Calculation of lattice sums and electrical field gradients for the rhombic and tetragonal phases of $YBa_2Cu_3O_x$

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The point charge model is used to calculate the lattice sums and determine the electrical field gradients (EFG) as well as the asymmetry parameters η for all cation sites of the rhombic and tetragonal phases of the superconductor $YBa_2Cu_3O_x$. The cases of copper of different valency at the Cu1 sites are considered separately and the EFG and η values are calculated in the vicinity of local defects caused by differences in the number and ordering of the oxygen vacancies at the Cu1 sites.

Experimental studies of high-temperature superconductors by resonance techniques (Mössbauer spectroscopy, NQR, NMR, EPR, etc.) encounter substantial difficulties in spectral-line identification and assignment of these lines to specific crystallographic positions of the atoms within the structure. For example, many authors[1–8] have assigned the quadrupole doublets with splitting ≈ 2.0 and ≈ 1.0 mm/s in the Mössbauer spectra of the $YBa_2Cu_3O_x$ system doped with ^{57}Fe to the iron atoms in positions Cu1 and Cu2, respectively. However an equal number of researchers[9–15] have argued in favor of a diametrically opposite identification. Such a situation has also occurred in the treatment of the NQR signals from ^{63,65}Cu nuclei at the Cu1 and Cu2 sites of the superconductor $YBa_2Cu_3O_x$.[16,19]

In order to simplify the interpretation of experimental data we calculate here the lattice contributions to the electrical field gradients (EFG) together with the asymmetry parameters η generated by external charges for all cation sites in the rhombic and tetragonal phases of $YBa_2Cu_3O_x$. The cases when the copper ions are trivalent (in the rhombic phase of $YBa_2Cu_3O_7$) and monovalent (in the tetragonal phase of $YBa_2Cu_3O_6$) are considered separately. Moreover the EFG and η values are calculated in the vicinity of local defects caused by the differences in the numbers and ordering of oxygen vacancies near the Cu1 site.

The lattice sums were calculated with the following assumptions. All cations and anions forming the lattice were assumed to be point charges equal to $+3$, $+2$ and -2 for Y, Ba, and O, respectively. All copper cations in positions Cu1 and Cu2 had a $+2$ charge in the initial approximation. The following variants were then considered: a) Copper in the rhombic phase of $YBa_2Cu_3O_7$ in the Cu2 positions have a $+2$ charge, while in the Cu1 positions they have a $+3$ charge; b) copper in the tetragonal phase of $YBa_2Cu_3O_6$ have a $+2$ charge in the Cu2 positions and a $+1$ charge in the Cu1 positions. The arrangement of the atoms in the unit cell were given by the following coordinates[20]: Y(0.5; 0.5; 0.5), Ba (0.5; 0.5; 0.1861), Cu1 (0; 0; 0), Cu2 (0; 0; 0.3574), O1 (0; 0.5; 0), O2 (0.5; 0; 0.3782), O3 (0; 0.5; 0.3782) and O4 (0; 0; 0.1573). Unit cell parameters of $a = 3.817$ Å, $b = 3.882$ Å, and $c = 11.671$ Å (Ref. 21) were used in the rhombic phase of $YBa_2Cu_3O_7$. We have $a = b = 3.869$ Å, $c = 11.723$ Å in the tetragonal phase of $YBa_2Cu_3O_6$.[22]

The EFG tensor components were calculated by the formulae

$$V_{\alpha\alpha}=\sum_i \frac{e_i}{r_i^3}\left(3\frac{\alpha_i^2}{r_i^2}-1\right), \qquad V_{\alpha\beta}=V_{\beta\alpha}=\sum_i \frac{3e_i\alpha_i\beta_i}{r_i^5}.$$

Here e_i is the ion charge, r_i is the distance from this site to the charge producing the EFG, and $\alpha, \beta = x, y, z$. In the principal coordinate system the EFG has three nonzero components, V_{xx}, V_{yy}, and V_{zz} that satisfy the Laplace equation $V_{xx} + V_{yy} + V_{zz} = 0$. Therefore the EFG can be entirely determined by two independent parameters: the maximum component V_{zz} ($|V_{zz}| > |V_{xx}| \geqslant |V_{yy}|$) and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ ($0 \leqslant \eta \leqslant 1$).

The computer calculations of the EFG tensor components incorporated all ions configured in a sphere of radius R. Control calculations in which R was varied from 0 to 94 Å in increments of 4 Å revealed that the calculation results converge rather rapidly (evidently due to the comparatively small number of atoms in a rather large unit cell). Therefore

TABLE I. The EFG parameters V_{zz} in units of $e/\text{Å}^3$ and η for the rhombic and tetragonal phases of $YBa_2Cu_3O_x$.

Variant number	Parameter	Cu1	Cu2	Y	Ba
1	V_{zz}	1,107 (*a*)	0,649	−0,140	−0,110 (*a*)
	η	0,270	0,133	0,199	0,617
2	V_{zz}	1,165 (*a*)	0,701	−0,091	−0,110 (*a*)
	η	0,397	0,123	0,305	0,575
3	V_{zz}	−1,394	0,734	−0,040	0,147
	η	0	0	0	0
4	V_{zz}	−1,286	0,683	−0,087	0,150
	η	0	0	0	0

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TABLE II. The EFG parameters V_{zz} in units of $e/\text{Å}^3$ and η at all cation sites near a "defect" at the Cu1 site (oxygen vacancies) for a rhombic structure.

Variant number	Parameter	Cu1	Cu2′	Cu2″	Y	Ba′	Ba″
1	V_{zz}	−0,977	0.679	0,657	−0.125	0.146	−0.112 (*a*)
	η	0,707	0.143	0,132	0.203	0.190	0,664
2	V_{zz}	−0,689	0.649	0,649	−0,139	0.092	−0.110 (*a*)
	η	0,250	0.166	0,135	0.163	0,815	0.621
3	V_{zz}	0,532 (*a*)	0.619	0,642	−0.154	0,034	−0,108 (*a*)
	η	0,563	0.156	0,136	0.163	0.819	0,573
4	V_{zz}	0,718 (*b*)	0.618	0,642	−0,144	0.099	−0.109 (*a*)
	η	0,118	0.191	0,138	0.180	0.507	0.588
5	V_{zz}	0,171 (*b*)	0.589	0,634	−0.159	−0.047	−0.107 (*a*)
	η	0,495	0.182	0,138	0.179	0,741	0.539

oscillations of V_{zz} and η about the mean will no longer exceed 1% when $R > 25$ Å. The final calculations listed in Tables I and II were therefore carried out for $R = 48$ Å.

Table I was compiled for the following variants of the rhombic and tetragonal phases of $\text{YBa}_2\text{Cu}_3\text{O}_x$.

1. The rhombic phase of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The copper is quadruply O-coordinated by oxygen atoms ordered in the *cb* plane (Fig. a) at the Cu1 sites; the copper charge is + 2 at all sites.

2. The same as in number 1 above, although the copper charge is + 3 at the Cu1 sites and is + 2 at the Cu2 sites.

3. The tetragonal phase of $\text{YBa}_2\text{Cu}_3\text{O}_6$. The copper is doubly O-coordinated at the Cu1 sites (the dumbell along the *c* axis, Fig. b); the copper charge is + 2 at all sites.

4. The same as in number 3 although the copper charge is + 1 at the Cu1 sites and + 2 at the Cu2 sites.

The crystallographic direction along which the principal axis of the EFG lies, if it does not lie on the *c* axis, is given in parentheses.

Table I clearly indicates that V_{zz} and η change appreciably for all sites in the transition from the rhombic phase to the tetragonal phase. The EFG not only has the greatest change in absolute value for the Cu1 sites but also has a change in sign. In the rhombic phase the parameter η is most substantial for the Ba sites; both the sign and direction of the principal axis of the EFG change here in the phase transition (as is the case for Cu1). A change in sign at the Cu1 sites ($\text{Cu}^{2+} \to \text{Cu}^{3+}$ or $\text{Cu}^{2+} \to \text{Cu}^{1+}$) noticeably alters the EFG parameters at all sites aside from Ba; the relative changes are particularly substantial for the Y sites.

The absolute value of V_{zz} for the Cu1 sites is approximately twice the value for the Cu2 sites in both the rhombic and tetragonal phases. Moreover, in the tetragonal phase V_{zz} has different signs at the Cu1 and Cu2 sites, while in the rhombic phase it has different directions. These features are very important for identifying the spectral lines belonging to these sites and provides a good method of analyzing the structural phase transition.

Table II lists all typical possible oxygen vacancy-arrangements on the Cu1 sites (see figure).

1. The triply O-coordinated Cu1 site. Of the three oxygen vacancies at the Cu1 site, two lie on the *a* axis and one lies on the *b* axis (Fig. c).

2. The quadruply O-coordinated Cu1 site: Distorted-tetrahedron or "quarter-octahedron" ("twin-boundary") coordination. Of the two oxygen vacancies at the Cu1 site one lies on the *a* axis and the other lies on the *b* axis (Fig. d).

3. The quintuply O-coordinated Cu1 site or the formation of a tetragonal pyramid at the Cu1 site with the axis running along the *a* axis. One oxygen vacancy lies on the *a* axis (Fig. e).

4. The quintuply O-coordinated Cu1 site or formation of a tetragonal pyramid at the Cu1 site with the axis lying on the *b* axis. One oxygen vacancy lies on the *b* axis (Fig. f).

5. The sextuply O-coordinated Cu1 site—local full octahedron at the Cu1 site. There are no oxygen vacancies (Fig. g).

The copper charge is + 2 at all sites in these five examples. Table II clearly shows that changes in the number or ordering of the oxygen atoms in the vicinity of the Cu1 sites radically alter the EFG parameters, primarily for the Cu1 sites. The Cu2 and Ba sites are also sensitive; the sites closest to the defect (labeled Cu2′ and Ba′ in Table II) are more sensitive to the type of defect structure than are the sites past

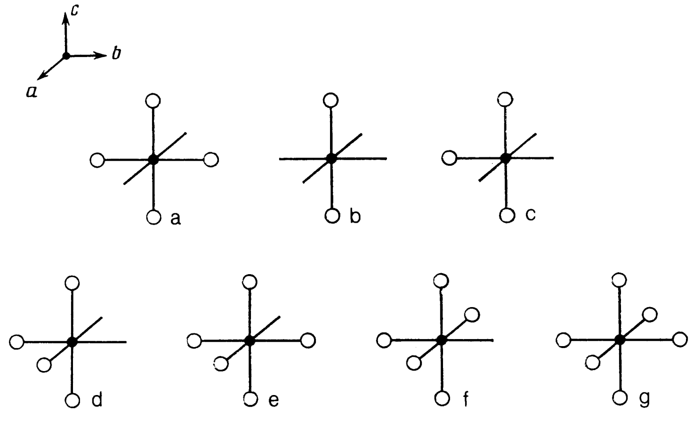

FIG. 1. Possible oxygen atom arrangements around the cation at the Cu1 site in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ structure (○—oxygen, ●—copper).

the neighboring sites (Cu2″ and Ba″). The EFG axis deviates substantially from the crystallographic axes for the Ba′ sites in all variants of the defect structure.

In comparing the calculated EFG values with the experimental data it is important to account for the fact that the values given in Tables I and II apply to an "empty" cation site rather than an occupied site. If the EFG parameters are measured by a nuclear probe (Mössbauer spectroscopy, NQR, the perturbed angular correlation technique) it is necessary to take account of the fact that the atomic shell of the electron to which the probing nucleus belongs may modify the EFG due to external charges (the anti-screening effect). The measured quadrupole splitting ΔE of nuclear levels in the general case is written as

$$\Delta E={}^1/_2e^2qQ(1-\gamma_\infty)(1-\eta^2/3)^{1/2},$$

where q is the EFG due to external charges ($eq\equiv V_{zz}$), Q is the quadrupole moment of the nucleus, and $1-\gamma_\infty$ is the anti-screening factor. It is also necessary to account for possible contributions to the EFG from the atomic electron shell and from the conduction electrons, which is particularly important for superconductors. Here we note that if we set $Q=0.2$b and $\gamma_\infty=-9.14$ (Ref. 23) for ^{57}Fe, the calculated quadrupole splitting values for the ^{57}Fe nuclei at the Cu1 and Cu2 sites of the rhombic phase will be 3.43 and 1.99 mm/s, respectively. A comparison of these values with experimental values from Ref. 11 indicates the need to account for the valency contributions to the EFG.

An analysis of these calculations suggests the following conclusions. The values of V_{zz} for the Cu1 sites are approximately twice those for the Cu2 sites in both the rhombic and tetragonal phases. In the tetragonal phase the values of V_{zz} for the Cu1 and Cu2 sites are not only substantially different in value but also have different signs. In the rhombic phase the signs of V_{zz} are identical for these sites, although the direction of the principal axis is different: It lies on the a axis for the Cu1 site and on the c axis for the Cu2 site.

The sign of V_{zz} and the direction of the principal axis of the EFG at the Cu1 and Ba sites change in the transition from the rhombic phase to the tetragonal phase. This may serve as an additional parameter for monitoring a structural phase transition.

The yttrium positions are very sensitive to the level of the cation charge at the Cu1 site while the Ba positions are insensitive to charge variations.

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