Atomic charges in $RBa_2Cu_4O_8$ lattices, determined by comparison of experimental and calculated nuclear quadrupole interaction parameters

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Abstract.   Nuclear quadrupole interaction parameters have been determined for the rare-earth and copper sites of the $RBa_2Cu_4O_8$ lattices (R = Sm, Y, Er) by $^{67}Cu(^{67}Zn)$ and $^{67}Ga(^{67}Zn)$ emission Mössbauer spectroscopy. The lattice electric field gradient tensors have been calculated for all sites of the above lattices using the point charge approximation. A comparison of the measured and calculated parameters has shown that in the $RBa_2Cu_4O_8$ lattices holes are predominantly confined to the oxygen chain sublattices.

1. Introduction

Comparison of experimentally determined and calculated parameters of nuclear quadrupole interaction, i.e. interaction of the electric quadrupole moment of a probe nucleus with the electric field gradient (EFG), allows the determining of charges of atoms in crystal lattices. The clearest results are obtained when such a comparison is carried out for the so-called 'lattice probes'. The EFG at the nuclei of such probes is created predominantly by lattice ions. For this reason, we have proposed and developed $^{67}Cu(^{67}Zn)$ emission Mössbauer spectroscopy (EMS) as a method for experimental determination of nuclear quadrupole interaction parameters at copper sites of high-temperature superconductor lattices [1]. In this method, the $^{67}Zn^{2+}$ lattice probe (spins of the ground and excited states: 5/2 and 1/2; quadrupole moment of the ground state: $Q = 0.15b$) occupies copper sites. The EFG tensor at the ^{67}Zn nuclei is determined by lattice ions only and can be calculated using the point charge model. This method proved to be the most effective for lattices with several non-equivalent copper positions. They allow the avoiding of problems associated with uncertainty in the Sternheimer factor for the Zn^{2+} centres. In particular, such a situation arises in the case of $RBa_4Cu_4O_8$ high-temperature superconductors (R is a rare-earth metal (REM) or yttrium). Their lattices have two copper positions Cu(1) and Cu(2). Another feature of these objects is that the nuclear quadrupole interaction parameters of the same $^{67}Zn^{2+}$ probe can be determined at the REM sites using $^{67}Ga(^{67}Zn)$ EMS [2]. In addition, the $YBa_2Cu_4O_8$ compound has been investigated in detail by the nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) techniques applied to the ^{17}O [3] and ^{63}Cu [4] isotopes. This expands the experimental basis for the interpretation of ^{67}Zn emission Mössbauer spectroscopy data.

* Deceased.

The aims of the present work were to measure nuclear quadrupole interaction parameters for the copper and REM sites in the $RBa_2Cu_4O_8$ lattices using the $^{67}Cu(^{67}Zn)$ and $^{67}Ga(^{67}Zn)$ EMS techniques, to calculate the lattice EFG tensors at these sites and to determine the atomic charge states in $RBa_2Cu_4O_8$ by comparing the measured and calculated parameters.

2. Experimental procedure

Ceramic samples of $RBa_2Cu_4O_{8+x}$ (R = Sm, Y, Er) were used for investigations. The ^{67}Cu and ^{67}Ga isotopes were introduced into the samples by diffusion in an oxygen atmosphere at $700\,^{\circ}C$ for two hours. A similar procedure has been shown to introduce ^{67}Ga atoms into the REM sites and ^{67}Cu atoms into the Cu(1) and Cu(2) sites of $YBa_2Cu_3O_7$ in accordance with their natural populations [1, 2]. A test annealing of an $YBa_2Cu_4O_8$ sample under the above conditions did not change its T_c-value of $\sim$80 K. $^{67}Cu(^{67}Zn)$ and $^{67}Ga(^{67}Zn)$ Mössbauer spectra were recorded at 4.2 K with the ^{67}ZnS absorber having a surface density of 1000 mg cm^{-2}.

3. Experimental results

Each of the $^{67}Cu(^{67}Zn)$ Mössbauer spectra obtained is a set of six lines of approximately equal intensities (figure 1(a)) which can be represented as two quadrupole triplets of the same
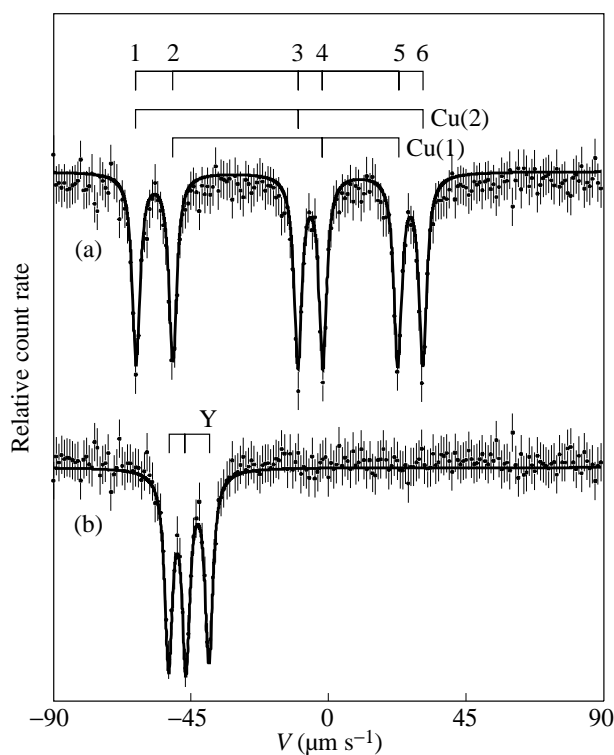

Figure 1. (a) $^{67}Cu(^{67}Zn)$ and (b) $^{67}Ga(^{67}Zn)$ emission Mössbauer spectra recorded at 4.2 K for $YBa_2Cu_4O_8$. The positions of all ions of the $^{67}Cu(^{67}Zn)$ spectrum (numbered) as well as the positions of the components of the quadrupole triplets corresponding to $^{67}Zn^{2+}$ at the Cu(1), Cu(2) and Y sites are shown.

intensity. The experimental spectra were resolved into two triplets identified with the ^{67}Zn^{2+} centres at the Cu(1) and Cu(2) sites on the basis of the similarity of the Cu(2) local environments in RBa$_2$Cu$_4$O$_8$ and RBa$_2$Cu$_3$O$_7$ compound groups. For this reason, we suggested that the asymmetry parameter of the EFG tensor for the Cu(2) sites in RBa$_2$Cu$_4$O$_8$ is zero, as it was found to be for RBa$_2$Cu$_3$O$_7$ [1]. This requirement was found to be satisfied only for the (2–4–5) triplet ascribed to ^{67}Zn^{2+} centres at Cu(2) sites (figure 1(a)). Therefore, the (1–3–6) triplet must correspond to ^{67}Zn^{2+} centres at Cu(1) sites. The equal intensities of the two triplets arise from equal populations of the two copper sites. The nuclear quadrupole interaction parameters for ^{67}Zn^{2+} centres in Cu(1) and Cu(2) are shown in table 1.

Table 1. Parameters of the ^{67}Cu(^{67}Zn) and ^{67}Ga(^{67}Zn) emission Mössbauer spectra.

Compound	Site	C(Zn) (MHz)	η
SmBa$_2$Cu$_4$O$_8$	Cu(1)	14.1(2)	0.75(5)
	Cu(2)	12.0(2)	$\leqslant 0.2$
YBa$_2$Cu$_4$O$_8$	Y	−2.5(2)	0.30(5)
	Cu(1)	14.3(1)	0.70(5)
	Cu(2)	12.3(1)	$\leqslant 0.2$
ErBa$_2$Cu$_4$O$_8$	Cu(1)	14.4(2)	0.68(5)
	Cu(2)	12.2(2)	$\leqslant 0.2$

The ^{67}Ga(^{67}Zn) spectra are quadrupole triplets (figure 1(b)) each corresponding to a single state of the ^{67}Zn^{2+} centre. On the basis of the data reported in [2], we assign these spectra to ^{67}Zn^{2+} centres at REM sites. Their nuclear quadrupole interaction parameters are given in the table, too.

4. Discussion

To determine the charges of atoms at sites of the RBa$_2$Cu$_4$O$_8$ lattices, it is necessary to compare the measured and calculated parameters of the nuclear quadrupole interaction for the ^{67}Zn^{2+} probe at copper sites. In general, the measured quadrupole interaction constant C can be represented as the sum

$$C = eQU_{zz} = eQ(1 - \gamma)V_{zz} + eQ(1 - R_0)W_{zz} \tag{1}$$

where U_{zz}, V_{zz} and W_{zz} are the principal components of the total, lattice (created by lattice ions) and valence (created by non-spherical valence electrons of the probe atom itself) EFG tensors, respectively; γ and R_0 are the Sternheimer factors for the probe atom.

The valence contribution to the total EFG tensor can be neglected for the ^{67}Zn^{2+} probe [1], and then equation (1) transforms into

$$C(\text{Zn}) \approx eQ(1 - \gamma)V_{zz}.$$

The lattice EFG tensor was found using the point charge model. Its components are calculated as follows:

$$\begin{aligned}
V_{pp} &= \sum_k e_k^* \sum_i \frac{3p_{ki}^2/r_{ki}^2 - 1}{r_{ki}^3} = \sum_k e_k^* G_{ppk} \\
V_{pq} &= \sum_k e_k^* \sum_i \frac{3p_{ki}q_{ki}}{r_{ki}^5} = \sum_k e_k^* G_{pqk}
\end{aligned} \tag{2}$$

where summation is over k and i for sublattices and sites within the sublattices, respectively, q and p are the Cartesian coordinates, e_k^* the charge of atoms of the kth sublattice and r_{ik} the distance from the ith site of the kth sublattice to a probe nucleus.

The lattice sums G_{ppk} and G_{pqk} were computed with the summation carried out within a sphere of radius 30 Å (test summations within spheres with radii of up to 100 Å gave the same results in accordance with the expected, better than r^{-3}, convergence of the lattice sums). Structural data [5] were used; the lattices were represented by the following formula: $RBa_2Cu(1)_2Cu(2)_2O(1)_2O(2)_2O(3)_2O(4)_2$.

Figure 2 shows the unit cell of the $RBa_2Cu_4O_8$ lattice with the designation of all of the sites. The index k in equation (2) had the following values for various sublattices:

k	1	2	3	4	5	6	7	8
atom	R	Ba	Cu(1)	Cu(2)	O(1)	O(2)	O(3)	O(4).

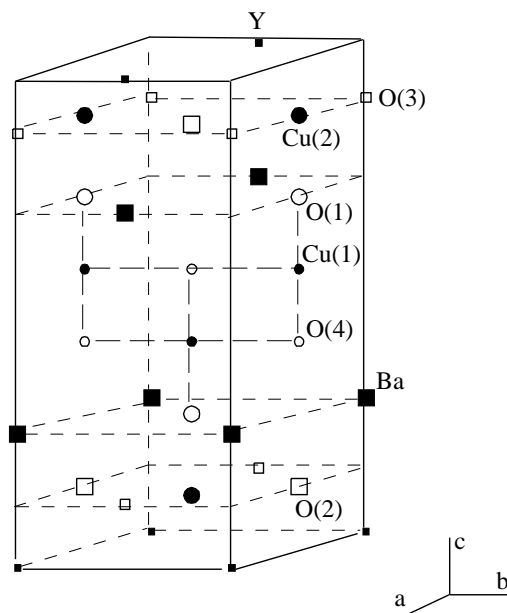**Figure 2.** The unit cell of the $RBa_2Cu_4O_8$ compounds with the designation of the sites.

The atomic charges in the $RBa_2Cu_4O_8$ lattices can be determined from $^{67}Cu(^{67}Zn)$ EMS data using a set of four equations proposed in [1]: the equation for the ratio between the quadrupole interaction constants of $^{67}Zn^{2+}$ at Cu(1) and Cu(2) sites $P_{34} = eQU_{zz3}/eQU_{zz4}$:

$$\sum_k e_k^* \left[G_{zzk3} - P_{34}G_{zzk4} \right] = 0 \tag{3}$$

and two equations for the asymmetry parameters η_3 and η_4 of the EFG tensors at Cu(1) and Cu(2) sites:

$$\sum_k e_k^* \left[G_{xxk3} - G_{yyk3} - \eta_3 G_{zzk3} \right] = 0 \tag{4}$$

$$\sum_k e_k^* \left[G_{xxk4} - G_{yyk4} - \eta_4 G_{zzk4} \right] = 0 \tag{5}$$

and also the electroneutrality equation:

$$e_1^* + 2e_2^* + 2e_3^* + 2e_4^* + 2e_5^* + 2e_6^* + 2e_7^* + 2e_8^* = 0. \tag{6}$$

All equations of the set (3)–(6) are homogeneous and, therefore, this set can define the atomic charges e_k^* only in units of one of them. It is convenient to choose as a unit of charge

that of the R ion, expected to be close to its formal chemical charge $+3e$. This choice is supported by data from the ^{155}Gd Mössbauer spectroscopy, revealing trivalent gadolinium in GdBa$_2$Cu$_4$O$_8$ [6].

The physical meaning of the effective charges e_k^* obtained from equations (3)–(6) is obvious. They are charges providing a Coulomb field equal to that observed at the crystal lattice sites. However, the e_k^*-values should not be considered exact electric charges of ions at lattice sites. Firstly, the charge scale is established quite arbitrarily in terms of the R ion charge. Secondly, equations (3)–(5) assume that there is no valence EFG for probe nuclei and this assumption is valid for real probes with limited accuracy only. Thirdly, the point charge model requires a spherical symmetry of ions which give rise to the EFG, and deviations of the charge distribution from the spherical one for ions of any sublattice will distort the effective charges for all sites. Nevertheless, the effective charges give a real notion of the valence states of ions at certain lattice sites and of essential deviations from the standard valence states.

Equations (3)–(6) are not enough to determine the charges of seven sublattices. However, the coefficients of the anion charges exceed those of the cation charges by an order of magnitude or more. For this reason, equations (3)–(6) permit finding the anion charges with some small uncertainties depending on the cation charges. We made several assumptions about the cation charges. Firstly, the R-to-Ba charge ratio was taken as 3:2, which followed from their conventional valence states. Secondly, the Cu(1)-to-Cu(2) ratio was varied from 1:3 to 3:1 in accordance with the possible valence states of copper.

In addition, account was taken of the following:

 (i) the Cu(2) local environment symmetry requires that the crystal axis c should be the principal axis of the lattice EFG tensor and
 (ii) $V_{zz4} > 0$ according to our measurements (see the table).

Agreement between the experimental data for the Cu(1) sites, $\eta_3 \approx 0.7$ and $V_{zz3} > 0$, and calculated values can be achieved in two ranges: range A with $e_5^*/e_8^* \approx 1.5$ and $|V_{bb3}| < |V_{cc3}|$; and range B with $e_5^*/e_8^* \approx 0.3$ and $|V_{bb3}| > |V_{cc3}|$. In both of these ranges the principal axis of the lattice EFG tensor for the Cu(1) sites coincides with the crystal axis a.

With the above assumptions made and standard charges taken for the R, Ba and Cu ions ($e_1^* = 3$, $e_2^* = e_3^* = e_4^* = 2$), we can find two sets of e_k^*-values consistent with the measured values of P_{34}, η_3 and η_4:

$$e_5^* = -2.025 \qquad e_6^* = -2.035 \qquad e_7^* = -1.986 \qquad e_8^* = -1.454 \qquad \text{(A1)}$$

in range A and

$$e_5^* = -0.715 \qquad e_6^* = -2.076 \qquad e_7^* = -2.031 \qquad e_8^* = -2.678 \qquad \text{(B1)}$$

in range B (all charges are given in electron charge units).

To make a choice between type A or B solutions, some independent criteria are required. For RBa$_2$Cu$_3$O$_7$ compounds, we previously used [1] for this purpose ^{17}O NMR data. As long as ^{17}O NMR data are also available for YBa$_2$Cu$_4$O$_8$ [3], these data can be used to select physically reasonable solutions.

Solution (A1) shows that the O(1), O(2) and O(3) atoms have effective charges corresponding to almost filled valence shells, i.e., the EFG at ^{17}O nuclei at these sites must be produced by lattice ions. Hence, equations (3)–(6) can be supplemented in range A with three equations similar to equations (3)–(5), but constructed for any of the following pairs of sites: O(1) and O(2), O(1) and O(3) or O(2) and O(3).

In contrast, model (B1) allows the use of similar equations for pairs of O(2) and O(3), O(2) and O(4) or O(3) and O(4) sites. In this way, several sets of seven equations for determining seven unknowns (e_2^* to e_8^*, with the R-site charge taken to be $+3e$) can be obtained.

The sets are different, depending on the chosen model (A or B) as well as on the sign of eQU_{zz} and the directions of the x- and y-axes of the EFG tensors. The last two groups of parameters are not provided by experiment [3]. However, all meaningful solutions for both A and B ranges give oxygen charges considerably different from $-2e$ even for those sites at which the oxygen electron shells were supposed to be closed in constructing the corresponding equations. In addition, the barium charge proved to be always different from its expected value of $+2e$. These properties of the solutions indicate that ^{17}O in $YBa_2Cu_4O_8$ cannot be considered a 'lattice probe' and, therefore, cannot serve as a criterion for choosing between solutions of types A and B.

As an alternative criterion for selecting A or B solutions, a correlation [7] between ^{67}Cu(^{67}Zn) EMS and ^{63}Cu NQR/NMR data for copper, found for a variety of copper oxides, can be used. Figure 3(a) shows $C(Cu)$ versus $C(Zn)$ obtained in [7] using the quadrupole interaction constants $C(Cu)$ and $C(Zn)$ measured by means of ^{63}Cu NQR or NMR and by ^{67}Cu(^{67}Zn) EMS at the same copper sites of complex copper oxides. The majority of the data [7] satisfied the linear equation

$$C(Cu) = 197 - 11.3C(Zn) \tag{7}$$

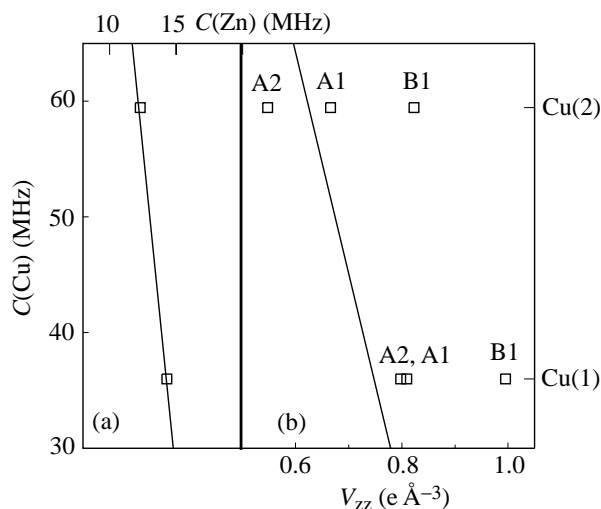where $C(Cu)$ and $C(Zn)$ are given in MHz. It is represented by the solid line in figure 3(a).

Figure 3. Diagrams showing (a) $C(Cu)$ versus $C(Zn)$ and (b) $C(Cu)$ versus V_{zz} for complex copper oxides. The points represent data for the Cu(1) and Cu(2) sites in $YBa_2Cu_4O_8$. The labels A1, A2 and B1 designate charge distribution models, used in the V_{zz}-calculations.

This linear dependence is a consequence of a constant valence contribution to the EFG for Cu^{2+} in various copper oxides. The main reason for a deviation of a point from the straight line (7) is a non-divalent state of copper.

In addition, a similar relation was found [7] between the values of $C(Cu)$ and V_{zz}:

$$C(Cu) = 179 - 191.4V_{zz} \tag{8}$$

where V_{zz} is the calculated principal component of the lattice EFG tensor for a site at which $C(Cu)$ is measured.

$C(Cu)$ versus V_{zz} is shown in figure 3(b). For this diagram, there is one more reason for deviation from the straight line (8): the calculation of the lattice EFG tensor may be incorrect

because of an inappropriate choice of charge distribution model. For this reason, the positions of the points corresponding to the same copper sites in the diagrams showing $C(Cu)$ versus $C(Zn)$ and $C(Cu)$ versus V_{zz} can be used for selecting several possible charge distributions in a lattice.

The points corresponding to Cu(1) and Cu(2) in YBa$_2$Cu$_4$O$_8$ (with ^{63}Cu NMR data from [4]) are shown in figure 3(a). It is seen that both of the points are in satisfactory agreement with equation (7) supporting the divalent state of copper at both positions in YBa$_2$Cu$_4$O$_8$. Figure 3(b) shows the points for the same sites in the diagram showing $C(Cu)$ versus V_{zz}. It is seen that the points are close to the straight line (8) when V_{zz} is calculated using model (A1), whereas in the case of calculation using model (B1) both of the points considerably deviate from the straight line (8). This seems to confirm the validity of A-type models.

A linear correlation has also been found [2] between the quadrupole interaction constants $C(Zn)$ measured by ^{67}Ga(^{67}Zn) EMS at REM sites of RBa$_2$Cu$_3$O$_7$ compounds and the principal components V_{zz} of the lattice EFG tensors calculated for the same sites using the point charge model. This linear correlation results from the lack of the valence EFG for the ^{67}Zn^{2+} probe. As it is seen from figure 4, the point corresponding to YBa$_2$Cu$_4$O$_8$ is away from this linear correlation (the V_{zz}-calculation for YBa$_2$Cu$_4$O$_8$ used model (A1)).
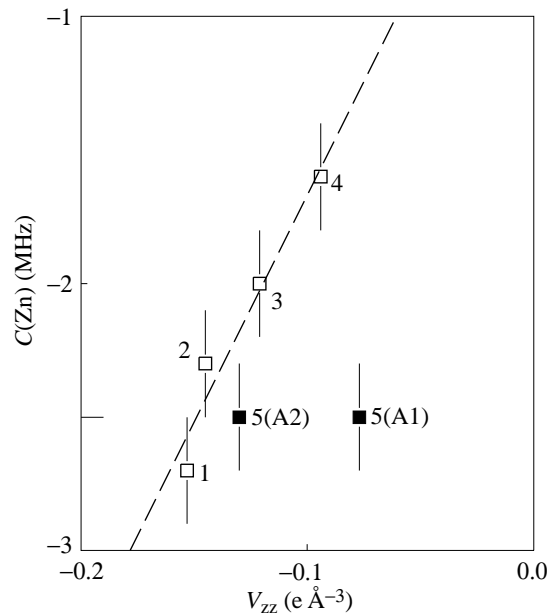
Figure 4. A diagram showing $C(Cu)$ versus V_{zz} for a REM site: EuBa$_2$Cu$_3$O$_7$ (1), YBa$_2$Cu$_3$O$_7$ (2), GdBa$_2$Cu$_3$O$_7$ (3), TmBa$_2$Cu$_3$O$_7$ (4) and YBa$_2$Cu$_4$O$_8$ (5). The labels A1 and A2 designate charge distribution models, used in the V_{zz}-calculations.

This deviation requires some corrections of model (A1) describing the charge distribution among the YBa$_2$Cu$_4$O$_8$ lattice sites. For a required increase in V_{zz}, it is necessary to place holes in the O(2) and O(3) sublattices. When independent sources of holes in RBa$_2$Cu$_4$O$_8$ are unknown, we are forced to redistribute charge between the O(1), O(2), O(3) and Cu(1) sublattices. Figure 4 shows the results following from a distribution obtained in this way:

$$
\begin{array}{llll}
e_1^* = 3 & e_2^* = 2 & e_3^* = 1.85 & e_4^* = 2 \\
e_5^* = -2.15 & e_6^* = -1.9 & e_7^* = -1.85 & e_8^* = -1.45.
\end{array} \tag{A2}
$$

A satisfactory agreement is seen with the linear $C(Zn)$–V_{zz} diagram. Model (A2) should be noted as hardly changing the position of the Cu(1) point in figure 3(b) but somewhat displacing the Cu(2) point, even though the displacement seems to be reasonably small.

The essential deviations of the effective charges of all oxygen atoms in model (A2) from $-2e$ explain the above-demonstrated impossibility of using ^{17}O NMR data in equations (3)–(9), requiring filled electron shells of oxygen probes.

This feature supports the general idea that the structure of the RBa$_2$Cu$_4$O$_8$ compounds is rather complicated. It can certainly be described in terms of the point charge model in a rough approximation only. Some additional problems may arise when account is taken of post-effects of β-decay of ^{67}Cu and electron capture by ^{67}Ga, producing the ^{67}Zn Mössbauer probe [8]. In this connection, it would be reasonable to compare our data with the results of quantum EFG calculations for the same compounds [9–13], which may be, in principle, more accurate and informative than the point charge approximation. However, direct comparison of our effective charge with the calculated electron densities is impossible, because it requires a knowledge of the details of the quantum calculation. In addition, there are some discrepancies between the NMR data and EFG values calculated in [9–13], especially for the Cu(2) sites. Similar discrepancies have been found for the RBa$_2$Cu$_3$O$_7$ compounds [14–16]. This points to the necessity for further improvement of the quantum calculations, on the one hand, and for development of alternative methods for determining the charge distribution in HTSCs, on the other.

5. Conclusions

The parameters of nuclear quadrupole interaction have been determined by ^{67}Cu(^{67}Zn) and ^{67}Ga(^{67}Zn) EMS for copper and REM sites of RBa$_2$Cu$_4$O$_8$ lattices. The lattice EFG tensors have been calculated for all sites of the lattices, using the point charge model. A comparison of the measured and calculated parameters has shown that holes in the RBa$_2$Cu$_4$O$_8$ lattices are mainly confined to the oxygen chain sublattice, although a significant fraction of them are also confined to the plane oxygen positions. This can explain the impossibility of using ^{17}O NMR data for determining the effective charges of atoms without taking account of the oxygen valence EFG.

Acknowledgment

References

[1] Masterov V F, Seregin P P, Nasredinov F S, Seregin N P and Sagatov M A 1996 *Phys. Status Solidi* b **196** 11
[2] Masterov V F, Nasredinov F S, Seregin N P and Seregin P P 1996 *Sov. Phys.–Solid State* **38** 1986
[3] Mangelschots I, Mali M, Roos J, Brinkmann D, Rusiecki S, Karpinski J and Kaldis E 1992 *Physica* C **194** 277
[4] Brinkmann D 1990 *Z. Naturf.* a **45** 393
[5] Morris D E, Nickel J H, Wei J Y, Asmar N G, Scott J S, Post J E, Heanly P J, Veblen D R and Hazen R M 1989 *Phys. Rev.* B **39** 7347
[6] Bornemann H J, Morris D E, Steinleitner C and Czjzek G 1991 *Phys. Rev.* B **44** 12 567
[7] Seregin P P, Masterov V F, Nasredinov F S and Seregin N P 1997 *Phys. Status Solidi* b **201** 269
[8] Seregin P P, Nasredinov F S and Vasilev L N 1978 *Phys. Status Solidi* a **45** 11
[9] Oguchi T, Sasaki T and Tarakura K 1990 *Physica* C **172** 277
[10] Yu J, Park K T and Freeman A J 1991 *Physica* C **172** 467

[11] Ambrosch-Draxl C, Blaha P and Schwarz K 1991 *Phys. Rev.* B **44** 5141
[12] Stachiotti M, Catlow C R A, Rodriguez C O and Christensen N E 1996 *Physica* C **269** 273
[13] Rodriguez C O, Fabricius G, Stachiotti M G and Christensen N E 1996 *Phys. Rev.* B **56** 14 833
[14] Schwarz K, Ambrosch-Draxl C and Blaha P 1990 *Phys. Rev.* B **42** 20 051
[15] Freeman A J, Podloucky R, Herzig P and Weinberger P 1991 *Phys. Rev.* B **43** 532
[16] Singh D J, Schwarz K and Blaha P 1992 *Phys. Rev.* B **46** 5849