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The investigations of Ag-contaning tennantite, belonging to the group of tetrahedrite-based sulfides, were performed by means of copper nuclear quadrupole resonance (NQR) in a temperature range from 4.2 K up to 60 K. These experiments showed that copper nuclear spin-lattice relaxation rate T_1^{-1} and nuclear spin-echo decay rate T_2^{-1} depend on temperature in the same way as earlier studied samples with other impurity compositions. The obtained data are interpreted from the viewpoint of internal motions in the structure of tennantite. The analysis of copper NQR data at low temperatures points to magnetic phase transition near 60 K from paramagnetic phase to the phase, which resembles spin-glass-like constitution.

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Keywords: NQR, tennantite, tetrahedrite, magnetic phase transition

1. Introduction

Tennantite is the representative of the *tetrahedrite*-group compounds, this family also called *fahlerz* or *fahlore*. Being one of the sources of economically important metals (Cu, Zn, Ag, Au and others), sensitive to physical-chemical conditions of ore-formation and having original crystal structure, these materials gave rise to numerous experimental and theoretical studies concerning their crystal chemistry (see [1], and references therein). However, in spite of intensive research during a long time (beginning from 18th century), many peculiarities of these compounds, their structure and properties haven't been clarified well enough. Thus, researchers are still concentrating their attention on the copper ions valence state and their distribution in the structure; lattice dynamics and its transport properties, isomorphous capacity of natural compounds.

In this report, we present the studies of ^{63,65}Cu NQR in natural crystal of Ag-containing tennantite in the temperature range 4.2 – 60 K. We found anomalies in the temperature dependences of nuclear spin-lattice relaxation (NSLR) rate T_1^{-1} and nuclear spin-echo decay (NSED) rate T_2^{-1}. The obtained data are interpreted from the viewpoint of internal motions in the structure of tennantite. Thereupon some peculiarities of tennantite crystal structure and its physical properties are considered.

2. Crystal-chemistry

The composition of tetrahedrite-based compounds is usually expressed by a unified chemical formula $Cu(I)_{10}Cu(II)_2X_4S_{13}$, where Cu(I)/Cu(II) are monovalent/divalent copper, X – semimetal atoms. The main minerals of this family are tennantite (X = As) and tetrahedrite (X = Sb). Since natural compounds show a certain composition range owing to different impurities (Zn, Fe, Ag, Hg and others), the more commonly used chemical formula for natural tetrahedrite-group compounds is $(Cu,Ag)_{10}(Cu,Fe,Zn,Hg)_2(Sb,As)_4S_{13}$.

The elementary cell of tetrahedrite-group compounds has a cubic symmetry corresponding to a T_d^6 - I43m; $Z = 2$ [2-4]. The crystal structure can be presented as the framework formed by the $[Cu(I)S_4]$-tetrahedrons, which are turned to one direction and jointed by vertexes (Fig. 1) [1]. In such combination the framework possesses interstices ("lanterns") in the form of three-dimensional twelve-apical polyhedron, sometimes referred to as "laves polyhedron" (Fig. 1). Each laves polyhedron contains six $[CuS_3]$-triangles. These triangles form a three-dimensional propeller with only one common apex – central sulfur atom S_2 (Fig. 1). The rest two sulfur apexes of each $[CuS_3]$-"vane" concurrently represent the vertexes of laves polyhedron. It is proposed that active valence of copper atoms in laves polyhedron have different value within the ratio Cu(I):Cu(II)=4:2 [1, 5]. Semimetal atoms, Sb and As, are arranged over the edges of laves polyhedron. In natural samples the tetrahedral coppers are partially substituted for impurity metals (Zn, Fe, Ag, Hg). The average interatomic distances in tennantite are reported in [2].

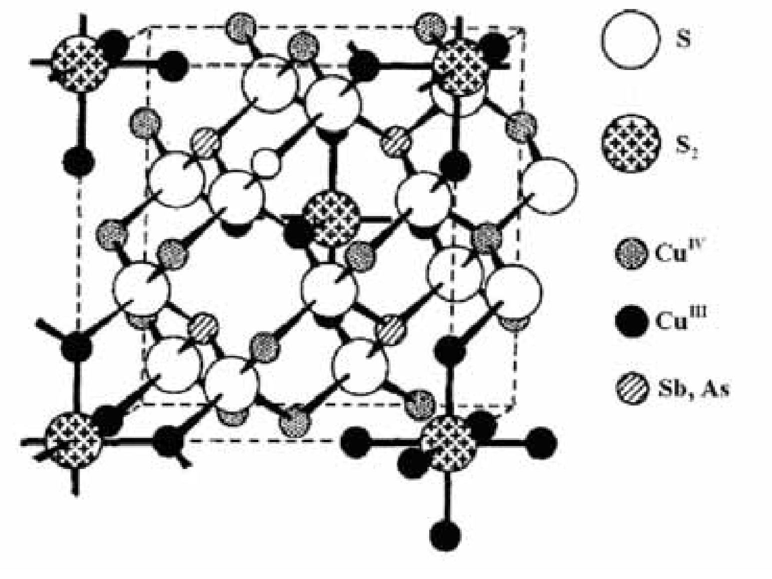

Fig. 1 The cell of tetrahedrite-group compounds. Triangular and tetrahedral coordinated copper atoms are signed as Cu^{III} and Cu^{IV}, respectively. The central sulfur atom in Cu_6S_{13} cluster in signed as S_2

3.Experimental part

The natural sample of tennantite, originating from Berezovskii gold-ore deposit (Middle Ural, Russia), was used in this study. The sample was in the form of polycrystalline aggregate and had iron–black color with a clear metallic glitter. Its phase homogeneity and tennantite structure were confirmed by X-ray diffractometry. The chemical composition of tennantite sample under study is presented by the formula: $(Cu_{10.04}Ag_{0.08})(Zn_{1.17}Fe_{0.94}Hg_{0.03})[As_{3.29}Sb_{0.98}]S_{12.44}$ (we denote this sample as *B*). For comparison, we show *T*-dependences of nuclear relaxation rates in another tennantite $Cu_{10.57}(Zn_{1.10},Fe_{0.69})[As_{3.50},Sb_{0.44}]S_{12.70}$ (sample *A*), which was studied earlier [6]. The NQR spectra of ^{63,65}Cu and nuclear relaxation were measured at T=4.2-65 K by a standard pulsed NQR method. For better penetration of the high-frequency magnetic field the sample was crushed in a mortar to a particle size of about 30 μm and packed in epoxy resin.

4. Results and discussions

The NQR resonance lines for both ^{63}Cu and ^{65}Cu isotopes were observed, with the NQR frequency ratio $F_Q(^{63}\mathrm{Cu})/F_Q(^{65}\mathrm{Cu}) = 1.081$ consistent with the ratio of nuclear quadrupole moments $Q(^{63}\mathrm{Cu})/Q(^{65}\mathrm{Cu})$. The presence of only one spectral line for both copper isotopes permits to attribute NQR spectra to the crystallographically single site of copper nuclei. As a rule, the ^{63,65}Cu NQR signals pertain to monovalent (diamagnetic) copper nuclei Cu(I) [7]. The monovalent copper atoms in tennantite are located at both the tetrahedral-based framework and Cu_6S_{13} clusters. There is no electric field gradient (EFG) at the sites with cubic local symmetry [8, 9]. This case is realized for the tetrahedral Cu(I) sites in diamagnetic framework, so only trigonal planar copper nuclei in clusters can serve as resonance centers exhibiting NQR.

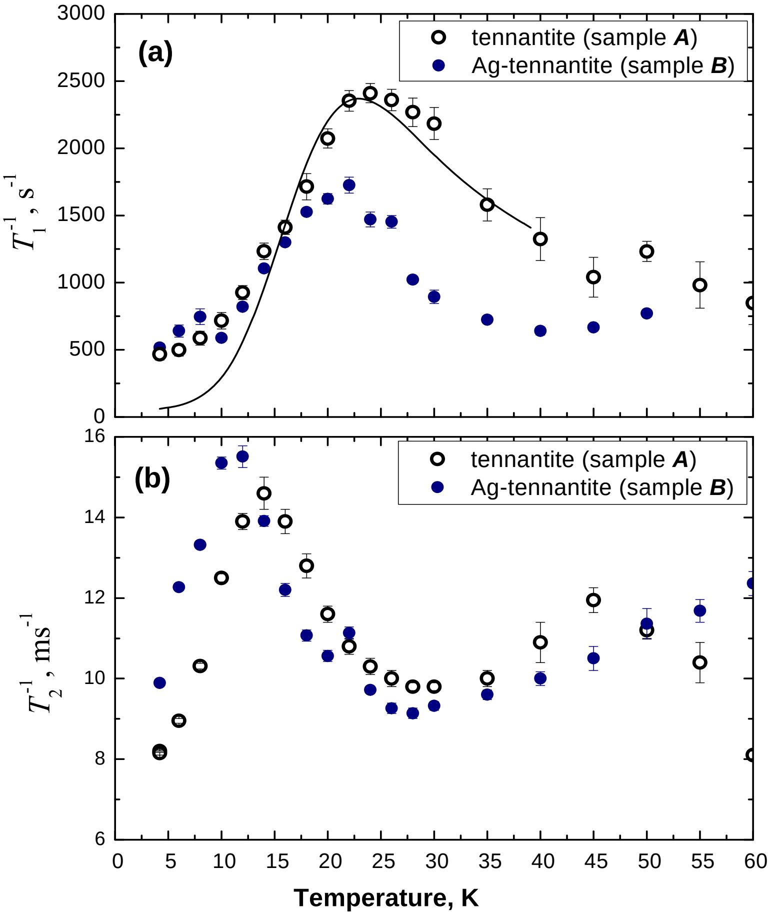

Fig.2. (a) The temperature dependence of the nuclear spin-lattice relaxation rates $1/T_1$ for ^{63}Cu, the curve shows a fit by (1) and (3), which predicts the activation energy of 65 K;
(b) the temperature dependence of the nuclear spin-echo decay rates $1/T_2$ for ^{63}Cu

The temperature dependence of NSLR rate $1/T_1$ is shown in Fig.2a. This parameter shows pronounced peak near 24 K. Although the NSED rate $1/T_2$ is almost independent of temperature above 75 K, there are strong peaks near 14 K (Fig.2b).

The peak in NSLR rate at 24 K points to the presence of field fluctuations [10-12] acting in our case on copper nuclear sites. As is known, the NSLR rate in case of relaxation due to fluctuating fields is determined by the correlation time τ_C of fluctuations:

$$\left(\frac{1}{T_1}\right)_{\mathrm{fluc}} = \frac{\Delta^2 \tau_C}{1+\omega_n^2 \tau_C^2} \qquad (1)$$

where Δ is a mean amplitude of fluctuations and ω_n is the NQR frequency. If Δ is constant but τ_C depends on temperature, $1/T_1$ attains the maximum value when $\omega_n \tau_C = 1$. Thus the peak of $1/T_1$ is naturally understood due to an increase of τ_C with decreasing temperature, i.e., slowing of the fluctuations at low temperatures. Usually, the correlation time is determined by a potential barrier according to Arrhenius law,

$$\tau_C = \tau_0 \exp\left(\frac{E_{\mathrm{ACT}}}{T}\right), \qquad (2)$$

where E_{ACT} is an activation energy. In general, there might exist two contributions to the NSLR of the ^{63,65}Cu nuclei:

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\mathrm{fluc}} + \left(\frac{1}{T_1}\right)_{\mathrm{sup}}, \qquad (3)$$

the first term reflecting contributions due to fluctuations, and the second one representing contribution typical for relaxation via the charge carriers. In case of a semiconductor [6],

$$\left(\frac{1}{T_1}\right)_{\mathrm{sup}} = A \cdot \sqrt{T}, \qquad (4)$$

where *A* is constant. We applied equation (3) to fit the experimental data (sample *A*) taking into account (1) together with (2) and (4). The best fits were obtained with the following parameters: $\Delta/2\pi = (128 \pm 4)$ kHz, $E_{\mathrm{ACT}} = (65 \pm 3)$ K, $\tau_0 = 4 \cdot 10^{-10}$ sec, $A = 20$ K$^{-1/2} \cdot$sec^{-1} (Fig.2a).

The NSED rate takes the maximum value when $\Delta \cdot \tau_C \sim 1$ [11]. Since Δ is 2 orders of magnitude smaller than ω_n, gradual slowing of the fluctuations accounts for the fact that the peak in $1/T_2$ occurs at lower temperature than the peak in $1/T_1$ (Fig.2b). Thus, the observed peaks in nuclear relaxation rates $1/T_1$ at 24 K and $1/T_2$ at 14 K are correlated and show the existence of internal motions in the crystal lattice. The possible nature of field fluctuations in the structure of tennantite is presented in earlier studies [6]. The same behavior of transverse and longitudinal nuclear relaxation rates in other samples studied in [6] together with non-trivial temperature dependence of NQR frequency and strong line broadening below 65 K allowed us to suppose that Laves polyhedron Cu_6S_{13} represents the mixed-valence cluster, similar to some extent to systems, described by Eremin and co-workers [13]. Experimental data were analyzed from the viewpoint of inhomogeneous electron distribution of Cu(II) in the Cu_6S_{13} cluster. The basic aspect in this consideration is that the electronic spins of Cu(II) at high-*T* are delocalized, whereas at low-*T* (namely, *T*<65 K) spins are frozen near Cu sites in the form of spin-glass like constitution.

However, since the sample *A* contains also impurities Fe, Zn (besides paramagnetic Cu(II)), it would be expedient to confirm experimentally that the revealed data are caused exactly by Cu(II). The main goal of this study is the reexamination of *T*-dependences of nuclear relaxation rates in another sample of tennantite (*B*) with amount of impurities, which differs from those in sample *A*. As is seen in Fig.2, the partial substitutions in sample *B* of magnetic Fe on non-magnetic Ag and Hg does not lead to appreciable change of *T*-dependences of nuclear relaxation rates $1/T_1$ and $1/T_2$. These facts, taking into account the high sensitivity of quadrupole interactions to any changes in the nearest crystal environment of quadrupole nucleus, indicate that the observed low-*T* peculiarities are not connected to different impurities or imperfections, but reflect the intrinsic properties of tetrahedrite-group compounds and are mainly determined by divalent ions Cu(II).

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