COMPARISON OF EXPERIMENTAL AND CALCULATION VALUES OF THE ELECTRIC FIELD GRADIENT TENSOR PARAMETERS FOR IMPURITY ATOMS $^{57}Fe^{3+}$ and $^{57m}Fe^{2+}$ B CuO

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Abstract. Absorption Mossbauer spectra of CuO samples: ^{57}Fe at 295K they are a superposition of two quadrupole doublets, the parameters of which are practically independent of the iron concentration.Discrepancy between calculated and experimental values of quadrupole splitting of CuO samples: ^{57} Fe may be a consequence of aliv a - ribbon replacement of the Cu $^{2+}$ ion with the Fe $^{3+}$ ion.

Keywords: Gradient, electric, Mossbauer spectroscopy, impurity, experimental, temperature, effective, magnetic, represent, parameters, generally.

Аннотация.Абсорбционные мессбауэровские спектры образцов CuO: 57Fe при 295К представляют собой суперпозицию двух квадрупольных дублетов, параметры которых практически не зависят от концентрации железа. Расхождение расчетных и экспериментальных значений квадрупольного расщепления образцов CuO: 57Fe может быть следствием замены в aliv a - ленте иона Cu2+ на ион Fe3+.

Ключевые слова: градиентный, электрический, мессбауэровская спектроскопия, примесь, экспериментальный, температура, эффективный, магнитный, представлять, параметры, в общем случае.

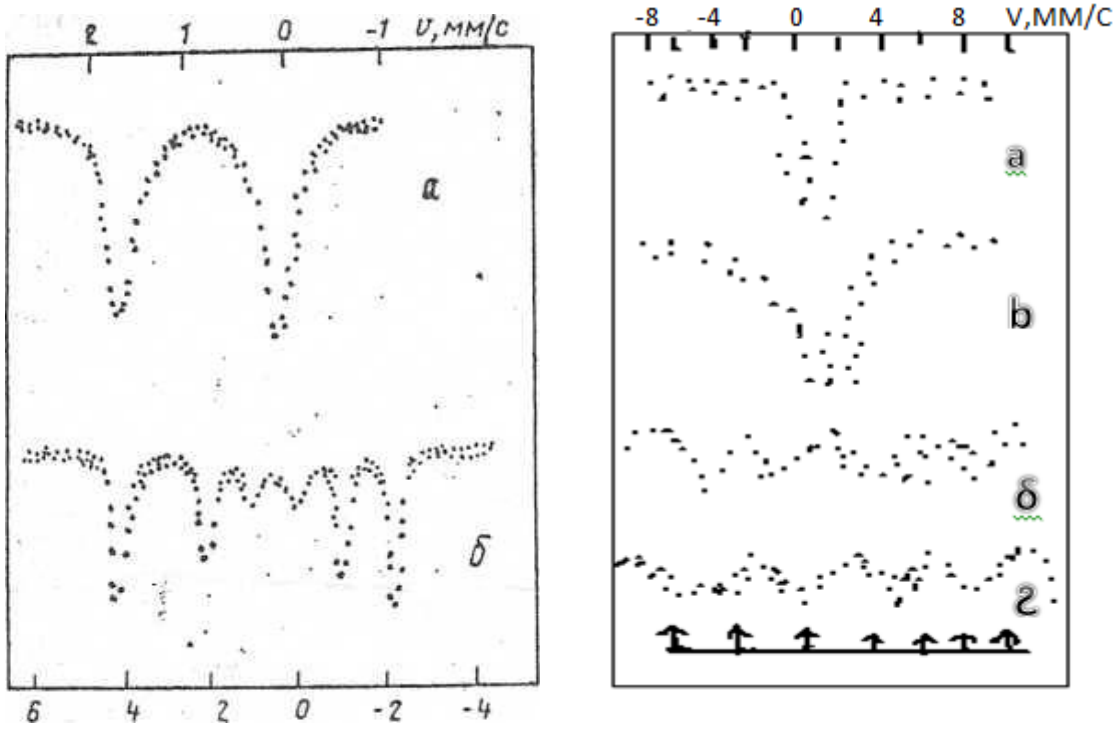
Using the Mossbauer spectroscopy it is shown that the iron impurity, atoms substitute the Cu^{2+} ions in CuO lattice as $^{57}Fe^{3+}$ and $^{57m}Fe^{2+}$ However the calculations of the electric field gradient(EFG) tensor parameters. On the; ^{57} Fe: nucleus are found to be uncorrect according to the appearance of the valence; electrons (in the case of $^{5.m}$ Fe 2+) or to the appearance of the additional EFG sources: (in the cape of ^{57} Fe $^{3+}$). Therefore it is doubtful to use the Mossbauer spectroscopy effecti vely in the case of the ^{57} Fe impurity atoms is the high-T_c superconductive lattices with- the aim of determing the EFG tensor parameters.

Mossbauer spectroscopy on ^{57}Fe impurity atoms widely used to study high-temperature superconductors [1]. It is assumed that ^{57}Fe impurity atoms replaces the m-copper atoms, so that the experimental value of the quadrupole splitting of the Mossbauer spectra of ^{57} Fe can be compared with the results of its theoretical calculation. However, to carry out such a comparison, it is necessary to know the location of the local atom in the lattice. That is why we tried to make such a comparison for the case of impurity iron atoms in the lattice of the simplest copper oxide CuO . Copper oxide has a Neel temperature T_N = 225 K [2], and therefore it was expected that when exogenous iron atoms enter copper sites, the Mossbauer spectrum will either be a magnetic sextet (at $T < T_N$), or quadrupole doublet (at $T > T_N$).

Copper oxide was obtained by precipitation of copper hydroxide from an aqueous solution of copper sulfate, followed by calcination of the precipitate at 450°C in air for 2 hours. Iron in the form of ferrous sulfate was introduced into an aqueous solution of copper sulfate and its concentration in CuO was 0.6 and 1,2 at %. All samples were single-phase. Samples of CuO doped with ^{57}Co were obtained (cobalt in the chemical form $57CoC1_2$ WAS INTRODUCED INTO AN AQUEOUS solution of copper sulfate, the concentration of cobalt in CuO ~10 17 at.m~ ^{3}).

Mossbauer spectra of ^{57}Fe were taken in the temperature range 5-295 K , isomer shifts are given relative to α - Fe , errors in determining isomer shift δ, quadrupole splitting Δ, linewidth Γ and effective magnetic field H_{ef} ^{57}Fe nuclei were ±0.01 mm/s, ±0.02 mm/s, ±0.02 mm/s and ±5 ke , respectively .

The Mossbauer emission spectra of CuO : ^{57}Co samples at 295K are well-resolved quadrupole doublets (δ = 0.78 mm/s, Δ = 1.56 mm/s), and at T≤225 K the spectra begin to broaden and at T <150K represent well resolved



Rice. 1, Mössbauer emission spectra of CuO : ^{57} Co at 295 *(a)* and 80 K *(b),g* Absorber K **.1** Re (C N) s • 3II $_2$ O.

Rice. 2. Absorption Mossbauer spectra of CuO : ^{57} Fe (0.6 at .%) at 295 *(a),* 150 *(b),* 50 *(c)* and 5 K *(G).* The positions of two quadraupole doublets (*a)* and two magnetic sextets *(d) are shown.* Source ^{57} Co (Pd).

magnetic sextets (at 4.2 K H_{ef}= 220 ke) (Fig. 1). Isomeric shifts, quadrupole splitting, and effective magnetic field are typical for ferrous iron, and we concluded that the daughter atoms of 57m Fe formed after the decay of ^{57} Co in CuO are in the form of 57m Fe $^{2+}$ in copper nodes.

Absorption Mossbauer spectra of CuO samples : ^{57}Fe at 295K they are a

superposition of two quadrupole doublets, the parameters of which are practically independent of the iron concentration. At an iron concentration of 0.6 at .% δ_1 = 0.32, Δ_1 = 1.45, Γ = 0.55,δ_2 = 0.34, Δ 2 = 0.79, 1 Γ= 0.47 mm/s the ratio of the areas under the doublets is 1.00±0.02 (Fig. 2, a). Lowering the measurement temperature below 230 K leads to broadening of the spectra with the subsequent manifestation of hyperfine structure in the form of superposition of two magnetic sextets (at 5K H_{ef} = 430, H_{ef} = 502 ke). At a fixed temperature, the resolution of the hyperfine structure deteriorates with increasing iron concentration. The magnitudes of isomer shifts, quadrupole splittings, and effective magnetic fields are typical for ferric iron. The presence of an obvious correlation between the transition of CuO to antiferrom g - thread state and appearance of ^{57}Fe on nuclei magnetic field allows us to conclude that impurity iron atoms enter the copper sites of the CuO lattice , forming two equally connected states of Fe^{3+} .

For iron centers at the copper sites of the CuO lattice, we calculated the parameter of the electric field gradient tensor (EFG) in the point charge approximation. The position of atoms in the unit cell and the parameters of the unit cell were specified according to [4]. Lattice sums m - (we calculated on a computer, the summation was carried out inside the sphere radius 30 A. Below are the main component of the Electric field gradient tensor eq_{KP}, the asymmetry parameter η_{kp} and the values of the quadrupole splittings of the Mossbauer spectra calculated on their basis, ^{57}Fe : $\Delta^{p} = -0.5 \cdot e^{2} q_{kp} Q (1 - \gamma) (1 + \eta_{kp}/3)^{1/3}$ and: for the quadrupole moment of the ^{57m}Fe nucleus value was used Q= 0.213 b [5], coefficient.

For CuO samples : ^{57}Co and CuO : ^{57}Fe There is no satisfactory agreement between the experimental and calculated values of quadrupole splitting. In the case of CuO : ^{57}Co this discrepancy is explained by the contribution to the Electric field gradient on ^{57m}Fe nuclei from the valence electrons of iron (Fe^{2+} ion has an electronic configuration of $3d^{6}$). If we use the data from [7] for the maximum possible value of quadrupole splitting due to one 3d electron of iron in Fe^{2+} compounds , 3.7 mm/s, then we obtain for the calculated value Δ_R = 1.4mm/s which is in good agreement with experimental Δ = 1.56 mm/s for CuO sample : ^{57}Co.

Discrepancy between calculated and experimental values of quadrupole splitting of CuO samples: ^{57}Fe may be a consequence of aliv a - ribbon replacement of the Cu^{2+} ion with the Fe^{3+} ion . This should be accompanied by the appearance of compensating centers (cation vacancies) in the lattice, which will be localized near the impurity atom and change the parameters of the Electric field gradient tensor. We calculated the Electric field gradient tensor at copper sites for various variants of the location of vacancies in the immediate environment of the Fe^{3+} ion . It turned out that the nearest cation vacancy, depending on its orientation relative to the main axes of the Electric field gradient tensor of the unperturbed lattice, leads to two values of the quadrupole splitting of the Mossbauer spectrum , ^{7}Fe ^{3} +. It follows that the experimental Mossbauer spectra of CuO : ^{57}Fe samples cannot be interpreted as superposition of spectra from isolated Fe^{3+} and associates Fe ^{3} vacancy, since in this case three quadrupole oak summers should be

observed. Due to the absence of isolated iron centers and to maintain the electrical neutrality of the lattice, all impurity Fe^{3+} ions.

Fe^{3}+—V—Fe^{3}+ must enter into associates and two structurally nonequivalent positions for iron atoms in the SI are associated with different orientations of these associates relative to the main axes of the electric field gradient tensor of the undisturbed lattice. Obviously, the populations of these states should be equal due to the equality of their electrostatic energy, and this explains the experimental fact that the areas under two quadrupole doublets are equal in the Mossbauer spectra of CuO; ^{67}Fe samples. The existence of two structurally unequal Fe^{3}+-V—Fe^{3}+ associates should lead to the appearance of two magnetically split sextets in Messebauer spectra at $T<T_N$, which is observed in experimental spectra. The fact that the resolution of these spectra depends on the concentration of iron indicates the existence of a spin-spin interaction between iron centers.

However, even for such a model, there is no agreement between the experimental and calculated values of the quadrupole splitting of the Mossbauer spectra of CuO:^{57}Fe samples. In principle, the agreement of these values can be achieved either by revising the generally accepted value of y(Fe^{3}+), or by lowering the charges of all lattice ions by the same number of times. Obviously, this will lead to a loss of Reliability of the information obtained by comparing the experimental and calculated values of the quadrupole splitting of the Mossbauer spectra. The problem of varying y(Fe3+) and lattice ion charges can be eliminated if the calculated $p=\Delta_1^p/\Delta_2^p$ and experimental $p^e=\Delta_1/\Delta_2$ quadrupole ratios are compared.

There is no cleavage for two iron centers. However, there is also no agreement between the values p and p3 (p- 1.38, p3 = 1.84±0.07). This indicates that when calculating the electric field gradient tensor, additional electric field gradient sources were not taken into account, leading to a decrease in the resulting electric field gradient tensor. The reason for the appearance of an additional source of electric field gradient on ^{57}Fe nuclei in SIO may be the absence of a cationic vacancy in the immediate environment of iron atoms due to this, oxygen ions shift in the first coordination sphere of impurity atoms and it is qualitatively obvious that this shift should lead to a decrease in the absolute value of the main quantitative calculation of the electric field gradient tensor in this case is hardly possible.

Thus, even for a simple SI lattice, the comparison of the calculated and experimental values of the parameters of the electric field gradient tensor turns out to be impossible if Mossbauer spectroscopy on ^{57}Fe impurity atoms is used. The obtained results cast doubt on the possibility of effective use of this spectroscopy in the lattices of complex high-temperature superconductors.

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