

# Magnetic phase transitions in two-dimensional frustrated $\text{Cu}_3\text{R}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ . Spectroscopic study

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**Abstract.** Using optical study of electronic spectra of rare-earth (RE) ions, magnetic phase transitions in the low-dimensional frustrated RE magnets  $\text{Cu}_3\text{R}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  ( $R = \text{Sm, Yb, Er, Nd, Pr, Eu}$ ) were investigated. Phase transitions were registered either by splittings of crystal-field (CF) doublets or by repulsion of CF levels of f-ions in a staggered magnetic field. Different scenarios of magnetic order in isostructural compounds of the francisite family are discussed.

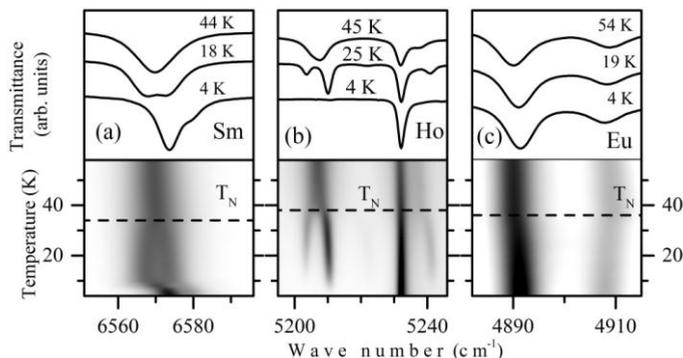
Magnetic system of a natural mineral francisite  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  [1] has attracted attention of scientists due to its unusual geometry. Copper ions in the orthorhombic  $Pm\bar{m}n$  crystal structure of francisite form a network of two-dimensional (2D) layers with a buckled Kagome lattice [2]. Due to weak interlayer interactions, an antiferromagnetic (AFM) ordering occurs in francisite at  $T_N = 24$  K [2]. Bismuth can be replaced by a rare-earth (RE) element, while the crystallographic structure remains the same [4]. The family of compounds  $\text{Cu}_3\text{R}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  ( $R = \text{RE}$ ) can be considered as a model system of 2D copper layers with different types of interactions, due to introduction of a second (RE) magnetic subsystem. In the case of  $R = \text{Y}$  [5] or  $\text{Sm}$  [6], the Néel temperature is also low ( $T_N = 35$  K), but higher as compared to parent francisite, which is due to a discrepancy in ionic radii of bismuth and RE ions. In addition to AFM ordering,  $\text{Cu}_3\text{Sm}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ , experiences a spin-reorientation second-order phase transition at  $T_R = 9$  K [6]. In this work, a comparative study of compounds with  $R = \text{Sm, Yb, Er, Nd, Pr, and Eu}$  is presented. We have carried out infrared spectroscopy study of f-f transitions in RE ions, with the aim to investigate magnetic ordering in compounds with different RE ions.

Transmittance spectra in a wide spectral range (1800 – 12000  $\text{cm}^{-1}$ ) were measured using a Fourier-spectrometer Bruker IFS125HR. Mixtures of  $\text{Cu}_3\text{R}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  and KBr powders were pressed into tablets, with an effective thickness of the substance  $\sim 10$   $\mu\text{m}$ . Low temperatures were achieved using a closed-cycle cryostat Cryomech PT403.

The CF energies of six  $R^{3+}$  ions were found in the spectral range studied. Spectroscopic data on temperature-dependent low-energy states of RE ions were used to calculate the RE contribution [7, 8] into magnetic susceptibility and heat capacity. Magnetic ordering was detected either by splitting of Kramers ( $T_N^{\text{Sm}} = 34$  K, Fig. 1 a;  $T_N^{\text{Yb}} = 34$  K;  $T_N^{\text{Er}} = 35$  K) or of casual ( $T_N^{\text{Ho}} = 37$  K, Fig. 1 b;  $T_N^{\text{Pr}} = 34$  K) doublets or by internal-magnetic-field-induced repulsion of CF levels ( $T_N^{\text{Eu}} = 36$  K, Fig. 1 c). The temperatures  $T_N$  obtained are very close to that in  $\text{Cu}_3\text{Y}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ . This fact was expectable, as d-d exchange interactions are the

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strongest ones in mixed d-f magnetic systems [9]. In the case of RE francisites, the d-d interactions are expected to be approximately the same for all the family, because the geometry of bonds does not change significantly due to closeness of ionic radii of RE ions.



**Fig. 1.** Transmission spectra of  $\text{Cu}_3\text{R}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ ,  $\text{R}=\text{Sm}$ ,  $\text{Ho}$ ,  $\text{Eu}$ , at several temperatures (upper panels) and intensity maps (lower panels) in the regions of the following multiplets, (a)  ${}^6\text{F}_{3/2}$  of  $\text{Sm}^{3+}$  ion, (b)  ${}^5\text{I}_7$  of  $\text{Ho}^{3+}$  ion, and (c)  ${}^7\text{F}_6$  of  $\text{Eu}^{3+}$  ion.

Francisites with Kramers ions studied demonstrate different temperature behavior of the RE ground doublet (GD). GD of erbium splits at  $T_N$ , while GDs of Sm and Yb do not. The last two split only at temperatures  $T < T_R$ ,  $T_R$  being 9 K in both cases. To understand the reason of such behavior, we address a relation for the splitting  $\Delta$  of a doublet state in a staggered magnetic field:

$$\Delta = \sqrt{\sum_{j=x,y,z} (g_j B_{\text{eff},j})^2}, \quad (1)$$

where  $g$  is the magnetic  $g$ -factor of the RE ion. The magnetic structure of copper ions in AFM phase for all the family is expected to be of the same type as in  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  [3] and  $\text{Cu}_3\text{Y}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  [4]. It follows from data on the magnetic structure of  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  [3] that in the case of symmetrical exchange the effective magnetic field acting on the RE ion is directed along the  $z$ -axis of a crystal ( $B_{\text{eff}} \parallel z$ ). In this case, Eq. (1) is reduced to  $\Delta = g_z B_{\text{eff},z}$ . As  $\Delta_{\text{GD,Sm(Yb)}} = 0$  at  $T_R < T < T_N$ ,  $g_z = 0$  for the ground doublets of both the  $\text{Sm}^{3+}$  and  $\text{Yb}^{3+}$  ions. Appearance of a splitting in the temperature range  $T < T_R$  means a change of  $B_{\text{eff}}$ , namely, the appearance of its component along a non-zero component of the magnetic  $g$ -factor of the RE ion. Thus, we conclude that spin-reorientational transitions take place in  $\text{Cu}_3\text{Sm}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  and  $\text{Cu}_3\text{Yb}(\text{SeO}_3)_2\text{O}_2\text{Cl}$  at  $T_R$ . The reason for that is a gain in energy that the system obtains due to the splitting of the ground doublet of the RE ion which exceeds loss in energy due to the reorientation of the spins of copper ions.

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