Mössbauer determination of the gradient of the electric-field at the cationic sites of $La_{2-x}(Sr, Ba)_xCuO_4$ lattice

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The parameters of the electric-field gradient (EFG) at the cationic sites of the $La_{2-x}(Sr, Ba)_xCuO_4$ lattice (the principal component of the EFG tensor *eq* and the asymmetry parameter) were determined experimentally by Mössbauer spectroscopy on the isotopes $^{57}Co(^{57m}Fe)$, $^{67}Cu(^{67}Zn)$, and $^{133}Ba(^{133}Cs)$. The computed values of *eq* (point-charge model) did not agree quantitatively with the experimental values of *eq*. This is explained by the lack of reliable data on the Sternheimer coefficients for the ions Fe^{3+}, Zn^{2+}, and Cs^{+} and the charge ratio of the $La_{2-x}(Sr, Ba)_xCuO_4$ lattice. It is shown by comparing the theoretically computed and experimental dependences of *eq* on *x* that holes, appearing when La^{3+} is replaced by Sr^{2+}, are localized predominantly on oxygen atoms located in the same plane as the copper atoms.

Alivalent substitution of Sr^{2+} or Ba^{2+} for La^{3+} leads to the appearance of the superconducting state in La_2CuO_4 crystals. It is obvious that holes and possibly other competing centers arising when such a substitution is made play the decisive role. The distribution of these centers over the lattice sites can in principle be determined from data on the nuclear quadrupole resonance (NQR) on the copper and lanthanum isotopes. The idea of this approach consists of comparing the parameters of the electric field gradient (EFG) on the nucleus being studied (the principal component *eq* and the asymmetry parameter η of the EFG tensor) determined from NQR with the values calculated in the approximation that the EFG is produced only by the ions of the crystal lattice (eq_{cr}, η_{cr}). However attempts to make such a comparison on the basis of NQR data for the isotopes $^{63,65}Cu$ (Ref. 1) and ^{139}La (Ref. 2) have been unsuccessful. This is attributable to the fact that in $La_{2-x}(Sr, Ba)_xCuO_4$ copper has a partially filled 3*d*-shell (Cu^{2+}, $3d^9$), and this makes it impossible to distinguish the EFG parameters from the NQR spectra in the crystal, while for lanthanum a reliable procedure for determining the quantities *eq* and η from the NQR spectra is not available.

Emission Mössbauer spectroscopy on the isotopes $^{67}Cu(^{67}Zn)$ and $^{133}Ba(^{133}Cs)$ does not have these drawbacks.[3] After the parent nuclei (^{67}Cu, ^{133}Ba) decay the Mössbauer nuclei (^{67}Zn, ^{133}Cs) form at the corresponding lattice sites, and in addition the daughter zinc and cesium atoms have a closed *d*-shell (Zn^{2+}, Cs^{+}) and this makes it possible to determine from the Mössbauer data the parameters of the EFG which is created at the cationic sites by the lattice ions. In principle, a very similar situation is realized with isovalent substitution of Cu^{2+} for $^{57}Co^{2+}$: after the ^{57}Co nucleus decays the daughter nucleus ^{57m}Fe forms at the site of the copper ion. In a material with hole conductivity, such as $La_{2-x}Sr_xCuO_4$, the daughter iron atom can be, with high probability, in the state Fe^{3+} with a spherical $3d^5$ shell. This makes it possible to determine from the Mössbauer spectra the parameters of the crystal EFG. On the other hand, the lifetime of the Mössbauer level of ^{57m}Fe is equal to $\sim 10^{-7}$s, which is too short for formation of defects which compensate the charge difference between Cu^{2+} and the substituent ion Fe^{3+}. For this reason, the environment of Fe^{3+} in the $La_{2-x}Sr_xCuO_4$ lattice can be considered to be the same as at a normal copper site.

For the investigations we synthesized by conventional ceramic technology the following samples: $La_{2-x}Sr_xCuO_4$: ^{57}Co ($x = 0.1, 0.2, 0.3$; cobalt concentration $\sim 10^{18}$ atoms/cm^3), $La_{2-x}Sr_x{}^{67}CuO_4$ ($x = 0.1, 0.15$, and 0.2), and $La_{2-x}{}^{133}Ba_xCuO_4$ ($x = 0.1$ and 0.3). The control samples were single-phase and their structure was of the type K_2NiF_4 with $T_c = 25, 37, 27$ and $\leqslant 4.2$ K, respectively, for $x = 0.1, 0.15, 0.2$, and 0.3. The Mössbauer spectra were obtained at 295 K (^{57}Co) and 4.2 K (^{67}Cu, ^{133}Ba) with the absorbers $K_4{}^{57}Fe(CN)_6 \cdot 3H_2O$, ^{67}ZnS, and $^{133}CsCl$.

The Mössbauer spectra of the $La_{2-x}Sr_x{}^{67}CuO_4$ samples consist of quadrupole triplets (Fig. 1 and Table I), corresponding to Zn^{2+} centers at the normal copper sites. For the sample with $x = 0.2$ an additional triplet appears in the spectrum (Fig. 1). This triplet has a relative intensity of $\sim 20\%$ and its appearance is probably connected with a nonuniform distribution of strontium atoms.

The Mössbauer spectra of the $La_{2-x}Sr_xCuO_4$:^{57}Co samples consist of quadrupole doublets (Fig. 2), whose parameters (Table II) are close to the parameters of the Mössbauer spectra of the samples La_2CuO_4:^{57}Co,[4] and by analogy to the results of Ref. 4 the spectra of the $La_{2-x}Sr_xCuO_4$:^{57}Co samples should be referred to $^{57m}Fe^{3+}$ centers at the normal copper sites.

The Mössbauer spectra of the $La_{2-x}{}^{133}Ba_xCuO_4$ samples consist of somewhat broadened single lines (the FWHH was $\Gamma_{exp} = 1.05 \pm 0.02$ mm/s, while the instrumental width of the spectral line for the spectrum with the ^{133}BaO source and the $^{133}CsCl$ absorber was $\Gamma_{ins} = 0.90 \pm 0.02$ mm/s) (Fig. 3), corresponding to $^{133}Cs^{+}$-centers at the barium sites. We attributed the broadening of the spectra to unresolved quadrupole splitting (Table III).

Using the relation

$$eq = (1-\gamma)\, eq^e_{cr} \qquad (1)$$

we determined from the experimental values of e^2qQ the experimental values of the principal tensor component of the EFG produced at the cationic sites by the lattice ions, eq^e_{cr} (for $^{67}Zn^{2+}$ the Sternheimer coefficient $\gamma = -12.2$ (Ref.

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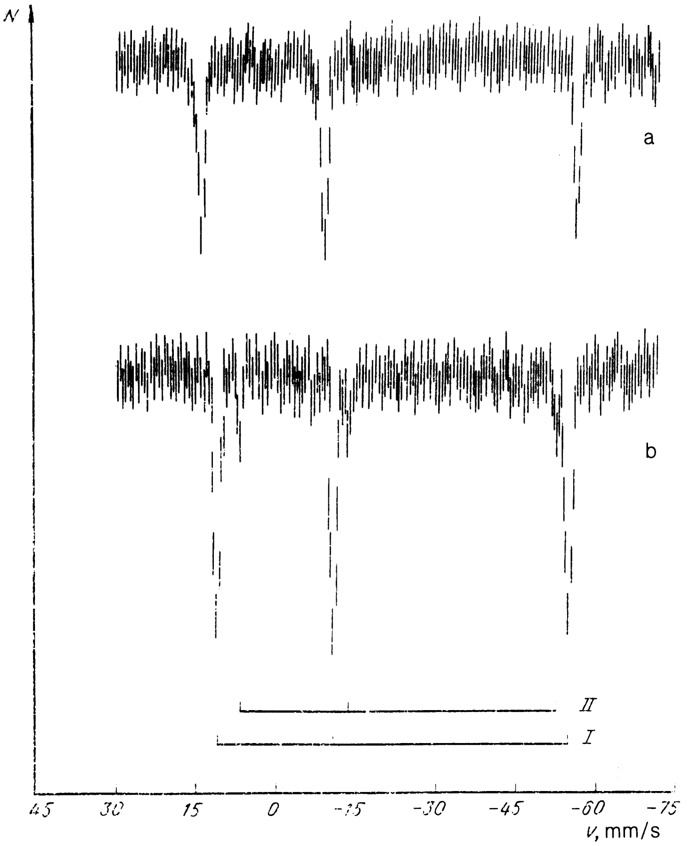

FIG. 1. The Mössbauer spectra of $La_{2-x}Sr_x{}^{67}CuO_4$ at 4.2 K: $x = 0.1$ (a) and 0.2 (b). I and II are the positions of the triplet lines in the spectrum *b*.

5), the quadrupole moment of the nucleus $Q = 0.17\ b$ (Ref. 6); for $^{57m}Fe^{3+}$ $\gamma = -7.97$ (Ref. 7), $Q = 0.213\ b$ (Ref. 8); for $^{133}Cs^+$ $\gamma = -121.3$ (Ref. 9), $Q = 0.003\ b$ for the ground state, and $Q = -0.22\ b$ for the excited state, Ref. 9).

In order to identify the compensating centers arising in the $La_{2-x}Sr_xCuO_4$ lattice we calculated the tensor components of the EFG at the cationic lattice sites on the basis of the point-charge model. The results were represented as a sum of the contributions from separate sublattices:

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

where k is the index of summation over the sublattices, i is the index of summation over the sites of a sublattice, α and β are Cartesian coordinates, e_k^* is the charge of the atoms in the kth sublattice, and r_{ki} is the distance from the ion to the copper (lanthanum) site under study.

The $La_{2-x}Sr_xCuO_4$ lattice consists of four sublattices, as described by the structural formula $(La, Sr)_2CuO(1)_2O(2)_2$. The positions of the atoms in the unit cell were given in the manner following Ref. 10:

(La, Sr)—(0, 0, 0.36046 *c*), (0, 0, 0.63954 *c*), (*a*/2, *b*/2, 0.13954 *c*), (*a*/2, *b*/2, 0.86046 *c*);

Cu—(0, 0, 0), (*a*/2, *b*/2, *c*/2);

O(1)—(0, 0, 0.1824 *c*), (0, 0, 0.8176 *c*), (*a*/2, *b*/2, 0.3176 *c*), (*a*/2, *b*/2, 0.6824 *c*);

O(2)—(*a*/2, 0, 0), (0, *b*/2, 0), (*a*/2, 0, *c*/2), (0, *b*/2, *c*/2).

The x-dependences of the unit-cell parameters were taken from Ref. 11. The lattice sums (2) were calculated numerically. The summation was performed inside a sphere with a radius of 30 Å.

The tensors of the lattice sums of U_k from separate sublattices are diagonal in the crystallographic axes (therefore,

TABLE I. Parameters of the Mössbauer spectra of $La_{2-x}Sr_x{}^{67}CuO_4$.

x	e^2qQ, MHz	η_{cr}	eq^c_{cr}, $e/Å^3$
0,1	11,8±0,3	≤0,2	0,150±0,004
0,15	11,4±0,3	≤0,2	0,146±0,004
0,2	11,1±0,3	≤0,2	0,142±0,004
	9,7±0,3	≤0,2	0,124±0,004

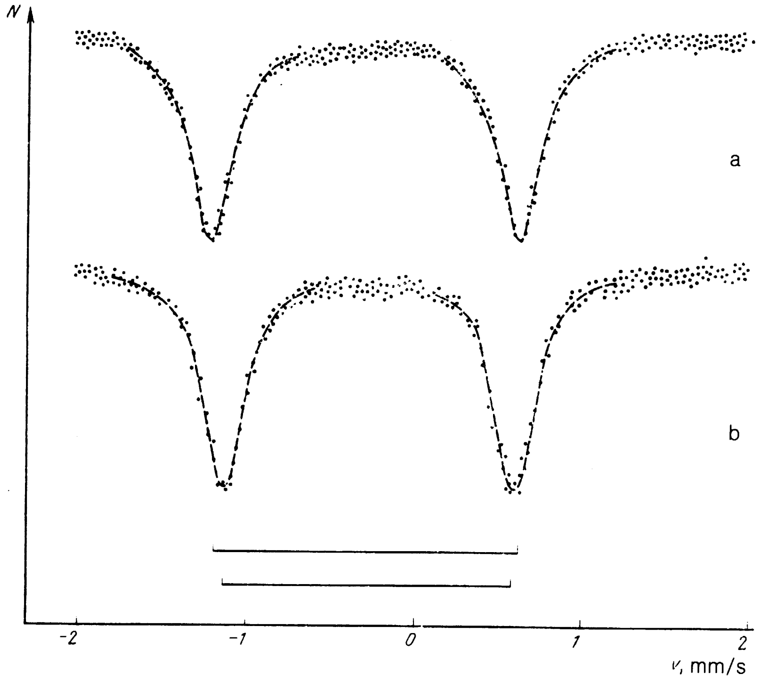

FIG. 2. Mössbauer spectra of $La_{2-x}Sr_xCuO_4$:^{57}Co at 295 K: $x = 0.1$ (a) and 0.3 (b).

the total EFG tensors are also diagonal). The principal axis of the EFG tensors is also the crystallographic *c* axis, and the tensors are axisymmetric. The computational results are presented in Table IV.

Agreement between the computed values eq_{cr} and the experimental values eq^{e}_{cr} for the copper and barium sites cannot be obtained for any combination of the La^{3+}, Sr^{2+}, Ba^{2+}, Cu^{2+}, Cu^{3+}, and O^{2-} ions in the $La_{2-x}(Sr, Ba)_xCuO_4$ lattice: the computed values for the cases of $^{67}Zn^{2+}$ and $^{133}Cs^{+}$ are larger than the experimental values, and the reverse pattern is observed for the case $^{57m}Fe^{3+}$.

This disagreement can be eliminated either by revising the generally accepted values of the Sternheimer coefficients for the Zn^{2+}, Fe^{3+}, and Cs^{+} ions or changing by the same factor the charges of all lattice atoms (changing the charge ratio of the lattice). However this leads to an obvious ambiguity of interpretation, and for this reason in order to determine the location of the hole appearing with alivalent substitution of Sr^{2+} for La^{3+}, we decided to compare the relations

$$P^{\text{э}}=(e^2qQ)_x/(e^2qQ)_{x=0,1}, \quad P=(q_{cr})_x/(q_{cr})_{x=0,1},$$

since these ratios should not depend either on the choice of Sternheimer coefficients or on the charge ratio of the lattice. Figure 4 shows the dependence $P(x)$ for the copper and lanthanum (barium) sites. The calculation was performed for four models: the hole is located in the copper sublattice, i.e., the charge of the hole is uniformly distributed over all sites of the lattice, so that the average charge of the sites is equal to $(2+x)e$; the hole is located in the O(1) sublattice, so that the average charge of the O(1) atoms is equal to $-(2-x/2)e$; the hole is located in the O(2) sublattice, so that the average charge of the O(2) atoms is equal to $-(2-x/2)e$; and, the hole is divided between the O(1) and O(2) sublattices and all oxygen atoms have a charge $-(2-x/4)e$. In all cases the charge of the atoms in the lanthanum sublattice was set equal to $(3-x/2)e$. As one can see from Fig. 4, the decrease of the value of e^2qQ as x increases for $^{67}Zn^{2+}$ and $^{57m}Fe^{3+}$ centers can be quantitatively explained, if the hole is localized in the O(2) sublattice (or predominately in this sublattice). The resolution of the Mössbauer spectroscopy on the isotope $^{133}Ba(^{133}Cs)$ does not make it possible to draw the same conclusion, but from Fig. 4 it follows that the decrease of the frequency of the quadrupole resonance on the ^{139}La isotope as x increases, as observed in Ref. 2, can also be explained, if the hole is localized in the O(2) sublattice.

Figure 4 also shows the results of Ref. 12, where $La_{2-x}Sr_xCu_{0.995}{}^{57}Fe^{3+}_{0.005}O_4$ samples were investigated by the method of Mössbauer spectroscopy. One can see that the quantity P^{e} for these materials decreases significantly more

TABLE II. Parameters of the Mössbauer spectra of $La_{2-x}Sr_xCuO_4$:^{57}Co.

x	e^2qQ, MHz	Isomeric shift relative to α-Fe, mm/s	eq^{e}_{cr}, e/Å^3
0,1	42,06±0,22	−0,27±0,02	0,633±0,007
0,2	40,20±0,22	−0,26±0,02	0,605±0,007
0,3	39,50±0,22	−0,25±0,02	0,594±0,007

Note: The sign of e^2qQ was assumed to be positive, following Ref. 4.

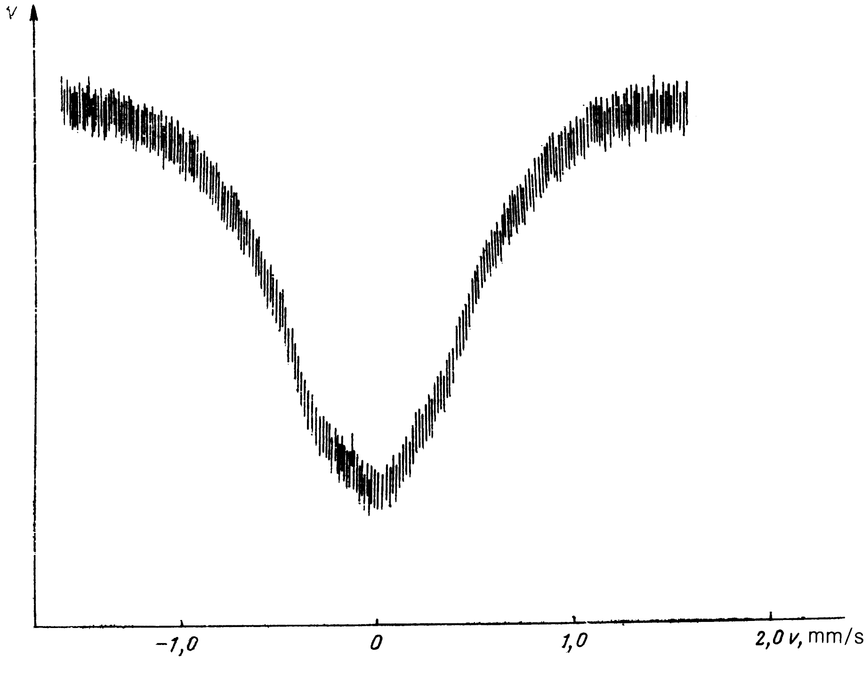

FIG. 3. Mössbauer spectrum of $La_{1.9}{}^{133}Ba_{0.1}CuO_4$ at 4.2 K.

TABLE III. The parameters of the Mössbauer spectra of $La_{2-x}{}^{133}Ba_xCuO_4$.

x	$\lvert e^2qQ \rvert$, MHz	$\lvert eq^e_{cr} \rvert$, $e/Å^3$
0,1	65±2	0,069±0,002
0,3	67±2	0,072±0,002

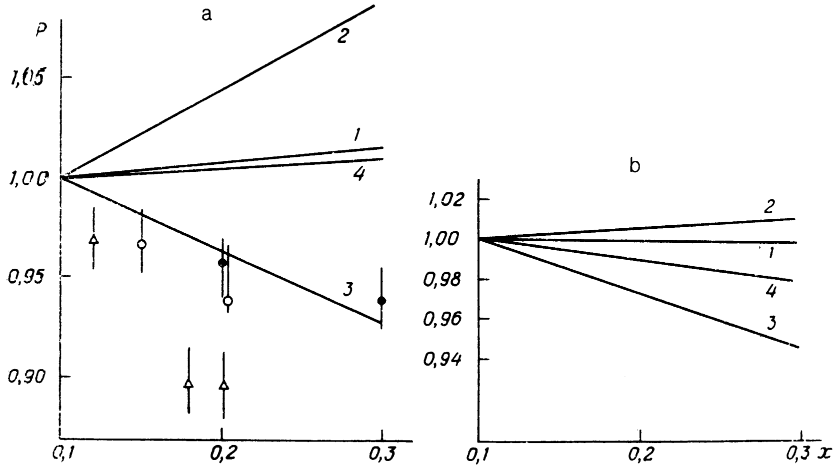

FIG. 4. P as a function of x for $La_{2-x}Sr_xCuO_4$ for copper (a) and lanthanum (b) sites: 1) the hole is localized in the Cu sublattice; 2) the hole is localized in the O(1) sublattice; 3) the hole is localized in the O(2) sublattice; 4) the hole is localized in the O(1) and O(2) sublattices; ○—data for $^{67}Zn^{2+}$ centers; ●—$^{57m}Fe^{3+}$; Δ—$^{57}Fe^{3+}$.[11]

TABLE IV. The contributions made by different sublattices to the EFG U_k at the copper and lanthunum sites of the $La_{2-x}Sr_xCuO_4$ lattice ($e/Å^3$).

Sublattice	$x=0,1$	$x=0,2$	$x=0,3$	$x=0,4$	$x=1,0$
copper sites					
(La, Sr)	−0,0775	−0,0784	−0,0790	−0,0796	−0,0788
Cu	0,0157	0,0164	0,0188	0,0174	0,0138
O(1)	0,3142	0,3138	0,3128	0,3146	0,3248
O(2)	−0,6840	−0,6894	−0,6950	−0,6978	−0,6951
lanthanum sites					
(La, Sr)	−0,0004	−0,0012	−0,0021	−0,0017	−0,0006
Cu	0,0078	0,0082	0,0088	0,0088	0,0069
O(1)	−0,0098	−0,0118	−0,0136	−0,0132	−0,0072
O(2)	0,0940	0,0956	0,0970	0,0972	0,0954

rapidly as x increases than is implied by the computed dependence. The difference of the behavior of the $^{57m}Fe^{3+}$ and $^{57}Fe^{3+}$ centers in the $La_{2-x}Sr_xCuO_4$ lattice is explained by their different local symmetry: the $^{57m}Fe^{3+}$ centers are formed from $^{57}Cu^{2+}$, located at the normal copper sites, while the $^{57}Fe^{3+}$ centers, replacing Cu^{2+} during synthesis, have in their immediate vicinity compensating centers (of the cationic vacancy type), which lead to a change of the parameters of the resulting EFG tensor. This proposition is also supported by the data of Ref. 13, where it was observed that for $^{57}Fe^{3+}$ centers at the copper sites of the $La_{1.85}Sr_{0.15}CuO_4$ lattice the principal axis of the EFG tensor is different from the crystallographic axis c.

In order to explain the reasons for the increase in $|e^2qQ|$ for $^{63,65}Cu^{2+}$-centers in $La_{2-x}Sr_xCuO_4$ as x increases (NQR data of Ref. 1) it is necessary to take into account the contribution made to the EFG on the copper nuclei not only by the lattice ions ($e^2q_{cr}(1-\gamma)Q<0$) but also by the valence electrons of the Cu^{2+} centers $[e^2q_{val}(1-R)Q>0]$, so that the experimental value of e^2qQ for $^{63,65}Cu$ nuclei is determined by the relation

$$e^2qQ=e^2q_{cr}(1-\gamma)Q+e^2q_{val}(1-R)Q. \tag{3}$$

Here eq_{val} is the principal tensor component of the EFG produced at the copper sites by the valence electrons of copper, R is the Sternheimer coefficient, and Q is the quadrupole moment of the copper nucleus ($Q<0$) for $^{63,65}Cu$ (Ref. 14).

If it is assumed that the quantity $e^2q_{val}(1-R)Q$ does not change significantly as a function of x, then a decrease of x will result only in a decrease of $|e^2q_{cr}(1-\gamma)Q|$ and therefore the quantity $|e^2qQ|$ increases. This is in fact observed in the NQR spectra of $^{63,65}Cu$ (Ref. 1).

Thus we have shown, by comparing the experimental and computed dependences $eq(x)$, that the compensating center appearing when La^{3+} is replaced by Sr^{2+}, is a hole, localized predominantly on the oxygen atoms located in the same plane as the copper atoms.

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