

Quasi-doublets of non-Kramers Ho^{3+} ion and magnetic ordering of holmium francisite-analog $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$

S. A. Klimin¹, P. S. Berdonosov², and E. S. Kuznetsova²

¹*Institute of Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow 108840, Russia*

E-mail: klimin@isan.troitsk.ru

²*Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow 119991, Russia*

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Optical spectroscopy of the f - f transitions in the non-Kramers Ho^{3+} ion was performed in a wide temperature range, from 4 K to room temperature, to study magnetic properties of the francisite-like holmium compound $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$. Despite the absence of symmetry doublets of the Ho^{3+} ion, its quasi-doublets were found, which are split in the exchange field acting on holmium ions in the magnetically ordered state of the crystal under study. From the splittings, the temperature of magnetic ordering was found, $T_N = 38$ K. Two quasi-doublets of Ho^{3+} ion, namely, the ground and the first excited ones, with the energy gap 25 cm^{-1} , contribute to the low-temperature magnetism of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$. The energy structure of crystal-field levels of the ground multiplet 5I_8 of the holmium ion was investigated, and the contribution of the rare-earth ion to the heat capacity of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ was calculated.

Keywords: Rare-earth francisite-like crystals, $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$, optical spectroscopy, quasi-doublets, Ho^{3+} crystal-field f - f transitions, magnetic ordering.

1. Introduction

Rare-earth (RE) synthetic compounds $\text{Cu}_3\text{RE}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ are structural analogs of the mineral francisite $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Br}$, with the replacement of bismuth by an RE element [1–3]. They belong to a big family of francisite-like compounds, which are widely studied due to the interesting structural [4–6], magnetic [7–12], metamagnetic [13–15], and spin-reorientation [16, 17] phase transitions, interesting interactions between magnetic d - and f -subsystems [16–18], and multiferroic behavior [5, 19–21]. The progenitor of the family of compounds, the francisite mineral [22], as well as its synthetic bromine analogue $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Br}$ are low-dimensional magnets with a low temperature of magnetic ordering ($T_N \approx 27.4$ K) [8, 9]. In $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Br}$, a complex six-sublattice magnetic structure with canted directions of magnetic moments in one the sublattices is realized [9], arising due to the complex competition of ferromagnetic and frustrated antiferromagnetic interactions in two-dimensional copper layers with a kagome-type lattice [21, 23].

RE analogs of francisite $\text{Cu}_3\text{RE}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ (RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) are also subject to magnetic ordering at low temperatures [12–14, 16–18]. The Néel temperature in them is higher

than in $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{BrX}$, X = Br, Cl, and varies in the range 32–38 K [7, 12]. It is interesting to mention that, since the temperature of magnetic ordering of the RE analogs is higher than that of the francisite itself, the presence of the RE ion weakens the interaction between the magnetic planes of copper, despite the fact that the interplanar distance equal to the lattice parameter c decreases for a number of rare earth analogs (6.927–7.074 Å in series Yb–Nd [2]) in comparison with $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Br}$ (7.220 Å [8]). The method of optical spectroscopy of the f - f transitions in the RE ions is important, since it contains information on the energy states of the electronic system of the f -ion. Data on the crystal-field (CF) energies of the ground multiplet, and their temperature behavior (displacement and splitting), makes it possible to calculate the contribution of the RE ion into the thermodynamic characteristics and to explain their low-temperature peculiarities [24–26]. In addition, these data are useful for understanding magnetic behavior of compounds under study. Exchange splittings of RE energy-doublets with a strongly anisotropic magnetic g factor are sensitive and can be used to analyze the direction of the effective magnetic field \mathbf{B}_{eff} acting on the RE ion from the side of the magnetically ordered d subsystem [27–31]. An interesting feature of the interaction between the d - and f -magnetic subsystems in crystals is that in the case of

strong single-ion magnetic anisotropy of the RE ion, spin-reorientation phase transitions can occur. It is namely the spectroscopic data on the temperature change in the splitting of the ground Kramers doublet of the RE ions in $\text{Cu}_3\text{Sm}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ [16] and $\text{Cu}_3\text{Yb}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ [17] that help to understand the nature of the low-temperature anomalies in these compounds, associated with the spin reorientation of the copper magnetic sublattice. The strongest $d-d$ interactions lead to magnetic ordering within the copper magnetic subsystem. In the compounds $\text{Cu}_3\text{Sm}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ and $\text{Cu}_3\text{Yb}(\text{SeO}_3)_2\text{O}_2\text{Cl}$, the effective field \mathbf{B}_{eff} , arising at Neél temperature T_N and acting on RE ions, has such direction that it cannot split the ground Kramers doublet of the RE ion. At the same time, the rotation of the effective field in the direction of the maximum component of the g -factor can potentially lead to an energy gain due to a splitting of ground Kramers doublet and corresponding decrease of the energy of the ground state of the RE ion. An increase in the effective field with decreasing temperature lower than T_N leads to an increase in the potential gain, since the energy splitting Δ of ground Kramers doublet is proportional to the field strength, $\Delta \sim g|\mathbf{B}_{\text{eff}}|$. As a result, at a temperature when this gain exceeds the energy that must be spent on the spin flip of the copper magnetic subsystem, a spin-reorientation phase transition occurs.

The crystal structure of the francisite-like compound $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ is shown in Fig. 1. This compound crystallizes in the orthorhombic space group $Pm\bar{m}n$ [2], and so does the mineral francisite [8, 22, 32–34]. A feature of the crystal structure is two-dimensional structure composed of copper layers (Fig. 1), and inside the layer, copper atoms form a corrugated Kagomé lattice. The RE ions are located in the eight-oxygen-coordinated polyhedra, and their crystallographic position has the C_{2v} symmetry.

Representatives of the rare-earth francisite-like family previously studied by us using optical spectroscopy of the $f-f$ transitions contained Kramers ions [10, 16–18], the energy spectrum of which consists of degenerate states (the so-called Kramers doublets). Spectroscopy of Kramers ions is a convenient tool for studying magnetic phase transitions [25, 30, 35, 36], as Kramers degeneracy can be lifted only under the action of a magnetic field. The Ho^{3+} ion, being a constituent of the $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$, is a non-Kramers ion. However, the ground multiplet 5I_8 of the Ho^{3+} ion is split by a crystal field with a symmetry below cubic (which is the case of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$) into $2J + 1 = 17$ CF levels, and among such a rich number of states, there are often occasionally degenerate or closely spaced states that can interact in a magnetic field (see, for example, [26]). Thus, it is of interest what is the energy structure of the CF levels of the holmium ion in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ and whether and how it will respond to the magnetic ordering of the crystal.

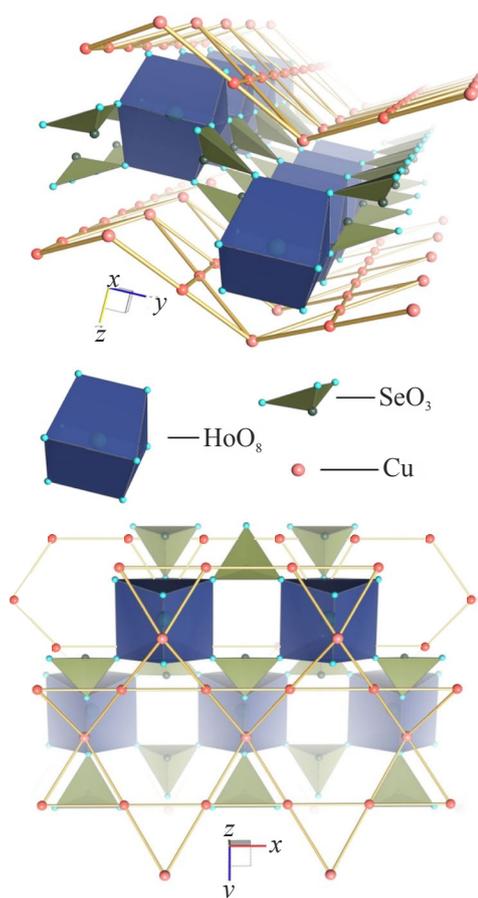


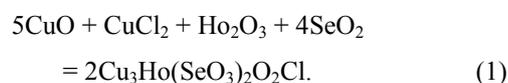
Fig. 1. (Color online) Crystal structure of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$. Two projections are given: top view along x axis demonstrating buckled 2D copper planes and bottom view along z axis, demonstrating Kagomé-like structure of copper planes.

In this work, the CF energy-structure of the non-Kramers Ho^{3+} ion in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ was studied by optical spectroscopy in order to obtain information on the magnetic ordering and magnetic properties of the crystal under study at low temperatures.

2. Experiment

Holmium (III) oxide Ho_2O_3 (Giredmet Russia, not less than 99.99%), copper (II) oxide CuO (purity 9–2), anhydrous copper (II) chloride CuCl_2 (Sigma-Aldrich $\geq 99.995\%$) and selenium (IV) oxide SeO_2 were used as precursors. Selenium (IV) oxide was preliminary obtained by dehydration of selenous acid H_2SeO_3 (pure) in mild conditions. The raw product was then sublimated in flow of dry air and nitrogen (IV) oxide NO_2 .

Compound with Ho was obtained from stoichiometric mixture prepared in glove box according to the equation:



The started compounds were thoroughly grinded in agate mortar, placed in quartz tube and sealed under vacuum ($\sim 10^{-2}$ Torr). The tube was heated in electronically controlled furnace at 300 °C for 12–24 h and finally at 575 °C for 72 h. As a result, green powder sample was obtained.

X-ray phase analysis performed on a STOE Stadi-p diffractometer (source $\text{CuK}\alpha_1$) confirmed the single-phase nature of the compound obtained. The parameters of the unit cells are fully consistent with the data of [2].

The transmission spectra of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ were measured on a BRUKER IFS125 Fourier spectrometer using an InSb detector cooled by liquid nitrogen and a CaF_2 beam-splitter. To carry out low-temperature measurements, the sample was placed in an indium envelope with a through hole 5 mm in diameter. The indium was mechanically pressed to the cold holder of a CryoMech ST403 closed-cycle optical helium cryostat. The sample was kept in a vacuum better than $5 \cdot 10^{-4}$ Torr; evacuation was carried out using a Varian V70 Turbo turbomolecular pump. Temperature control with an accuracy of 0.1 K was carried out using a Scientific Instruments controller.

3. Symmetry analysis

The energy levels of a free RE ion are degenerate regarding the projections of the total moment J . Under the influence of the crystal field, their degeneracy is completely or partially lifted. In the general case, the level with the angular momentum J splits into $2J+1$ CF sublevels. Symmetry analysis for the holmium C_{2v} site in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ shows that the CF states of a non-Kramers Ho^{3+} ion are singlets characterized by four different irreducible representations (IrR), namely, Γ_1 , Γ_2 , Γ_3 , and Γ_4 [37, 38]. Table 1 shows how a level with the total momentum J (for selected values corresponding to the multiplets participating in transitions studied in this work) splits in a crystal field of the C_{2v} symmetry. The selection rules for electric dipole (ED) and magnetic dipole (MD) transitions are summarized in Tables 2 and 3, respectively. In particular, it follows from the Table 2 that all ED transitions are allowed except $\Gamma_1 \leftrightarrow \Gamma_3$ and $\Gamma_2 \leftrightarrow \Gamma_4$ ones and, from the Table 3, that the levels with the identical symmetry do not interact in magnetic field.

4. Experimental results and discussions

Diffuse transmittance spectra of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ are shown in Fig. 2 at temperatures 4, 175, and 300 K. Two groups of narrow lines, nicely visible at 4 K spectrum, belong to two intermultiplet transitions in the Ho^{3+} ion, namely, to transitions from ground 5I_8 multiplet to excited 5I_7 (spectral region around 5300 cm^{-1}) and 5I_6 (8800 cm^{-1}) ones. The energy positions of the multiplets in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ are very close to that from the Dieke scheme for the holmium multiplets in LaCl_3 (see Fig. 1). Spectral lines become wider and weaker with warming up the sample, as well as new low-frequency lines appear due to the appearance of new transitions originating from excited CF levels

Table 1. The number of the CF levels of the non-Kramers ion R^{3+} and their symmetry in the C_{2v} crystal field of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ for selected values of the total moment J

J	C_{2v}	
	IrR	Number of levels
6	$4\Gamma_1 + 3\Gamma_2 + 3\Gamma_3 + 3\Gamma_4$	13
7	$4\Gamma_1 + 4\Gamma_2 + 3\Gamma_3 + 4\Gamma_4$	15
8	$5\Gamma_1 + 4\Gamma_2 + 4\Gamma_3 + 4\Gamma_4$	17

Table 2. Selection rules for the electric dipole (ED) optical transitions of a non-Kramers ion in a site with the C_{2v} symmetry, d_i ($i = x, y, z$) refer to the components of the electric dipole moments

C_{2v}	ED			
	Γ_1	Γ_2	Γ_3	Γ_4
Γ_1	d_z	d_x	—	d_y
Γ_2	d_x	d_z	d_y	—
Γ_3	—	d_y	d_z	d_x
Γ_4	d_y	—	d_x	d_z

Table 3. Selection rules for the magnetic dipole (MD) optical transitions of a non-Kramers ion in a site with the C_{2v} symmetry, μ_i ($i = x, y, z$) refer to the components of the magnetic dipole moments

C_{2v}	MD			
	Γ_1	Γ_2	Γ_3	Γ_4
Γ_1	—	μ_y	μ_z	μ_x
Γ_2	μ_y	—	μ_x	μ_z
Γ_3	μ_z	μ_x	—	μ_y
Γ_4	μ_x	μ_z	μ_y	—

of ground Ho^{3+} multiplet which are populated only at elevated temperatures.

There is a decrease in the transmission of the sample with increasing frequency (see Fig. 1). This is an effect of diffuse scattering of light in a polycrystalline sample distributed in potassium bromide, the magnitude of which increases with frequency. However, against the background of a smooth decrease in transmission, an increase in the slope is observed with increasing sample temperature in the high-frequency part of the spectra. This behavior is associated with the presence of strong absorption bands of the copper d -ion. One such band is in the red region of the spectrum. This absorption is characteristic of the entire large family of francisite-like compounds and determines their green color (see insert in Fig. 2 for the color of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$). With decreasing temperature, this band

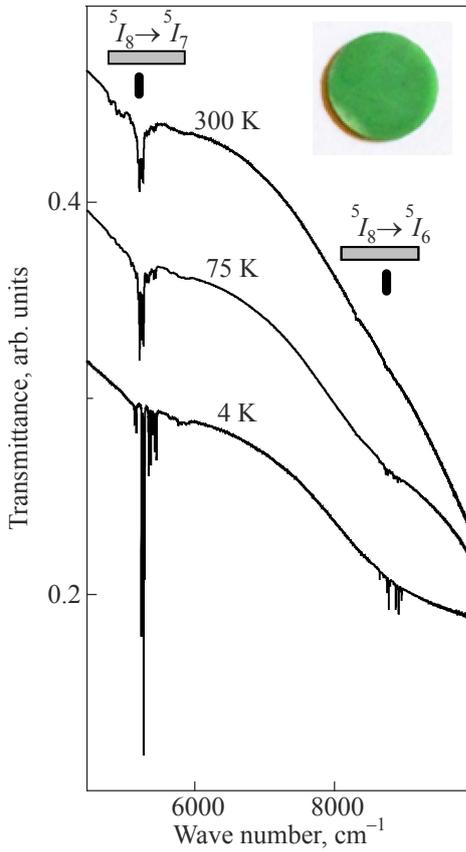


Fig 2. Diffuse transmittance spectra of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ at selected temperatures. Ordinate scale refers to 4 K spectrum. Two other spectra are linearly shifted along vertical axis. Black vertical sticks denote the positions of 5I_7 and 5I_6 multiplets of the Ho^{3+} ion in LaCl_3 matrix [39]. In the insert general view of the sample as prepared for optical measurements is shown ($\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ filled with optically transparent potassium bromide).

narrows and the sample becomes more transparent in the spectral region close to the red visible light. Below, to analyze the spectra in a narrower spectral region of two multiplets, in order to get rid of the spectral slope, the normalized spectra will be used that are divided by a smooth baseline.

Figures 3 and 4 show detailed temperature dependences of the transmission spectra in the region of intermultiplet transitions $^5I_8 \rightarrow ^5I_7$ and $^5I_8 \rightarrow ^5I_6$, respectively. The most interesting thing is that near a temperature of magnetic ordering T_N , almost all spectral lines are split. This is in contradiction with the expectation that all CF energy states of the Ho^{3+} ion are singlets and leads to the assumption that the ground CF level of the Ho^{3+} ion in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ is a quasi-doublet, which splits in the exchange field \mathbf{B}_{eff} acting on holmium from the side of the ordered copper magnetic subsystem.

This assumption is confirmed by comparing the temperature behavior of the most characteristic spectral lines shown in Fig. 5. All six selected lines presented are split in the same way: (i) there are two split components; (ii) the distances between the components are equal for all exam-

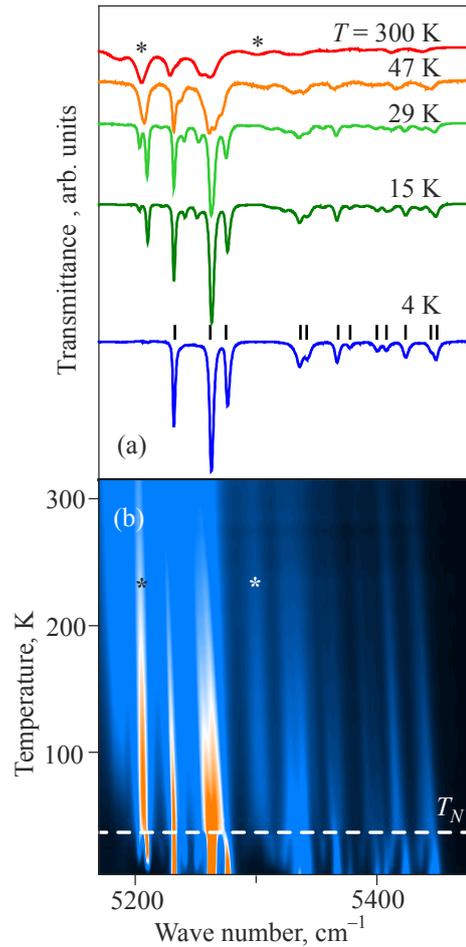


Fig 3. (Color online) Temperature changes in the spectral region of $^5I_8 \rightarrow ^5I_7$ intermultiplet transition of the Ho^{3+} ion as (a) normalized spectra at various temperatures and (b) color map. Vertical ticks in (a) denote the energy positions of CF levels of 5I_7 multiplet at 4K. Asterisks denote lines corresponding to transitions originating from the first excited (25 cm^{-1}) quasi-doublet of ground Ho^{3+} multiplet 5I_8 .

ples of split lines for any given temperature; (iii) the intensity of the high-frequency component increases with decreasing temperature, and that of the low-frequency component decreases. This behavior clearly fits into the scheme presented as an inset to Fig. 5(b): the ground state of the holmium ion is a quasi-doublet, which splits upon magnetic ordering of the crystal. Due to that each spectral line split into two components, the low-frequency one “freezes out” as it is associated with the transition starting from the upper component of the split ground quasi-doublet, the population of which goes to zero at low temperatures.

The splitting of the ground quasi-doublet was found as a function of temperature from the spectra presented in Fig. 6. The insets show the spectra of the one of the lines in the same spectral range at different temperatures. At low temperatures, when two components of the split spectral line are visible in the spectrum, the values $\Delta_0(T)$ were determined as the distances between the components. In the region of

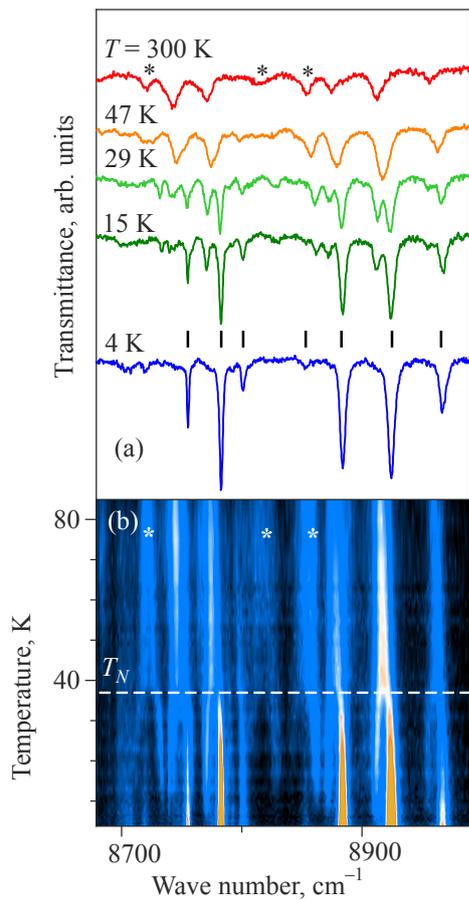


Fig. 4. Temperature changes in the spectral region of $^5I_8 \rightarrow ^5I_6$ intermultiplet transition in the Ho^{3+} ion as (a) spectra at various temperatures and (b) color map. Vertical ticks in (a) denote the energy positions of CF levels of 5I_6 multiplet. Asterisks denote lines corresponding to transitions originating from the first excited quasi-doublet of ground Ho^{3+} multiplet 5I_8 .

higher temperatures, when the components were not resolved, Δ_0 was taken as the excess of the half-width over its value at a temperature of 170 K, starting from which the spectral line began to broaden with decreasing temperature. Comparison of the two spectra in the insets to Fig. 6, at $T = 45$ K and $T = 165$ K, clearly shows how much the spectral line broadened at a lower temperature. It turns out that the splitting of the ground quasi-doublet Δ_0 begins in the paramagnetic phase. The function $\Delta_0(T)$ has a pronounced “tail” spreading to high temperatures. This situation is typical for low-dimensional systems in which magnetic correlations in the paramagnetic phase survive at very high temperatures [40]. In crystals with a low-dimensional magnetic subsystem, magnetic correlations are observed at temperatures much higher than the magnetic ordering temperature and can be on the order of $5 T_N$ [41] and even $10 T_N$ [42]. The temperature of magnetic ordering was determined from the point of maximum of the derivative of the function $\Delta_0(T)$, it equals to 38 K. The function $\Delta_0(T)$ is also important for calculating the contribution of holmium to the thermodynamic characteristics.

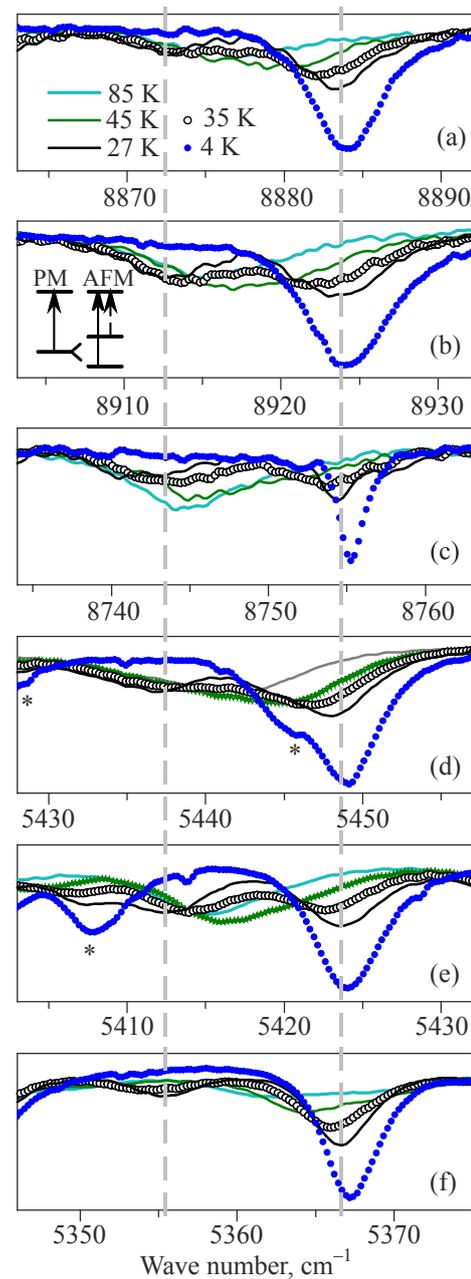


Fig. 5. Transmission spectra at various temperatures for the several selected spectral lines. The lines are given in the same scale, namely, 29 cm^{-1} across the x axis for each drawing. All lines presented split in the similar way according to the energy-level scheme given as insert to (b) for paramagnet (PM) and antiferromagnet (AFM) states. Grey vertical lines are drawn to underline the sameness of the distances between two components in all the transitions presented. Asterisks denote the lines belonging to another independent transitions.

In order to analyze the possibility of interaction of two energy states in a magnetic field, let us turn to Table 3. To compose doublet there are ten combinations of possible pairs of states with given symmetries Γ_i , $i = 1 \dots 4$. From the Table 3 it can be seen that a pair of levels described by the identical representations (for example, $\Gamma_1 + \Gamma_1$, or, e.g., $\Gamma_2 + \Gamma_2$) do not interact in a magnetic field. Thus, for

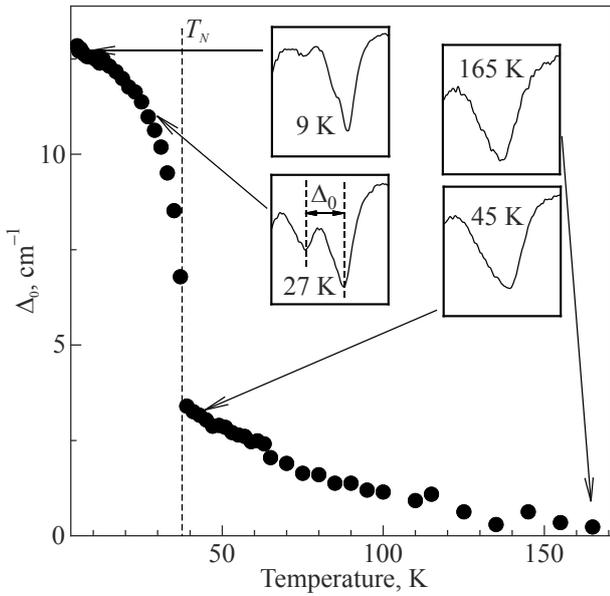


Fig 6. Splitting Δ_0 of the ground quasi-doublet of the Ho^{3+} ion in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ as a function of temperature. The inserts show the temperature evolution of the absorption line near 5437 cm^{-1} , an equal spectral interval of 34 cm^{-1} is shown for all inserts, the scale along the ordinate axis is arbitrary.

ground Ho^{3+} multiplet we are already limited in interacting pairs of levels and there are six of them left. One conclusion can be drawn, that for the transitions originating from quasi-doublet that split, there are no ED forbidden transition, as this doublet consists of CF levels with not-identical IrR. So, transitions to any CF level from the ground state are allowed as ED ones. This means that, e.g., for multiplet 5I_6 consisting of 13 CF levels transitions to all of them from the ground doublet are allowed. Nevertheless, number of lines registered in multiplet 5I_6 , as well as in 5I_7 one, is less than it is expected for $2J+1$ number. We propose that quasi-doublets can also exist in the energy structure of those two excited multiplets as well as they are present in a ground 5I_8 one.

Further, if the direction of the effective field \mathbf{B}_{eff} were known, someone could further restrict possible pairs of IrR in quasi-doublet. For example, in the compound $\text{Ho}_2\text{BaNiO}_5$, with the same symmetry C_{2v} of the holmium center and with a magnetic ordering temperature of 59 K, there is also a quasi-doublet in the ground state [26] splitting in magnetically ordered state. Since the magnetic structure for $\text{Ho}_2\text{BaNiO}_5$ has already been investigated, it was possible to limit the possible symmetry to two variants. In the case of francisite-like phases, the magnetic structure was determined for $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Br}$ [9] and it was shown that it is the same for $\text{Cu}_3\text{Y}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ [11]. This fact demonstrates that change in lattice parameters of two compounds do not change much magnetic interactions in copper magnetic system and the magnetic structure remains unchanged.

If we assume that the same structure is realized in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$, then, the effective exchange field acting on holmium will be directed along the crystallographic c axis, $\mathbf{B}_{\text{eff}} \parallel c$. In this case, the main doublet will consist of either the pair $\Gamma_1 + \Gamma_3$ or $\Gamma_2 + \Gamma_4$. However, this assumption can be confirmed only by extra experiments.

In the transmission spectra, there are other spectral lines, splitting near a temperature of magnetic ordering T_N , which differ qualitatively in temperature changes. These lines are marked with asterisks in Figs. 3 and 4. They split, and then both components “freeze”, and their intensity drops to zero as the temperature drops. These lines are associated with transitions originating at the first excited level of the ground multiplet (see the scheme in Fig. 7, dotted arrows). Moreover, the high-frequency component freezes first, low-frequency one survives at lower temperatures, this is in agreement with the Boltzmann populations of initial states of transitions. Thus, the energy of the first excited CF state (which occurs to be also doublet) can be determined, it is 25 cm^{-1} and its splitting at lowest temperatures equals 20 cm^{-1} . Further analysis of the temperature-dependent transmission spectra and line intensities allowed us to find the energies of the higher levels of the main multiplet: four CF levels around 143 cm^{-1} , and, further, four levels above 450 cm^{-1} . Resting five of seventeen CF levels, according to our data, lie higher than 600 cm^{-1} . The energy structure of ground multiplet 5I_8 of the Ho^{3+} ion in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ is summarized in Fig. 7.

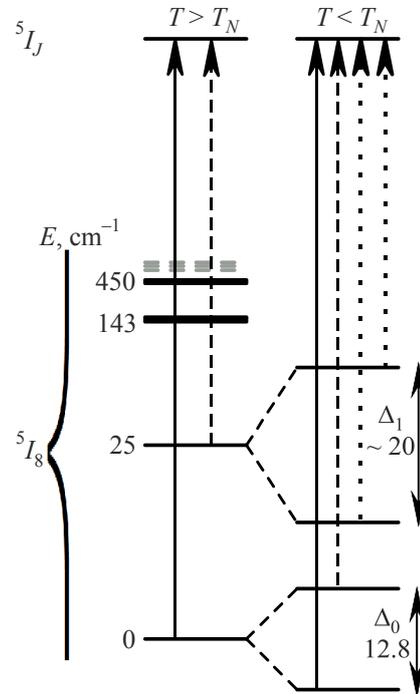


Fig. 7. CF energy-level scheme for the ground multiplet of the Ho^{3+} ion in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ in magnetically disordered ($T > T_N$) and ordered states ($T < T_N$).

The set of CF level energies of the ground multiplet of the Ho^{3+} ion found in this work was used to calculate holmium contribution into the heat capacity $C(T)$ of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$. For this aim the following formulae was used:

$$C_{\text{Ho}} = R \sum_{i,j=1,N;j<i} \left(\frac{E_i - E_j}{kT} \right)^2 n_i n_j, \quad (1)$$

where R and k are the gas and the Boltzman constants, respectively, T — temperature, E_i are the energies of CF levels of the ground multiplet, N is their number, n_i and n_j are the populations of i th and j th CF levels determined by the following relations (Boltzmann distribution):

$$\frac{n_1}{n_2} = e^{\frac{E_1 - E_2}{kT}}, \quad (2)$$

$$\sum_{i=1,N} n_i = 1. \quad (3)$$

Equation (1) having a very compact and simple form was derived in [26] and can be easily used for calculation when CF energies are known.

The following set of energies was used in our calculations of $C_{\text{Ho}}(T)$: 0 (2), 25 (2), 143 (4), 450 (4), 600 (5). In calculation, shown in Fig. 8 by solid line, we took into account also experimental data on the splitting of the ground state $\Delta_0(T)$. The calculated contribution is separated into two parts, namely, low-temperature, relatively narrow peak with maximum at 10.3 K and high-temperature wide part with growing values of $C_{\text{Ho}}(T)$ in the temperature region from 50 to 100 K. Evidently, the low-temperature peak, known also as Schottky-anomaly, is associated with

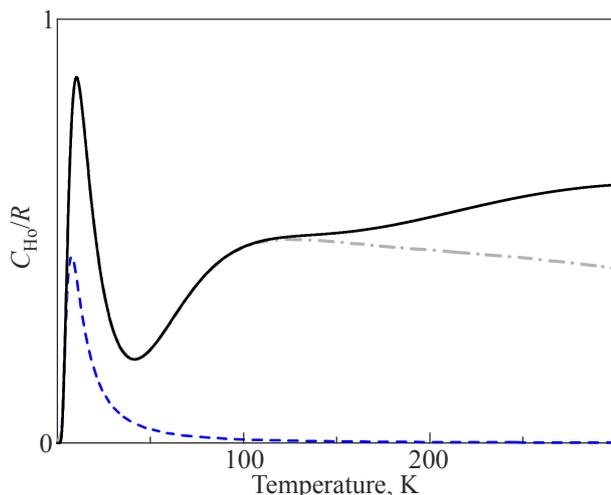


Fig. 8. The contribution of holmium C_{Ho} into the heat capacity $C(T)$ of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ calculated using data on the energies of the CF levels of the Ho^{3+} ion obtained in this work. All 17 CF energies (solid curve), 12 CF energies (dash-dotted line) and the only data on Δ_0 (dashed line) were used in calculation.

low-energy CF-states (split upper component of ground quasi-doublet and split components of CF level at 25 cm^{-1}). Usually, this low-temperature part of $C_{\text{Ho}}(T)$ is considered as magnetic part of heat capacity. To demonstrate the influence of the separated high-energy CF levels (600 cm^{-1} and higher) we have calculated C_{Ho} using just first 12 CF levels found in this work. The resulting curve shown in Fig. 8 by dash-dotted line. There is no influence of these levels at temperatures lower than 120 K. In this temperature range these levels are not populated. So, the Schottky anomaly does not depend on the highest-energy CF levels of holmium ground multiplet.

Finally, we have to underline that in the case of $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ the presence of two low-lying quasi-doublets does not allow to use standard formulae for the calculation of holmium contribution into the heat capacity. Equation (4) is a particular case of Eq. 1 for two-level system:

$$C(T) = R \left(\frac{\Delta_0(T)}{kT} \right)^2 n_0 n_1 = \frac{1}{4} R \left(\frac{\Delta_0(T)}{kT} \right)^2 \left(\cosh \frac{\Delta_0(T)}{2kT} \right)^{-2}. \quad (4)$$

Calculation with the use Eq. 4 is shown in Fig. 8 by dashed curve. The curve has maximum at 7.6 K, which is much lower than in solid curve and the value of C_{Ho} contribution of “two-level” Schottky anomaly is approximately two times less than in the case of taking into account CF-quasi doublet at 25 cm^{-1} .

Conclusion

We have presented the first study of the f - f transitions of the Ho^{3+} ion in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$. Observed splittings of spectral lines announcing an AFM ordering at $T_N = 38 \text{ K}$ unambiguously confirm that the ground state of holmium in the compound studied is a quasi-doublet. The experimental set of CF levels of the ground multiplet of the Ho^{3+} ion in $\text{Cu}_3\text{Ho}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ is given. Calculation of the holmium contribution into the heat capacity is presented which takes into account experimental low-lying CF levels of the Ho^{3+} ion.

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Квазідублети некрамерсовського іона Ho³⁺
та магнітне впорядкування структурного аналога
франциситу Cu₃Ho(SeO₃)₂O₂Cl

S. A. Klimin, P. S. Berdonosov, E. S. Kuznetsova

Для дослідження магнітних властивостей франциситоподібного з'єднання гольмію Cu₃Ho(SeO₃)₂O₂Cl проведено вивчення $f-f$ переходів у некрамерсовського іона Ho³⁺ методом оптичної спектроскопії в широкому діапазоні температур від 4 К до кімнатної. Незважаючи на відсутність симетричних дублетів іона Ho³⁺, виявлено його квазідублети, що розщеплюються в обмінному полі, яке діє на іони гольмію в магні-

товпорядкованому стані досліджуваного кристала. Встановлено температуру магнітного впорядкування $T_N = 38$ К. Два квазідублети іона Ho³⁺, а саме, основний і перший збуджений з енергією 25 см⁻¹, вносять вклад у низькотемпературний магнетизм кристала. Досліджено енергетичну структуру рівнів кристалічного поля основного мультиплету ⁵I₈ іона гольмію та розраховано внесок рідкоземельного іона в теплоємність кристала Cu₃Ho(SeO₃)₂O₂Cl.

Ключові слова: рідкоземельні франциситоподібні кристали, Cu₃Ho(SeO₃)₂O₂Cl, оптична спектроскопія, квазідублети, $f-f$ переходи кристалічного поля Ho³⁺, магнітне впорядкування.