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Low-temperature magnetic properties of chalcopyrite (CuFeS2) studies by 63,65Cu NMR and 57Fe Mössbauer spectroscopy

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Chalcogenide minerals exhibit a fascinating variety of crystal-chemistry and physical properties that is of both scientific interest and potential practical application value. The role of ternary chalcogenide CuFeS2 (referred to as chalcopyrite) should be specially emphasized. On the one hand, chalcopyrite is known as a very important commercial source of copper ore. On the other hand, chalcopyrite-based chalcogenide group of minerals is considered as a perspective generation of solar cells. This is due to their high optical absorption coefficient when compared with known materials, with their energy band gap varied within the range of 0.8-3.5 eV by controlling chemical composition. This is also the reason for these materials finding wider application in optoelectronic devices.
From scientific point of view, CuFeS2 has drawn strong interest as an antiferromagnetic semiconductor. One of known specific features of CuFeS2 is the occurrence of polymer-like structure consisting of –Cu–S–Fe– chains. This structure leads to the presence of several unusual properties of electronic and magnetic origin. Particularly, the values of Fe magnetic moments in CuFeS2 with 3.85μB are significantly less than those for the magnetic trivalent Fe, necessitating considerations of valence states of iron and copper ions [1]. Unusual behavior of electrical resistivity of chalcopyrite leads to the discussions about the nature of its electronic type (for example, zero-gap semiconductor [2] or unusual insulator of Haldane–Anderson type [3]). Neutron diffraction examination reveals phase transition in CuFeS2 at 50K temperature [4], however earlier Mössbauer studies provide no evidence of such behavior [5]. Thus, clarification of the points mentioned above requires comprehensive study of local properties of CuFeS2 and local methods providing experimental information at micro- and nano-scale are most suitable for this purpose. In addition, combination of different local methods appears to be more expedient in complex studies due to the possibility of observing and comparing electron-nuclear interactions using different nuclei probes [6]. Joint application of nuclear resonance spectroscopic methods (Mössbauer Effect and NMR, NMR and NQR, Mössbauer Effect and ENDOR and other) are some of the examples of such joint experimental techniques.
In this report, we present some preliminary results of chalcopyrite studies by simultaneous application of two nuclear resonance spectroscopic methods at low temperatures: 63,65Cu nuclear magnetic resonance (NMR) and 57Fe Mössbauer Effect. In particular, at approximately 50K temperature we have experimentally observed rapid deviation of CuFeS2 relaxation parameters from what is normally considered as standard behavior typical for the majority of semiconductors. On the basis of the experimental data obtained and their analysis, some aspects of electronic structure and physical properties of CuFeS2 are presented and discussed.

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