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Abstract

Full Text

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STUDY OF ARTIFICIAL MIARGYRITE ($AgSbS_2$) BY THE METHOD OF NUCLEAR QUADRUPOLE RESONANCE

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Sulfantimonide of composition $AgSbS_2$ is known in two modifications: cubic (β) and monoclinic (α) (^{1}, ^{2}). The high-temperature β form has a galena-type lattice, in which the positions of Pb atoms are statistically occupied by Ag and Sb. In the β form, nuclear quadrupole resonance (NQR) was not observed, and this, apparently, is a consequence of disorder in the distribution of Ag and Sb atoms. In the low-temperature α form, stable below 390°, an NQR spectrum has been found, which is discussed below.

Fig. 1. Unit cell of the low-temperature modification of miargyrite according to data of (^{5}). Interatomic distances are indicated in angstroms.

Low-temperature miargyrite has the theoretical composition (in %): Ag 36.72, Sb 41.56, and S 21.83. Natural specimens often contain impurities of As, Cu, and Pb (^{3}). Its structure was established by Hofmann (^{4}) and recently reconsidered by Knowles (^{5}). The unit cell contains 8 formula units and has the parameters: $a = 12.862$, $b = 4.411$, and $c = 13.220$ Å; $\beta = 98°38'$; space group $C2/c$. The Ag, Sb, and S atoms form chains elongated in the direction [101] (Fig. 1). The Ag atoms occupy two crystallochemically independent positions. In the first, their nearest neighbors are two S atoms; in the second, four. One of the bonds in the AgS_4 tetrahedron is a bridging one, fastening neighboring chains. This determines the absence in miargyrite of the noticeable cleavage characteristic of some chain-layer lattices of sulfides and sulfosalts. The Sb atoms are also of two kinds, each of them having three S atoms as nearest neighbors. The SbS_3 polyhedra (trigonal pyramids) are combined into binuclear complex radicals

$[Sb_2S_4]_n$. It may be noted (Fig. 1) that both SbS_3 polyhedra are somewhat distorted and differ little from one another in interatomic distances.

The object of the investigation was a specimen of miargyrite obtained by pyrosynthesis in the following way. First, from highly purified elemental Ag, Sb, and S, taken in stoichiometric proportions, there was obtained

cubic modification. Its synthesis regime is as follows: heating to 550° at a rate of 200° per hour, holding at this temperature for 1 hour, cooling from 550 to 500° at a rate of 50° per hour, rapid cooling to 430°, and annealing at this temperature for 72 h. The monoclinic modification was obtained from the cubic one as a result of subsequent annealing for 384 h at a temperature of 300°. The prolonged annealing in this case is due to the fact that the cubic modification, stable above 390°, is readily quenched and therefore can exist for a long time also at a lower temperature (^{1}). The initial annealing at a temperature of 430° is necessary in order to obtain a homogeneous material.

Under the microscope, a polished section of artificial miargyrite has a high reflectivity, but somewhat lower than that of galena. Its color is white with a faint greenish tint. The effects of bireflectance and anisotropy are clear; the anisotropy colors vary from dark brown to blue. The internal reflections are red. On the thermogram of the obtained miargyrite sample, two endothermic effects are distinctly recorded. The first is observed at a temperature of 390° and corresponds to the polymorphic transformation of the monoclinic modification into the cubic one; the second, at a temperature of 528°, corresponds to the onset of melting of the material. Table 1 gives the interplanar-spacing data for the sample investigated by us and for the standard, which was a natural sample (^{6}). Good agreement of the principal lines is evident, indicating the structural analogy of the samples.

Table 1

Interplanar spacings of miargyrite (α-$AgSbS_2$)

Sample No. 1. Natural miargyrite		Sample No. 2. Artificial miargyrite		Sample No. 1. Natural miargyrite		Sample No. 2. Artificial miargyrite		Sample No. 1. Natural miargyrite		Sample No. 2. Artificial miargyrite	
I	d_α/n	I	d_α/n	I	d_α/n	I	d_α/n	I	d_α/n	I	d_α/n
9	3.42	8	3.413	6	1.682	3	1.686	4	1.250	2	1.268
6	3.16	4	3.164			2	1.654			4	1.254
6	3.08	4	3.080	4	1.625	2	1.631	4	1.228	3	1.231
10	2.88	10	2.873	4	1.588	3	1.590			1	1.223

Sample No. 1. Natural miargyrite		Sample No. 2. Artificial miargyrite		Sample No. 1. Natural miargyrite		Sample No. 2. Artificial miargyrite		Sample No. 1. Natural miargyrite		Sample No. 2. Artificial miargyrite	
8	2.74	10	2.733	4	1.550	3	1.550			1	1.201
4	2.64	1	2.634			2	1.493			1	1.183
4	2.20	1	2.188	2	1.425	1	1.444	2	1.145	1	1.165
7	2.01	8	2.010	4	1.415	2	1.421	2	1.130	2	1.144
7	1.965	8	1.965	2	1.372			2	1.105	3	1.130
6	1.910	4	1.909			4	1.373			4	1.109
		1	1.867	3	1.330	3	1.357			1	1.098
7	1.800	3	1.808	2	1.301	3	1.338			1	1.088
		3	1.789	2	1.285			2	1.065	3	1.079
4	1.715	2	1.714		.	2	1.285			3	1.066

Note. CoK_α, Fe filter, 40 kV, 6 mA, 6 h, $D = 57.3$ mm.

The NQR spectrum of the nuclei Sb^{121} (nuclear spin $I = 5/2$) and Sb^{123} ($I = 7/2$) was studied at temperatures of 77 and 300°K in a polycrystalline sample with a volume of about 2 cm^3. The main parameters of the spectrum are summarized in Table 2, where, for comparison, some characteristics are also given for the NQR spectrum in pyrargyrite (Ag_3SbS_3), studied previously (^{7}).

It follows from the table that the NQR spectrum of the nuclei Sb^{121}, ^{123} in low-temperature miargyrite consists of 5 lines. Taking into account the number of allowed quantum transitions, such a spectral pattern unambiguously indicates that in the unit cell of this compound all Sb atoms occupy crystallochemically equivalent positions. The magnitude of the asymmetry parameter η, equal to 34%, demonstrates a strong distortion of the SbS_3 polyhedra. Although the Debyegram of the artificial sample is identical to the standard one, the NQR data

Table 2

Parameters of the NQR spectrum of miargyrite and pyrargyrite

Isotope	Quantum transition	NQR frequencies, ν_{res}, MHz: experimental, 77° K	NQR frequencies, ν_{res}, MHz: experimental, 300° K	NQR frequencies, ν_{res}, MHz: calculated for $\eta = 34.1\%$, 77° K	Quadrupole coupling constant, eQq, MHz, 77° K
Miargyrite	**Miargyrite**	**Miargyrite**	**Miargyrite**	**Miargyrite**	**Miargyrite**
Sb^{121}	$^1/_2 \leftrightarrow {}^3/_2$	54.00	52.80	54.00	~ 337
Sb^{121}	$^3/_2 \leftrightarrow {}^5/_2$	94.44	91.83	94.44	~ 337
Sb^{123}	$^1/_2 \leftrightarrow {}^3/_2$	39.57	–	38.81	~ 337
Sb^{123}	$^3/_2 \leftrightarrow {}^5/_2$	55.80	54.20	56.21	~ 337
Sb^{123}	$^5/_2 \leftrightarrow {}^7/_2$	86.82	84.47	86.86	~ 337
Pyrargyrite	**Pyrargyrite**	**Pyrargyrite**	**Pyrargyrite**	**Pyrargyrite**	**Pyrargyrite**
Sb^{121}$\eta = 0$	$^1/_2 \leftrightarrow {}^3/_2$	49.84	–	–	332.3
Sb^{121}$\eta = 0$	$^3/_2 \leftrightarrow {}^5/_2$	99.70	–	–	332.3

do not agree completely with the X-ray determinations of the structure, according to which the unit cell of miargyrite should contain two nonequivalent positions for Sb atoms. In our view, the reason for this discrepancy lies in an insufficiently accurate determination of the coordinates of the atoms (electron densities) in the X-ray structural analysis. The most probable source of errors in the present case is the incorrect determination of the magnitude of the temperature correction B_s, which reflects the root-mean-square displacement of an atom from its equilibrium position ([8]). The scatter of the values of B_s in miargyrite is especially large for sulfur atoms ([5]). This fact, as well as the large value of the asymmetry parameter η of the electric-field gradient at Sb nuclei, indicates a strongly pronounced anisotropy of atomic vibrations. Meanwhile, the existing methods for estimating the magnitude of B_s are based on the assumption of the isotropic character of such vibrations. It is natural to conclude that, under these conditions, the question of the exact localization of atoms (especially light ones) in the unit cell of miargyrite can be satisfactorily resolved only by the combined use of a number of methods.

The indicated features in the lattice dynamics of miargyrite are reflected in the temperature gradient of the frequency,

$$\frac{1}{\nu}\frac{d\nu}{dT}.$$

According to theory, the resonance frequencies ν_{res} and the asymmetry parameter η for an absolutely rigid lattice are related to one another by definite relations (^{9}). However, thermal motions of atoms and functional groups make these quantities temperature-dependent. In other words, if $\eta \neq 0$, the values of

$$\frac{1}{\nu}\frac{d\nu}{dT}$$

for different transitions prove to be unequal. Table 3 gives the values of

$$\frac{1}{\nu}\frac{d\nu}{dT}$$

for asymmetric groups $SbS_3(SbS_5)$ in stibnite, bournonite, and miargyrite. Their scatter is evident, and it is especially noticeable in miargyrite. As a consequence, the NQR frequencies in the latter differ substantially from the theoretical set of frequencies for an absolutely rigid lattice. A more thorough study of the dependence of the resonance frequencies on temperature could probably clarify the nature of the anomalous behavior of the X-ray structural parameter B_s in the case under consideration.

The NQR spectral data and the discussion presented above show that the structure of low-temperature miargyrite has a somewhat higher symmetry than follows from the X-ray structural analysis. The equivalence of the Sb positions in the unit cell established by NQR requires a refinement of the space group.

In the structural-chemical aspect, miargyrite is a coordination polymer. On the basis of the NQR spectrum one can give the following ca-

Table 3

Isotope	Quantum transition	antimonite Sb_2S_3 ($\eta = 38\%$)	bournonite $CuPbSbS_3$ ($\eta = 23\%$)	miargyrite α-$AgSbS_2$ ($\eta \simeq 34\%$)
Sb^{121}	$1/2 \leftrightarrow 3/2$	0.208	0.076	0.115
Sb^{121}	$3/2 \leftrightarrow 5/2$	0.226	0.081	0.095
Sb^{123}	$1/2 \leftrightarrow 3/2$	0.190		0.078
Sb^{123}	$3/2 \leftrightarrow 5/2$	0.222	0.078	0.121
Sb^{123}	$5/2 \leftrightarrow 7/2$	0.221	0.079	0.115

$\frac{1}{\nu}\frac{d\nu}{dT}$, deg^{-1}

a qualitative description of the state of the chemical bonds in this compound. The complex radical $[Sb_2S_4]_n$ may be regarded as a dimer of SbS_3 groups with strongly localized sp^3-hybrid orbitals of Sb atoms. The strengthening of this complex is promoted to a certain degree by donor–acceptor bonds formed by unshared pairs of sulfur-atom s- and p-orbitals and vacant d-orbitals of antimony atoms (^{10}). The Sb atoms carry a certain effective positive charge, i.e., the Sb—S bonds have a noticeable share of ionic character. As indicated in (^{10}), metallic atoms of the copper type, located in the second coordination sphere, exert a substantial influence on the state of the bonds in SbS_3 (SbS_5) groups of sulfosalts. The latter draw part of the electron cloud toward the sulfur atoms with which they are directly bonded in the structure. Such charge transfer (the inductive effect) along a chain of bonded atoms increases noticeably with increasing coordination number of the metal atom. In this sense, the increase in the ionicity of the Sb—S bonds in miargyrite does not seem unexpected in comparison with pyrargyrite, where the Ag atoms have twofold coordination. Accordingly, the quadrupole-interaction constant eQq in $AgSbS_2$ is somewhat larger than that for Ag_3SbS_3.

In polymeric structures of sulfosalts, nuclear quadrupole spin-lattice relaxation is in most cases determined by the mobility of SbS_3 groups. However, in miargyrite these groups are constituent parts of the complexes $[Sb_2S_4]_n$, which are rather rigidly bound to the Ag sublattice. On this basis one may suppose that, in the relaxation of Sb^{121}, ^{123} nuclei of miargyrite, lattice vibrations are the most effective (^{11}). This apparently explains the fact that the relaxation time T_1 for antimony nuclei in miargyrite (at 77° K) is approximately an order of magnitude longer than the corresponding value in pyrargyrite ($T \simeq 60$ and 6 msec), in whose structure the SbS_3 groups can execute more or less free torsional vibrations about the c_3 axis. Since both compounds, $AgSbS_2$ and Ag_3SbS_3, possess semiconductor properties, at room temperatures other relaxation mechanisms become effective, for example charge diffusion.

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