

Determination of properties of electric-field-gradient tensor at $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ lattice sites by emission Mössbauer spectroscopy

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The quadrupole interaction constant and the asymmetry parameter of the electric-field-gradient tensor at copper and barium sites in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ lattices have been determined by emission Mössbauer spectroscopy with the help of the isotopes ^{67}Cu (^{67}Zn) and ^{133}Ba (^{133}Cs).

An experimental determination of the properties of the electric-field-gradient (EFG) tensor at the lattice sites in high- T_c superconductors makes it possible to test the validity of theoretical models which predict these properties and thus to identify the charge state of the atomic centers and their distribution among the lattice sites of the metal-oxide ceramic. The most comprehensive information about the properties of the EFG at lattice sites can be found by the methods of nuclear quadrupole resonance, perturbed angular correlation, and Mössbauer spectroscopy. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, these methods involve either copper centers (nuclear quadrupole resonance of $^{63,65}\text{Cu}$ isotopes¹) or impurity centers at the positions of copper atoms [the Mössbauer effect involving the isotopes ^{57}Fe (^{57}Co) (Ref. 2) or ^{119}Sn (Ref. 3); perturbed angular correlation involving the isotopes ^{111}Cd (^{111}In , ^{111}Ag) (Refs. 4 and 5), or centers of rare-earth metals at the positions of yttrium atoms (the Mössbauer effect involving the isotopes ^{151}Eu (Ref. 6), ^{155}Gd (Ref. 7), ^{161}Dy (Ref. 8), ^{166}Er (Ref. 9), ^{169}Tm (Ref. 10), and ^{170}Yb (Ref. 11)]. All these methods, however, suffer from substantial shortcomings. In the first place, the use of impurity atoms²⁻⁵ raises the problem of the positions of these atoms in the lattice and also the problem of the cancelation of the excess charge of an "alivalent" impurity (i.e., the local appearance of a canceling center near an impurity atom leads to the appearance of an EFG different from the EFG produced by ions of the unperturbed lattice, eq_{cr}). Second, in none of the cases cited¹⁻¹¹ have the experimental values of e^2qQ been compared with theoretical predictions of eq_{cr} , because of the uncertainty in the valence-electron component of the EFG at the nucleus of interest, eq (here eQ is the quadrupole moment of the nucleus of interest). To obtain information about the value of eq_{cr} , it is evidently necessary to satisfy the following conditions: The probe which is used must be at the position of the atom of interest at the outset. The probe must have a closed valence shell, so that it is possible to determine eq_{cr} from the experimental value of e^2qQ . The introduction of an alivalent probe at a lattice site must not be accompanied by the formation of canceling centers.

All these conditions are satisfied in the case of emission Mössbauer spectroscopy involving ^{67}Cu (^{67}Zn) and ^{133}Ba (^{133}Cs) isotopes. In each case, Mössbauer nuclei are

formed in an excited state at the corresponding lattice sites after the decay of the parent nuclei. The daughter zinc and cesium atoms have closed valence shells, Zn^{2+} , $3d^{10}$ and Cs^+ , $4d^{10}$. The Mössbauer γ rays are emitted $\sim 10^{-5}$ – 10^{-9} s after the daughter nucleus forms, so there is no possibility that canceling centers will form in the lattice. The use of ^{67}Cu (^{67}Zn) atoms as the probe is of obvious and fundamental importance since the superconductivity of the metal-oxide ceramics is determined to a large extent by the state of the copper centers. A ^{133}Ba (^{133}Cs) probe essentially makes possible the first determination of the properties of the EFG tensor at barium atom sites.

We selected ceramics with the compositions $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ for this study. Samples with the radioactive isotope ^{67}Cu or ^{133}Ba were prepared by the standard procedure.¹² The control $YBa_2Cu_3O_7$ samples had an orthorhombic structure with $T_c \sim 85$ K, while the control $YBa_2Cu_3O_6$ samples had a tetragonal structure and remained in a semiconducting state at $T > 4.2$ K. Mössbauer spectra were recorded at

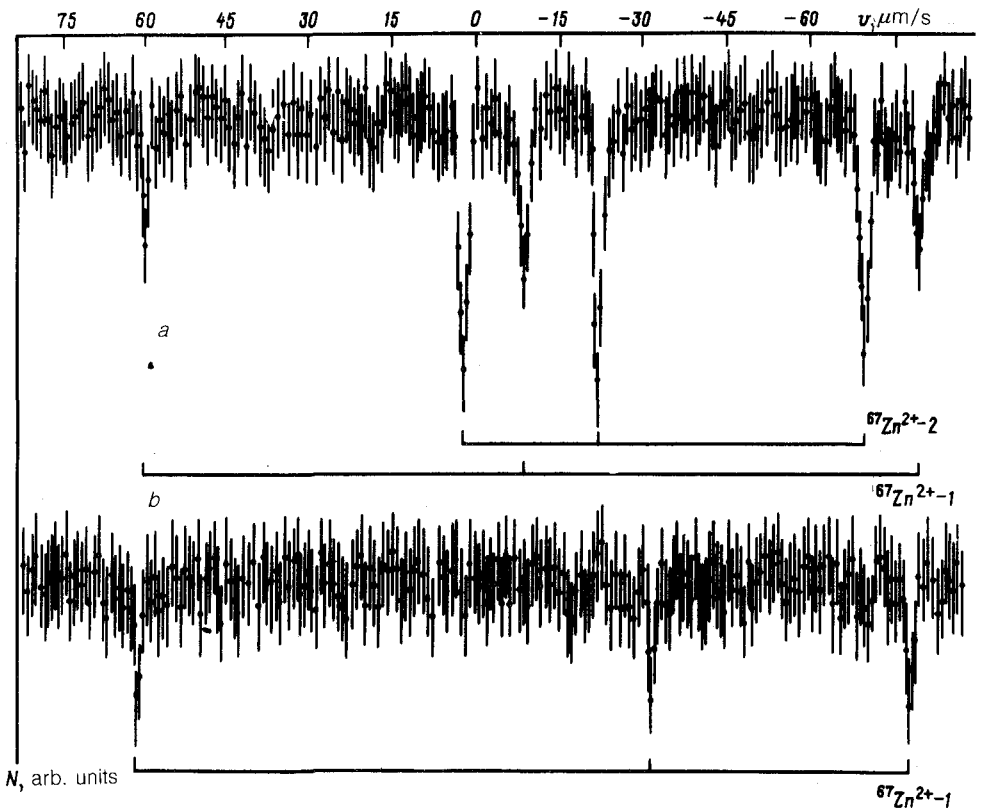


FIG. 1. Emission Mössbauer spectra of ^{67}Cu at 4.2 K. *a*— $YBa_2Cu_3O_7$; *b*— $YBa_2Cu_3O_6$. The positions of the quadrupole triplets corresponding to $^{67}Zn^{2+-1}$ and $^{67}Zn^{2+-2}$ centers are shown.

4.2 K with ^{67}ZnS absorbers for the samples containing ^{67}Cu and $^{133}\text{CsCl}$ absorbers for the samples containing ^{133}Ba .

The copper atoms in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ have two structurally nonequivalent positions, Cu-1 and Cu-2, with a 1:2 population ratio.¹² We accordingly expected the appearance of two quadrupole triplets with different values of e^2qQ in the emission Mössbauer spectrum of $\text{YBa}_2^{67}\text{Cu}_3\text{O}_{7-x}$. It can be seen from Fig. 1a that this is indeed what is observed for the spectrum of a $\text{YBa}_2^{67}\text{Cu}_3\text{O}_7$ samples: The spectrum is a superposition of two quadrupole triplets with an intensity ratio $\sim 1:2$. The less intense spectrum should be attributed to $^{67}\text{Zn}^{2+}$ -1 centers at Cu-1 sites, and the more intense spectrum to $^{67}\text{Zn}^{2+}$ -2 centers at Cu-2 sites. For the $\text{YBa}_2^{67}\text{Cu}_3\text{O}_6$ sample, the spectrum has a single triplet (Fig. 1b), which should be attributed to $^{67}\text{Zn}^{2+}$ -1 centers at Cu-1 sites (for the Cu-2 sublattice in $\text{YBa}_2\text{Cu}_3\text{O}_6$ an antiferromagnetic ordering is observed¹³ at $T < 450$ K, and the Mössbauer spectrum of $^{67}\text{Zn}^{2+}$ -2 centers is spread out over a large velocity interval). The properties of the EFG tensor for the $^{67}\text{Zn}^{2+}$ centers in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ are shown in Table I.

The barium atoms in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ lattice occupy a single position,¹² so the emission Mössbauer spectra of the $\text{Y}^{133}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ ceramics (Fig. 2) should be attributed to $^{133}\text{Cs}^+$ centers at barium sites. The broadening of the experimental spectra results from an unresolved quadrupole splitting. The values of e^2qQ for these centers are listed in Table I. In calculating e^2qQ we allowed for the circumstances that the Mössbauer spectrum of the ^{133}BaO sample is an isolated line with a width at half-maximum of 0.90 ± 0.02 mm/s. This value was adopted as the instrumental width of the spectral line.

In general, the EFG at the nuclei in a crystal lattice is produced by the surrounding ions q_{cr} and by nonspherical host atomic valence electrons, $q_{\text{val}}:q = (1 - \gamma)q_{\text{cr}} + (1 - R)q_{\text{val}}$, where γ and R are Sternheimer coefficients. For the Zn^{2+} and Cs^+ ions, there is no valence component of the EFG, so q_{cr} at the copper and barium sites can be determined from the Mössbauer data through the use of the known Sternheimer coefficients [$\gamma(\text{Zn}^{2+}) = -12.2$ (Ref. 14), $\gamma(\text{Cs}^+) = -121.3$ (Ref. 15)] and the known quadrupole moments of the ^{67}Zn nucleus

TABLE I. Properties of the electric-field-gradient tensor of ^{67}Zn and ^{133}Cs centers in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

Compound	Center	e^2qQ , MHz	η	q_{cr} , expt	$e/\text{\AA}^3$, theo	Center	e^2qQ , MHz	q_{cr} , expt	$e/\text{\AA}^3$, theo
$\text{YBa}_2\text{Cu}_3\text{O}_7$	$^{67}\text{Zn}^{2+}$ -1	20.1 ± 0.5	0.95 ± 0.05	0.283	1.165	$^{133}\text{Cs}^+$	45 ± 5	0.048	-0.110
	$^{67}\text{Zn}^{2+}$ -2	11.8 ± 0.5	< 0.2	0.151	0.701				
$\text{YBa}_2\text{Cu}_3\text{O}_6$	$^{67}\text{Zn}^{2+}$ -1	-23.5 ± 0.5	< 0.2	0.299	-1,286	$^{133}\text{Cs}^+$	65 ± 5	0.069	0.150

Here e^2qQ is the quadrupole interaction constants; eq_{cr} is the principal component of the EFG tensor at the nuclei under study, created by lattice ions; and η is an asymmetry parameter. Data from Ref. 16 were used in the calculation of eq_{cr} .

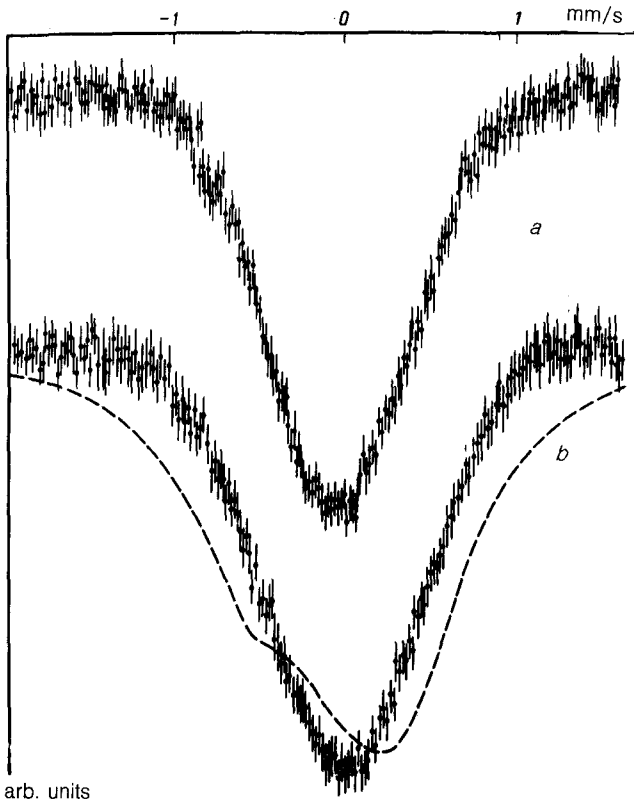


FIG. 2. Emission Mössbauer spectra of ^{133}Cs at 4.2 K. *a*— $\text{YBa}_2\text{Cu}_3\text{O}_6$; *b*— $\text{YBa}_2\text{Cu}_3\text{O}_7$. The dashed line shows a theoretical prediction based on the assumption $q_{\text{cr}} = 0.150 \text{ e}/\text{\AA}^3$.

($Q = 0.17 \text{ b}$ for the ground state and $Q = 0$ for the excited state¹⁴) and of the ^{133}Cs nucleus ($Q = 0.003 \text{ b}$ for the ground state and $Q = -0.22 \text{ b}$ for the excited state¹⁵). The values found for q_{cr} in this manner are listed in Table I. They can be compared with theoretical predictions of q_{cr} for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Ref. 16). In this table we see a qualitative agreement between the experimental and theoretical values of q_{cr} [for $\text{YBa}_2\text{Cu}_3\text{O}_7$, for example, the theoretical ratio $q_{\text{cr1}}/q_{\text{cr2}} \sim 1.6\text{--}2.0$ agrees with the experimental value ~ 1.8 (here eq_{cr1} and eq_{cr2} are the principal components of the EFG tensor at the Cu-1 and Cu-2 sites, respectively); the transition from $\text{YBa}_2\text{Cu}_3\text{O}_7$ to $\text{YBa}_2\text{Cu}_3\text{O}_6$ is accompanied by not only a change in the absolute value of eq_{cr} for the copper and barium sites but also a change in the sign of eq_{cr} for the copper sites]. On the other hand, the agreement does not extend to the quantitative level. The situation is illustrated by the dashed line in Fig. 2b, which shows a theoretical Mössbauer spectrum for a $\text{Y}^{133}\text{Ba}_2\text{Cu}_3\text{O}_6$ sample. This calculation used the value of eq_{cr} from Ref. 16. The theoretical spectrum has a clearly defined structure, in contrast with the experimental spectrum. We believe that the discrepancy between the experimental and

theoretical values of eq_{cr} is a consequence of imperfections of the initial assumptions used in the EFG calculations.

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