of copper at both positions and to localization of a hole mainly at the O(4) centers.

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