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Evidence for low-temperature internal dynamics in $Cu_{12}As_4S_{13}$ according to copper NQR and nuclear relaxation

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Abstract

^{63,65}Cu nuclear quadrupole resonance (NQR) was applied to study the natural mineral $Cu_{12}As_4S_{13}$ (tennantite) in the temperature range 4.2–210 K. The obtained results point to the presence of field fluctuations caused by internal motions in tennantite. Consistently with the crystal structure, the experimental data can be described by an occurrence of a magnetic phase transition, which takes place near 65 K. The low-temperature phase is characterized by Cu(II) electron magnetic moments freezing in the form of a spin-glass-like constitution.

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1. Introduction

Tennantite is the representative of the tetrahedrite-group compounds, the latter also called fahlerz. 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 an original crystal structure, these minerals 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 the 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 ion valence state and their distribution in the structure; lattice dynamics and its transport properties, and the isomorphous capacity of natural compounds.

In this paper, we report detailed studies of ^{63,65}Cu NQR and nuclear relaxation in natural tennantite in the temperature range 4.2–210 K. We found anomalies in the temperature dependences of nuclear spin-lattice relaxation (NSLR) rate T_1^{-1}, nuclear spin-echo decay (NSED) rate T_2^{-1}, nuclear quadrupole frequency F_Q, and NQR linewidth $\mathrm{d}F_Q$. 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. Composition and structure

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, Cd, Co, Au, Mn and others), the more commonly used chemical formula for natural tetrahedrite-group compounds is $(Cu, Ag)_{10}(Cu, Fe, Zn, Hg)_2(Sb, As)_4S_{13}$. Copper is the leading metal; other metals constitute the isomorphous components. In natural samples the ratio Cu(I):Cu(II) varies from 10:2 down to 9:3.

The elementary cell of tetrahedrite-group compounds has a cubic symmetry corresponding to a T_d^6-$I\bar{4}3m$; $Z = 2$ [2–4].

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