РОССИЙСКАЯ АКАДЕМИЯ НАУК
Уральское отделение

Российское минералогическое общество
Комиссия по кристаллохимии, рентгенографии и спектроскопии минералов
Международный Союз кристаллографов
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Санкт-Петербургский государственный университет
Уральский федеральный университет

Материалы XVIII Международного совещания

КРИСТАЛЛОХИМИЯ, РЕНТГЕНОГРАФИЯ И СПЕКТРОСКОПИЯ МИНЕРАЛОВ - 2014

13–15 октября 2014 г.

РОССИЯ, ЕКАТЕРИНБУРГ

STRUCTURAL PROPERTIES OF CHALCOCITE PROBED BY NQR SPECTROSCOPY

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Binary copper sulfides of $Cu_{1+x}S$ ($0 \le x \le 1$) family are numerous (approximately 15) and amazing owing to variety of their physical properties. Among them only two represent the stoichiometric compounds with established structures: covellite CuS and chalcocite Cu_2S. Other compounds are non-stoichiometric. Some of these sulfides form ores from which a metallic Cu is extracted (CuS, Cu_2S, djurleite $Cu_{\approx 1,95}S$, digenite $Cu_{\approx 1,8}S$, roxbyite $Cu_{\approx 1,78}S$, anilite $Cu_{1,75}S$) [1]. Many of them are employed in optical and photoelectric devices, used in synthesis of high-temperature superconductors, considered as materials for cathodes in Li-batteries and for nanotechnologies.

The structure and the physical-chemical properties of $Cu_{1+x}S$ compounds depend strongly on their stoichiometry [1]. Many binary sulfides $Cu_{1+x}S$ are hardly identified by their optical properties and might be easily missed if one is to rely on the X-ray diffraction data only [1]. Therefore the structural properties of some $Cu_{1+x}S$ compounds, including chalcocite Cu_2S, are not completely known or even unclear up to date. Generally, 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 Cu_2S. One of the earlier studies suggested the space group Pc and 48 non-equivalent Cu sites [2], whereas other studies pointed to the space group $P2_{1/c}$ and 24 non-equivalent Cu sites [3-5]. The most Cu atoms are located at the triangular sites Cu-S3 and linear units Cu-S_2 with different Cu-S lengths and bond angles. A small number of Cu occupy the tetrahedral Cu-S_4 units.

^{63,65}Cu-NQR spectroscopy can play an important complementary role in phase-structural diagnostics of $Cu_{1+x}S$ sulfides and their physical studies [6]. NQR effect is due to the interaction of electric field gradient (EFG) of the crystal with the quadrupole moment of nuclei (for example, Cu). Cu NQR frequencies depend on the EFG and quadrupole moments and, as a result, are sensitive to local environment of quadrupole nuclei and their variations. Two natural polycrystalline Cu_2S specimens from Djezgazgan (Kazakhstan) and Donbass (Ukraine) deposits have been studied by copper NQR spectroscopy at temperature of liquid nitrogen (77 K). The goals of measurements are the comparison of data for two samples (variability depending on the nature of samples), the clarification of crystal structural features of chalcocite Cu_2S and the consideration of the NQR parameters as the possible database for next-generation portative NQR/NMR spectrometers for geological exploration. As it was found, both natural samples exhibit the similar complicated NQR spectra, providing evidence for 24 non-equivalent copper sites. Some of the NQR spectral lines could be used as references for express analysis of copper ore by NQR spectrometers.

In this report, the investigation of Cu_2S specimens in the context of previous results for covellite CuS and digenite $Cu_{1,8}S$ is presented and discussed.

This work is supported partly by Academy of Sciences of the Republic of Tatarstan (grant No. 06-149m/Г).

REFERENCES

1. Gablina I.F.: Mineraly sistemy med'-sera (Minerals of the copper-sulfur system). Geoinformmark ed., M., 46 p. (1993) (in Russian).
2. Evans H.T., Science, v.203, p.356-358 (1979).
3. Evans H.T., Nature. Phys. Science, v.232, pp.69-70 (1971).
4. Evans H.T., Zs. Krist, v.150, p.299-320 (1979).
5. Evans H.T., Amer. Min., v.66, p.807-818 (1981).
6. Abdullin R.S. et al., Phys. Chem. Minerals, v.14, p.258-263 (1987).