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Yb^{3+} optical-transitions probability change at magnetic phase transitions in the multiferroic $Cu_3Yb(SeO_3)_2O_2Cl$

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The infrared transmission spectra of $Cu_3Yb(SeO_3)_2O_2Cl$, an ytterbium analogue of the natural mineral francisite, have been studied in a wide temperature range. Two phase transitions (at $T_N = 35$ K and $T_R = 9$ K) were registered by studying the splittings of Yb^{3+} Kramers doublets. It is shown that the low-temperature transition is spin-reorientational one. An analysis within the framework of the mean field theory allows us to conclude that the single-ion magnetic anisotropy of ytterbium does not coincide with the anisotropy of the copper magnetic subsystem. An estimate of the energy required for the reorientation of the copper magnetic subsystem has been obtained, it is 864 J mol^{-1}. It was found that the probability of a 0–0 transition in the Yb^{3+} ion changes in the temperature range of both phase transitions, presumably due to spontaneous magnetostriction.

Keywords: francisite, multiferroic, optical spectroscopy, *f–f* transitions, Kramers doublets.

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Introduction

Ytterbium copper oxochloroselenite $Cu_3Yb(SeO_3)_2O_2Cl$ is an isostructured synthetic analog of the natural mineral francisite $Cu_3Bi(SeO_3)_2O_2Cl$. The mineral, discovered in 1987, quickly attracted the attention of chemists and physicists as well. From a chemical point of view, it turned out that it has a unique combination of chemical elements observed for the first time [1]; it can be synthesized in laboratory conditions [2]; it allows for a variety of replacement of chemical elements [3–5]. In particular, it is possible to replace bismuth with rare earth (RE) elements [2,6,7]. Francisite, like its RE analogues, crystallizes in the space group *Pmmn*, $a = 6.354$ Å, $b = 9.63$ Å, $c = 7.22$ Å [1,4,7]. One of the features of the structure is the space arrangement of Cu^{2+} ions, which form two-dimensional layers in the ab plane, while inside the layer they form a deformed Kagome lattice (Fig. 1). This feature, together with experimental confirmation, allows us to attribute francisite, as well as its isostructural related compounds, to the class of low-dimensional frustrated magnets [3,8,9].

The study of the magnetic properties of francisite and related compounds is the focus of both experimental and theoretical studies [6,8–12]. It has been established that francisite and its bromine analogue $Cu_3Bi(SeO_3)_2O_2Br$ are ordered antiferromagnetically (AFM) at low temperatures ($T_N \sim 24$ K [2] and ~ 27 K [12], respectively), its RE analogues — at temperatures in the range of 35–41 K [6,9,13–19]. The trivalent RE ion is an excellent optical probe for studying magnetic properties [20–22]. Kramers ions are especially interesting, in particular Yb^{3+}, which is part of $Cu_3Yb(SeO_3)_2O_2Cl$, since their crystal-field levels are at least twice degenerate. As it is known, Kramers degeneracy is removed only by a magnetic field, for example, an internal field arising in a magnetic-ordered state in a crystal. Thereby , spectroscopic study of *f–f* transitions of Kramers ions is an informative means of studying magnetic phase transitions [23,24]. Replacing bismuth by a rare earth with a non-zero magnetic moment leads to the appearance of a second magnetic subsystem, and interesting phenomena associated with the interaction of subsystems arise. Thus, in samarium [13] and ytterbium [14] francisites, there are spin-flip transitions, caused by the strong single-ion magnetic anisotropy of RE ions. It is necessary to estimate the magnitude of such anisotropy; it can be done based on optical data.

In addition, the fracisite family is of interest from the point of view of their multiferroic properties, which have now already been discovered in the crystal $Cu_3Bi(SeO_3)_2O_2Cl$ [25–30]. In particular, a linear magnetoelectric effect [27], spontaneous polarization [26], and spontaneous magnetostriction [28] were observed in $Cu_3Bi(SeO_3)_2O_2Cl$. Multiferroic behavior could also be observed in RE francisites, but they are less studied. Optical spectroscopy of *f–f* transitions is an adequate method for studying both magnetic ordering and the possible interaction of the magnetic and charge subsystems (the appearance of electric polarization) [22,31], with the latter influences the energy levels of the RE element ion through the crystal field.

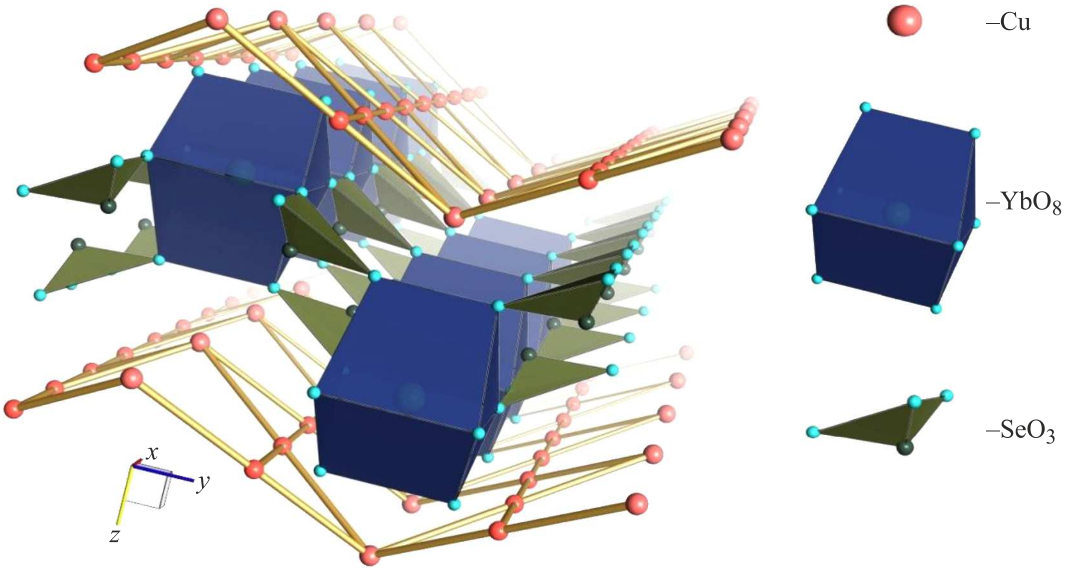

Figure 1. Fragment of the crystal structure of $Cu_3Yb(SeO_3)_2O_2Cl$. In the xy plane, copper ions form a corrugated Kagome lattice. There are copper layers parallel to the xy plane and YbO_8 and SeO_3 polyhedra located between the planes.

In this paper, we present the results of studying the magnetic properties of $Cu_3Yb(SeO_3)_2O_2Cl$ using optical spectroscopy of f–f transitions in the trivalent ytterbium ion. Our goal was to study magnetic ordering and the effects of interaction between magnetic and charge subsystems.

Experiment

Polycrystalline samples of $Cu_3Yb(SeO_3)_2O_2Cl$ were obtained by solid-phase synthesis at the Faculty of Chemistry of Lomonosov Moscow State University. The synthesis is described in detail in the papers [2,7]. The results of the X-ray study showed that the sample has a structure with space group $Pmmn$ and does not contain other phases.

For optical measurements, a powder was prepared in an agate mortar from a mixture of 5–10 mg $Cu_3Yb(SeO_3)_2O_2Cl$ and 150–200 mg KBr of optical quality. The mixture was located in a mold in a hydraulic press and held for 5 min at a pressure of approximately 5 at. The result was a thin tablet, which was located in a holder for measurements on a spectrometer. An indium substrate was used to ensure thermal contact between the sample and the cold finger of cryostat.

The transmittance spectra of the samples were measured using a Bruker Fourier spectrometer model IFS 125HR. A CryoMechST403 closed-cycle optical helium cryostat was used for measurements at low temperatures. The holder with the sample was located inside the cryostat and fixed in a position parallel to the plane of the inlet. The cryostat was located in the cell compartment of the device, after which air was pumped out from the internal cavities of the cryostat. Measurements were carried out at pressures below 10^{-4} torr inside the cryostat. Before starting measurements, the cooling system was turned on and the temperature required for measurements was set using the device software and temperature controller. The device software, in particular the OPUS program, allowed to perform a series of measurements with specified parameters (temperature, measurement accuracy, scanning time) in automatic mode. This was also used for sequential measurements of transmittance spectra with smaller temperature steps at low temperatures than at high temperatures, as well as for measurements while heating and cooling the sample.

Experimental results and discussion

Figure 2 shows the transmittance spectra of ytterbium francisite in the region of electronic transitions in the ytterbium ion at high (300 K) and low (5 K) temperatures. These spectra were obtained by subtracting a broad structureless baseline from the transmission spectrum of a tablet filled with KBr, since due to light scattering in the tablet, there is a smooth drop in transmittance with increasing wave numbers. In addition, the wing of the broad absorption band of divalent copper also contributes to the baseline. The latter is located in the near-IR and visible red areas of the spectrum, as a result of which francisites have a green color. The spectra obtained in this way, presented in Fig. 2, contain narrow lines due to f–f transitions in the Yb^{3+} ion. The given spectra were discussed in detail in the paper [14]. Here we will briefly present the conclusions of the paper [14] regarding the description of the spectra, their temperature changes and interpretation and move on to a discussion of two points not touched upon in the paper [14], namely, attention will be paid to single-ion anisotropy of the Yb^{3+} ion and the temperature dependence of the intensities of spectral lines near the temperatures of two phase transitions.

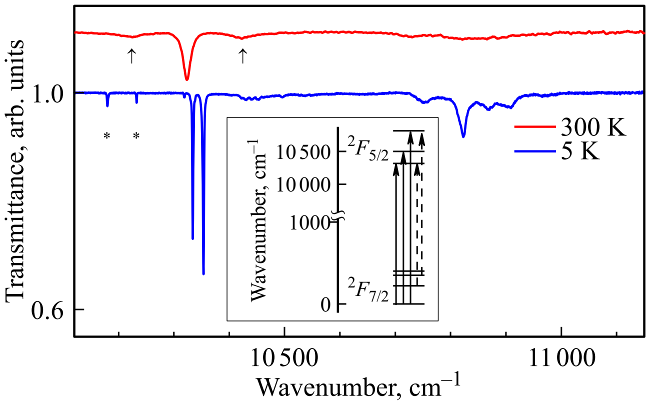

Figure 2. Transmittance spectra of $Cu_3Yb(SeO_3)_2O_2Cl$ in the region of the intermultiplet transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$ in the Yb^{3+} ion at high (300 K) and low (5 K) temperatures. Asterisks indicate lines associated with the impurity phase. Arrows point to vibronic bands. The spectra are arbitrarily shifted along the ordinate axis for clarity. The insert shows — a diagram of the crystal-field levels of the Yb^{3+} ion. Arrows show optical transitions, dashed arrows show transitions that „freeze " out at low temperatures due to population depletion.

The Yb^{3+} ion (electronic configuration $4f^{13}$) has the simplest energy scheme of electronic levels in the lanthanide series with two multiplets: the ground $^2F_{7/2}$ and the excited $^2F_{5/2}$, as shown in the insert to Fig. 2. A crystal field with symmetry C_{2v} splits multiplets into 4 ($^2F_{7/2}$) and 3 ($^2F_{5/2}$) Kramers doublets. In addition to transitions between the crystal-field levels of multiplets, the spectrum contains vibronic bands (electron-phonon transitions) characteristic of the Yb^{3+} ion. The most intense line 10332 cm^{-1} corresponds to the transition from the ground state of the $^2F_{7/2}$ multiplet of the Yb^{3+} ion to the first level of the excited $^2F_{5/2}$multiplet (the so-called 0–0-band). Detailed temperature changes for it are presented in Fig. 3.

At temperatures below $T_N = 35$ K, the 10332 cm^{-1} line experiences splitting into two components, and in a narrow temperature range near $T_R = 9$ K, a sharp change in the nature and magnitude of the splitting occurs, and four components are observed in the spectrum, two of which „freeze out" with a further decrease in temperature. The splitting of spectral lines is due to the removal of Kramers degeneracy in the effective exchange field that appears during magnetic ordering. In the $Cu_3Yb(SeO_3)_2O_2Cl$ crystal, two magnetic phase transitions occur: magnetic ordering at the temperature $T_N = 35$ K and a spin-flip transition at $T_R = 9$ K.

We assume that the phase transition at a temperature of 35 K is associated with the ordering of the copper magnetic subsystem. Firstly, in an isostructural compound with non-magnetic yttrium, the entire magnetic system consists only of copper ions, and it is ordered at a temperature of 36.3 K [12]. The closeness of the AFM transition temperatures in the two compounds suggests that ytterbium has little effect on the exchange integral of the interplanar interaction. Secondly, the exchange magnetic d–d-interactions are much much stronger than the f–d ones. Therefore, it should be expected that it is the copper subsystem, when ordered, that creates an internal field, which splits the Kramers doublets of ytterbium. In the framework of the mean-field theory, the splitting Δ of the Kramers doublet can be represented as a quasi-Zeeman expression

$$\Delta = \mu_B \sqrt{\Sigma_{i=x,y,z} (g_i B_{\mathrm{ef},i})^2},$$

where μ_B is Bohr magneton, g_i and $B_{\mathrm{ef},i}$ are ith components of the magnetic g factor of the RE-ion and the internal effective field, respectively. The sharp change in the value of Δ at the temperature $T_R = 9$ K is associated with a change in the direction of the effective field acting on the RE ion. Thus, the magnetic structure realized during the initial ordering, due to the magnetic anisotropy of the copper magnetic lattice, changes to another one.

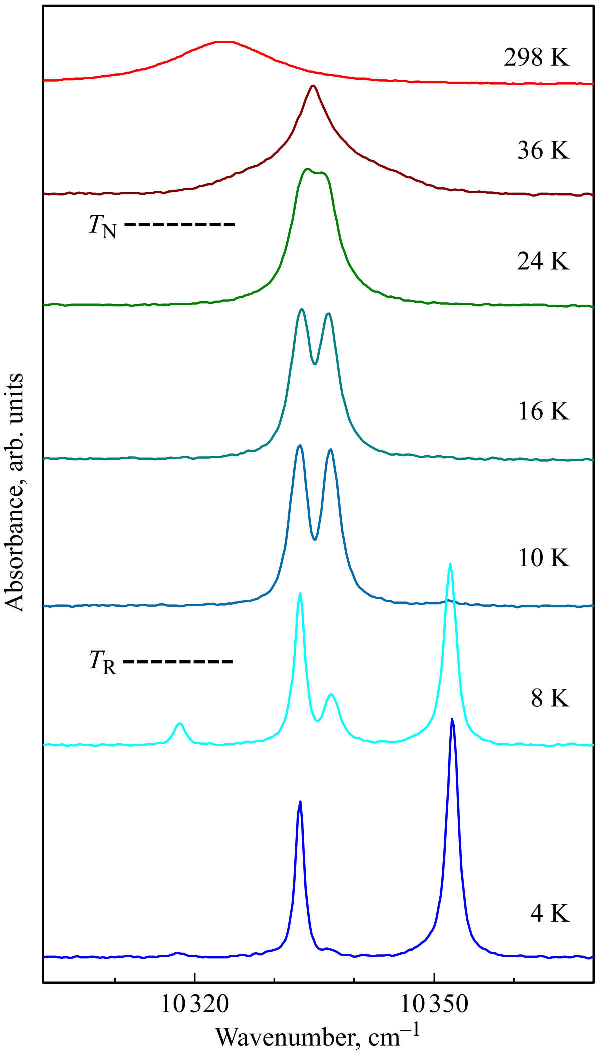

Figure 3. Absorption spectra of $Cu_3Yb(SeO_3)_2O_2Cl$ at several temperatures in the region of the 0–0 transition in the Yb^{3+} ion. The spectra are shifted along the y-axis for clarity.

Our data allow to conclude that at a temperature $T_N = 35$ K the ground Kramers doublet of ytterbium does not undergo splitting, but the upper doublet of the transition from the multiplet $^2F_{7/2}$ splits, as shown in the level diagram in Fig. 4. Otherwise, if the splitting of the ground doublet was responsible for the splitting of the line $10332\,\text{cm}^{-1}$ ($\Delta_{0-0} = 4\,\text{cm}{-}1$), the ratio of the intensities m of the two components into which the line splits would change due to the temperature change in the populations and would amount to

$$m = \exp(hc\Delta_{0-0}/kT),$$

where h is Planck's constant, c is the speed of light, k is Boltzmann's constant. A simple estimate shows that at a temperature of 10 K near the spin-flip transition $m = 1.77$, i.e. the intensity ratio of the two lines — component of the split 0−0–line should change from 1:1 to 1:1.77 upon cooling from 35 K to 10 K. The observed spectra (Fig. 3, *a*) show that the ratio of the components, close to 1:1, is maintained throughout the entire specified temperature range. Thus, we can conclude that the splitting of the 0−0 line into two components in the temperature range 35−9 K is due to the splitting of the upper doublet of the transition from the $^2F_{7/2}$ multiplet. The absence of splitting of the ground doublet in the temperature range $T_R < T < T_N$ is due to the fact that, according to the quasi-Zeeman formula, the component of the magnetic factor g along the field direction B_{ef} is equal to (or close to) zero.

Both doublets participating in the optical transition split below the temperature T_R, and the magnitude of their splitting is easily calculated from the distances between the spectral components. The values Δ_0 and Δ_a are 15 and $20\,\text{cm}^{-1}$, respectively, at a temperature of 5 K.

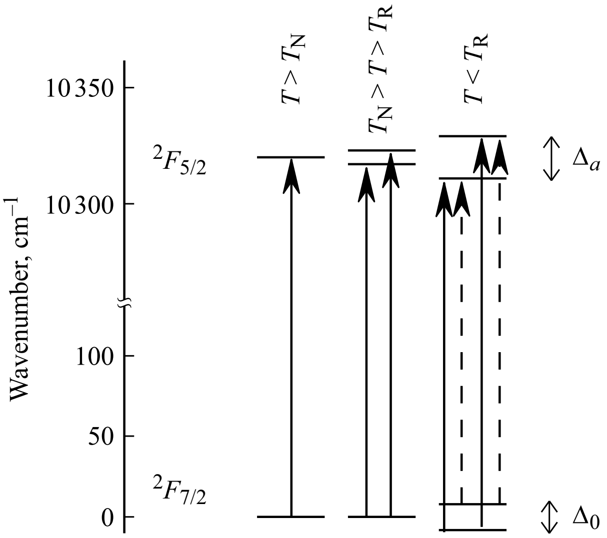

Figure 4. Diagram of Kramers doublets participating in the 0−0 transition in the Yb^{3+} ion in three magnetic phases: paramagnetic ($T > T_N$), AFM1 ($T_N > T > T_R$) and AFM2 ($T < T_R$).

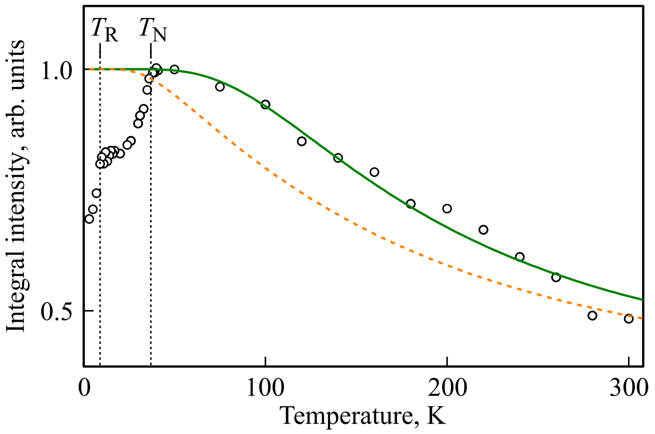

Figure 5. Integrated intensity of absorption lines in the area of 0−0-transition in the range $10300-10360\,\text{cm}^{-1}$ depending on temperature. The lines represent the population calculation of $n_0 + n_1$ (see the text).

As can be seen from the Fig. 4, the ground state of the Yb^{3+} ion decreases in energy by $\Delta_0/2$, giving an energy gain to the entire crystal. At the same time, it is obvious that part of this gain $\mathscr{E}_{SR,Yb}$ should be spent on reorientation of the copper magnetic system. At the moment of reorientation itself, these energies are compared in magnitude. Thus, we can estimate the gain of the ytterbium subsystem and thus determine the energy required to reorient the copper spins. Obviously, the gain $\mathscr{E}$ (which is also the energy expression of the value of the single-ion magnetic anisotropy of a rare earth ion) per mole will be

$$\mathscr{E} = \frac{1}{2} x N_A hc\Delta_0, \tag{1}$$

where x is a number of RE ions in a formula unit (in the case of $Cu_3Yb(SeO_3)_2O_2Cl$ $x = 1$), N_A is the Avogadro constant. Since the splitting Δ_0 depends on temperature, the magnetic anisotropy of the RE ion also changes with temperature. At a temperature of 9 K after reorientation, the value Δ_0 is $14.5\,\text{cm}^{-1}$, and we obtain $\mathscr{E}_{SR,Yb} = 864\,\text{J mol}^{-1}$. The latter value is also an estimate of the spin-flip energy of the copper subsystem $\mathscr{E}_{SR,Cu}$, which is of interest for comparison with data from other possible studies that are currently missing in the literature.

We investigated how the total integral intensity of absorption lines in the region of the 0−0 transition changes with temperature in the range $10300-10360\,\text{cm}^{-1}$. The obtained dependence is shown in Fig. 5. It has two obvious features in the temperature ranges of T_N and T_R, corresponding to two magnetic phase transitions in $Cu_3Yb(SeO_3)_2O_2Cl$.

The intensity of the absorption line I is described by the relation $I = P(n_0 + n_1)$, where n_i — the population of two energy states (0 and 1) of the split ground doublet, P — the transition probability, which is determined by the following expression:

$$P = \left|\langle\Psi_i\left|\hat{d}\right|\Psi_f\rangle\right|^2. \tag{2}$$

Here $\hat{d}$ — dipole moment operator, Ψ_i and Ψ_f — wave functions of the initial and final states of the transition.

The total population of $n_0 + n_1$ is determined from the Boltzmann distribution law:

$$n_0 + n_1 = \frac{1}{1 + \Sigma_i e^{-E_i/kT}}, \qquad (3)$$

where E_i are the energies of the crystal-field levels of the ground multiplet $^2F_{7/2}$ of the Yb^{3+} ion.

In the spectra we obtained in a wide temperature range from 5 K to room temperature on the low-frequency side of the $10330\,cm^{-1}$ line, we were unable to detect other lines except a broad band near the frequency $10230\,cm^{-1}$, which we presumably attributed to the vibronic transition. This is confirmed by the fact that an attempt to describe experimental points in the paramagnetic phase by equation (3) under the condition that $E_2 = 100\,cm^{-1}$ does not give a good result (see the dashed curve in Fig. 5), since this energy level begins to be noticeably populated, starting from temperatures of about 30 K. A good adapting is obtained with the value $E_2 = 220\,cm^{-1}$ ($E_3 = 250\,cm^{-1}$, $E_4 = 300\,cm^{-1}$).

The deviation of the experimental points of the integral intensity of the $10330\,cm^{-1}$ line from the curve describing the population clearly indicates a change in the transition probability precisely at the temperatures of two phase transitions. The transition probability changes when an internal magnetic field appears in the crystal, as well as during spin-flip. According to equation (2), this is only possible at the wave function renormalization due to the effects of interaction of the charge and magnetic subsystems in the internal magnetic field. An analogue of the magnetoelectric effect arises, but not in an external field, but in an internal field B_{ef}, arising in a magnetic-ordered state. The splitting of multiplets in a crystal field is associated with the electric field created both by the charges surrounding the RE ion and by the exchange charges. It is the appearance of electric polarization that may be the reason for the change in the probability of optical transitions in the Yb^{3+} ion during magnetic phase transitions in $Cu_3Yb(SeO_3)_2O_2Cl$. This scenario is supported by the fact that the magnetoelectric effect is actually observed in the mineral francisite [25–30]. One of the reasons for non-zero electric polarization may be spontaneous magnetostriction. Thus, we associate the observed changes in the probability of optical transitions with the effect of interaction between the magnetic and charge subsystems $Cu_3Yb(SeO_3)_2O_2Cl$, which is a manifestation of its multiferroicity.

Conclusions

A spectroscopic study of the $Cu_3Yb(SeO_3)_2O_2Cl$, ytterbium structural analogue of the mineral francisite, was carried out in a wide temperature range (5–300 K). The splitting of the Kramers doublets of Yb^{3+} ion unambiguously indicates the presence of two phase transitions, in accordance with the previously published paper [14]. Ordering of the copper magnetic subsystem takes place at the temperature of $T_N = 35$ K. There is one more phase transition at the temperature of $T_R \approx 9$ K.

The temperature behavior of the splitting of the ground Kramers doublet of ytterbium allowed to make the conclusion about the nature of the low-temperature transition: it is a first-order spin-flip transition. The ground Kramers doublet of the Yb^{3+} ion splits only at temperatures below T_R. The splitting absence in phase AFM in the temperature range $T_R < T < T_N$ can only be explained by the fact that the direction of the internal magnetic field acting on the Yb^{3+} ion from the ordered copper subsystem coincides with the direction along which the magnetic $g$factor of the ground state of ytterbium is minimum (has zero value). In the low-temperature phase AFM at $T < T_R$ the field turns toward the direction along which g-factor is maximum, and the ground samarium doublet splits. As a result, the energy of the ground state of the ytterbium ion decreases, and the system receives an energy gain, which is spent on flipping the spins of the copper magnetic lattice. Thus, the significant magnetic anisotropy of ytterbium is the cause of the spin-flip transition. We were able to estimate the amount of energy required to position the copper magnetic subsystem: $\mathscr{E}_{SR,Yb} = 864\,J\,mol^{-1}$.

A change in the probability of optical transitions in the Yb^{3+} ion was detected, accompanying each of the magnetic phase transitions in $Cu_3Yb(SeO_3)_2O_2Cl$. The probable reason for this is the renormalization of the wave functions of the crystal-field states of the Yb^{3+} ion, which arises due to the interaction of the magnetic and charge subsystems of ytterbium francisite, which allows to classify the compound under study as a multiferroic. With a high probability, spontaneous striction can occur in a crystal during magnetic phase transitions, as happens in the crystal of the mineral francisite. Meanwhile, the displacement of the ions causes a change in the crystal field acting on the Yb^{3+} ion, created both by the displaced nearby ions and by the exchange charges changing due to the displacements.

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Conflict of interest

The authors declare that they have no conflict of interest.

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