CRYSTAL CHEMISTRY OF THE STANNITE-GROUP COMPOUNDS (EPMA, EPR, SQUID, MÖSSBAUER SPECTROSCOPY)

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In order to check the model of complex isomorphous replacement "Cu → Fe" (EVSTIGNEEVA et al., 2003), and to determine the metal valence states, EPMA, EPR, SQUID, and Mössbauer spectroscopy were performed on 10 synthetic analogues of the kuramite - stannite series, $Cu_{3-x}Fe_xSnS_4$ ($0 < x < 1$). The Cu valence and the character of chemical bond were studied with EPMA on the base of self-absorption of the measured copper X-ray emission. According to the first results the contribution of Cu 3*d* electrons to the chemical bond increases if the Fe content increases from 0 to 0.5 afu. It is caused by the Cu–Fe interaction due to the short Cu-Fe distance between Cu_{Tetr} and Fe_{Oct}. The general dependency of experimental magnetic susceptibility on the temperature corresponds to the theoretical high-temperature limit of the Curie constants calculated on the base of the proposed model of isomorphism (EVSTIGNEEVA et al., 2003). The magnetic susceptibility line is bent at [Fe] ~0.5 afu, and consists of two positive linear trends. The Curie constant values are located below the theoretical line at [Fe] < 0.5 afu, while above 0.5 Fe afu they plot slightly above this line. The first trend should be explained by the intermediate spin state of Fe^{3+}, the best fit agrees with S = 3/2. The second trend, parallel to the theoretical one, but shifted to higher emu/mol values, corresponds to the Fe^{3+}/ Fe^{2+} exchange model considering that a small spin-orbit interaction increases the Fe^{2+} contribution in comparison with stannite, 3.15 in spite of 3 emu/mol., as was shown by BERNARDINI et al. (2000). These results can prove the Fe spin transition between 0.5 – 0.6 Fe afu. The Fe spin state and antiferromagnetic interactions like those established for natural and synthetic stannites (BERNARDINI et al., 2000) are discussed. The data obtained are in good agreement with results of Mössbauer spectroscopy, but the schemes of isomorphism in stannite family compounds proposed earlier need to be precised.

References

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