

СТРУКТУРНЫЕ СВОЙСТВА НИЗКОТЕМПЕРАТУРНОГО ХАЛЬКОЗИНА
Cu₂S

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STRUCTURAL PROPERTIES OF LOW-TEMPERATURE CHALCOCITE Cu₂S

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Binary copper sulfides of Cu_{1+x}S (0 ≤ x ≤ 1) family are numerous and amazing owing to variety of their physical properties. These sulfides form ores from which a metallic Cu is extracted (covellite CuS, chalcocite Cu₂S, djurleite Cu_{~1,95}S, digenite Cu_{~1,8}S, roxbyite Cu_{~1,78}S, anilite Cu_{1,75}S) [1]. Many of them are employed also in optical and photoelectric devices, used in synthesis of high-temperature superconductors, considered as materials for cathodes in Li-batteries and for nanotechnologies.

In general, Cu_{1+x}S compounds are hardly identified by their optical properties and might be easily missed if one is to rely on the X-ray diffraction data only (Gablina, 1993). This effect is due to the fact that crystal-chemical properties of Cu_{1+x}S minerals, in spite of relationship, depend strongly on their stoichiometry (Gablina, 1993). Therefore the structural properties of some Cu_{1+x}S compounds, including chalcocite Cu₂S, are not completely known or even unclear up to date. For example, there are difficulties to determine both the symmetry space group and the structural features in the case of numerous non-equivalent sites of atoms. This happens for Cu₂S. One of the earlier studies suggested the space group *Pc* and 48 non-equivalent Cu sites (Evans, 1979a), whereas other studies pointed to the space group *P2₁/c* and 24 non-equivalent Cu sites (Evans, 1971; Evans, 1979b; Evans, 1981). The most Cu atoms are located at the triangular sites Cu-S₃ and linear units Cu-S₂ with different Cu-S lengths and bond angles. A small number of Cu occupies the tetrahedral Cu-S₄ units.

^{63,65}Cu nuclear quadrupole resonance (NQR) spectroscopy has been applied for highlight the structural features of Cu₂S. Cu NQR frequencies depend on the crystal electric field gradient (EFG) and quadrupole moments of nuclei (for example, Cu) and, as a result, are sensitive to local environment of quadrupole nuclei and their variations. In order to reach reliability, two natural polycrystalline

Cu₂S samples from have been studied by NQR at temperature of liquid nitrogen (77 K). In addition, theoretical calculations of NQR frequencies have been made on the base of crystallographic data (Evans, 1979b) and point charge model. As it was found, both natural samples exhibit the similar complicated NQR spectra, providing evidence for 24 non-equivalent copper sites. Moreover, experimental and computed values of NQR frequencies are very similar to each other. This supports the crystallographic data of (Evans, 1971; Evans, 1979b; Evans, 1981).

It seems, however, that the combination of NQR and Neutron spectroscopic methods is a best way for Cu_{1+x}S compounds to investigate their not only the structural properties but the dynamical effects, including ionic motion and vibrations. Temperature-dependent measurements of NQR relaxation could be useful to determine the type of internal motions, whereas Neutron diffraction together with Neutron spectroscopy could find the fine features of these motions. Selenide analogs of Cu_{1+x}S compounds with their interesting thermoelectric properties are being example of this. In particular, Neutron spectroscopic studies of Cu_{2-δ}Se show the correlated thermal vibrations of Se and Cu atoms and the diffusion of Cu atoms between the nearest 8c sites through the 32f sites (Danilkin et al., 2011; Danilkin et al. 2012). As result, the combinational Neutron and NQR spectroscopic studies of Cu₂S and other representatives of Cu_{1+x}S compounds are important to elucidate their fine features and technological properties.

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