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Complete List of Authors:	Sadovnikov, Stanislav; Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, Laboratory of Nonctoichiometric compounds Gusev, Aleksandr; Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences Ekaterinburg, Russian Federation, Chukin, Andrey; Ural Federal University named after the First President of Russia B.N. Yeltsin Rempel, Andrey; Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences,

High-Temperature X-Ray Diffraction and Thermal Expansion of Nanocrystalline and Coarse-Crystalline Acanthite α-Ag_2S and Argentite β-Ag_2S †

S. I. Sadovnikov,[a] A. I. Gusev,[a] A. V. Chukin[b] and A. A. Rempel[a]

An *in situ* study of thermal expansion of polymorphic phases of coarse-crystalline and nanocrystalline silver sulfide – monoclinic acanthite α-Ag_2S and cubic argentite β-Ag_2S – has been carried out for the first time using the high-temperature X-ray diffraction method. The temperature dependences of the unit cell parameters of acanthite and argentite in the interval 300-623 K have been determined, and the thermal expansion coefficients of acanthite and argentite have been found. It is shown that the observed difference in the thermal expansion coefficients for nano- and coarse-crystalline acanthite is due to small particle size of nanocrystalline silver sulfide leading to the growth of anharmonicity of atomic vibrations. It is established by differential thermal analysis that a reversible polymorphic acanthite – argentite phase transformation takes place at ~449-450 K and the phase transformation enthalpy is equal to ~3.7-3.9 kJ mol^{-1}.

Key words: Silver sulfide, Nanocrystalline and coarse-crystalline powders, Thermal expansion, Atomic vibration anharmonicity, Acanthite - argentite phase transformation

[a] *Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg 620990, Russia*. *E-mail: gusev@ihim.uran.ru*
[b] *Ural Federal University named after the First President of Russia B.N. Yeltsin, Ekaterinburg, 620002, Russia*
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I. Introduction

Silver sulfide Ag_2S attracts much interest as a semiconductor owing to high chemical stability and ease of synthesis. Semiconducting nanocrystals and nanostructured films of silver sulfide found application in optoelectronics, infrared equipment, and power engineering. Thin films of silver sulfide are used in photochemical cells, thin-film transistors and infrared detector.[1-4] Nanostructured silver sulfide Ag_2S can be used in photochemical cells,[3,5] in resistance-switches and nonvolatile memory devices.[6-8] Ag_2S nanoparticles can be used as photocatalysts in various redox-processes and for producing nanocomposite photocatalysts.[9-11] Silver sulphide is a promising material for conversion of solar energy into electrical energy.[12-15] For application of silver sulfide in infrared equipment and solar energy converters, it is necessary to have information about the variation of the thermal expansion coefficient as a function of temperature.

It is known that silver sulfide Ag_2S has three basic polymorphic modifications. Low-temperature monoclinic phase α-Ag_2S (acanthite) exists at a temperature below ~450 K.[16] Second phase β-Ag_2S (argentite) has body centered cubic (bcc) lattice and exists in the temperature range 452-859 K. High-temperature face centered cubic (fcc) phase γ-Ag_2S stable from ~860 K up to melting temperature. For technical application as a semiconducting photoluminescent material, of most interest is low-temperature acanthite and argentite phases in nanosized state.

Natural acanthite mineral α-Ag_2S has a monoclinic (space group $P2_1/c$ ($P12_1/c1$)) crystal structure.[17]

The crystal structure of monoclinic silver sulfide powders synthesized by chemical deposition has been recently determined in works.[18,19] According to,[18] the coarse-crystalline powder of silver sulfide with the average particle size of ~500 nm has a monoclinic (space group No. 14 - $P2_1/c$ ($P12_1/c1$)) structure of α-Ag_2S acanthite type and is stoichiometric. The unit cell of acanthite α-Ag_2S includes four formula units of Ag_2S ($z = 4$). A thorough study of nanocrystalline silver sulfide revealed that it has the same monoclinic (space group $P2_1/c$) acanthite-type structure, but is nonstoichiomertic and has the composition ~$Ag_{1.93}S$.[19]

According to,[20] the unit cell of argentite β-Ag_2S has a body centered cubic (space group No. 229 - $Im\bar{3}m$ ($I4m\bar{3}2/m$) (O_h^9)) structure and includes two formula units of Ag_2S ($z = 2$). Two sulfur atoms occupy the crystallographic position 2(a) and form a bcc sublattice. Four silver atoms Ag are statistically distributed in 42 positions 6(b), 12(d), and 24(h). Later on the probabilities of occupation of 6(b), 12(d), and 24(h) positions were assumed to be equal to 2/9, 1/9, and 1/18, respectively. The model structure of β-Ag_2S argentite proposed in work[20] is very similar to that of AgI. However the neutron diffraction study[21] of AgI monocrystal showed that the distribution of silver atoms

in it cannot be described by random distribution, and therefore the model[20] is not suitable for bcc β-Ag_2S.

The neutron diffraction study[22] of artificial β-Ag_2S argentite crystal in the temperature interval 459-598 K considerably refined the distribution of Ag atoms. Note that the examined monocrystal β-Ag_2S features large twinning. According to data,[22] four silver atoms are statistically distributed in 18 positions 6(*b*) and 12(*d*) at a temperature from 459 to ~500 K. The occupation of 6(*b*) and 12(*d*) positions by Ag atoms depends on temperature. At 459 K, these positions in the unit cell contain 0.81 and 3.19 Ag atoms, and at 473 K these positions contain 0.66 and 3.34 Ag atoms, respectively. At a temperature $T \geq 533$ K all 4 silver atoms are statistically distributed only in 12(*d*) positions. According to the neutron diffraction data[23] collected for β-Ag_2S at $T = 558$ K two S atoms are located in the 2(*a*) positions with coordinates (0 0 0), and four Ag atoms are statistically distributed over the 12(*d*) tetrahedral sites with coordinates (1/4 0 1/2).

According to high-temperature XRD data,[24] as distinct from data,[22,23] four silver atoms are statistically distributed in 54 positions 6(*b*) and 48(*j*) with the occupation probabilities ~0.097 and ~0.0715, respectively.

Under equilibrium conditions, a polymorphous phase transformation of monoclinic acanthite α-Ag_2S into bcc argentite β-Ag_2S takes place at a temperature about 448-453 K.[16,25-27]

Until recently, scanty information about acanthite – argentite phase transformation was obtained only for bulk samples of coarse-grained silver sulfide Ag_2S.[26,27] Lately,[28,29] an electron microscopic study of the acanthite – argentite phase transformation in nanocrystalline silver sulfide was carried out. Using scanning electron microscopy (SEM), the authors of the study[28] recorded for the first time a video film showing how the acanthite - argentite transformation occurs in nanocrystalline silver sulfide in real time.

The information about thermal expansion of silver sulfide is very limited, although such data are necessary for application of Ag_2S at elevated temperatures and for selecting substances with close thermal expansion coefficients. The data on thermal expansion of different phases of silver sulfide are needed for the creation of resistance-switches and nonvolatile memory devices, whose operation is based on the acanthite – argentite transformation. According to,[30] the linear thermal expansion coefficient α_{ac} of acanthite is equal to $\sim 20 \times 10^{-6}$ K^{-1}. The temperature interval, to which this coefficient corresponds, and the method of its measurement in work[30] are not given. According to,[31] at a room temperature the linear thermal expansion coefficient α_{ac} of bulk acanthite is equal to 16.8×10^{-6} K^{-1}. The data on the thermal expansion coefficient of argentite or nanocrystalline acanthite are not available in the literature.

Although there are three publications[32-34] devoted to electronic structure calculation of monoclinic silver sulfide, no quantum chemical calculations of the phonon spectrum of silver sulfide allowing one to estimate the thermal expansion of Ag_2S are available.

In this work, using the high-temperature X-ray diffraction (XRD) method, we performed for the first time an *in situ* systematic study of the thermal expansion of coarse-crystalline and nanocrystalline powders of silver sulfide in the region of existence of monoclinic acanthite α-Ag_2S and bcc argentite β-Ag_2S.

II. Experimental

Nanocrystalline powder of silver sulfide Ag_2S was synthesized by chemical deposition from aqueous solutions of silver nitrate $AgNO_3$, sodium sulfide Na_2S and sodium citrate $Na_3C_6H_5O_7$ with concentrations 50, 25 and 12.5 mmol·l^{-1}, respectively. The synthesis technique is described earlier[19,35] (*see also* ESI† for experimental details). Deposited Ag_2S powder was washed with distilled water by decanting, filtered and dried in air at 323 K. The coarse-crystalline Ag_2S powder was produced by hydrothermal synthesis from aqueous solutions of $AgNO_3$ and thiourea $(NH_2)_2CS$ with identical concentrations 50 mmol·l^{-1}. The sulfide formation reaction took place in a closed vessel at 453 K for 4 h. The air and saturated vapor pressure over the solution was ~$1\cdot10^6$ Pa.

In situ high-temperature XRD (HT-XRD) experiments were performed using a X`Pert PRO MPD (Panalytical) diffractometer equipped with a Anton Paar HTK-1200 Oven furnace. HT-HRD patterns were recorded in the angle interval $2\theta$ = 20-67.5° with a step of $\Delta(2\theta)$ = 0.026° and scanning time 200 s in each point. X`Pert PRO MPD diffractometer was equipped with a position-sensitive fast sector detector PIXCEL, which simultaneously measures the intensity of reflection not at a separate point as an ordinary proportional counter, but in a 2θ range with a width of 3.154°. The use of this detector allowed one to reduce considerably the XRD pattern survey time with no compromise in quality. The reduction of the survey time is also an essential condition of investigation, since silver sulfide nanopowder is very hygroscopic and during heating it is quickly oxidized by adsorbed water. The diffraction measurements were performed at a temperature from 295 to 623 K with a step of ~25-30 K. When the assigned heating temperature was reached, the XRD pattern was recorded during 30 min.

The synthesized powders of silver sulfide were examined on a Shimadzu XRD-7000 and STADI-P (STOE) diffractometers in Cu$K\alpha_1$ radiation. X-ray measurements were performed in the angle interval 2θ = 20-95° with a step of $\Delta(2\theta)$ = 0.02° and large scanning time 10 s in each point. The determination of the crystal lattice parameters and final refinement of the structure of the synthesized silver sulfide powders were carried out with the use of the X'Pert Plus software suite.[36]

The microstructure and particle size of the silver sulfide powders and their elemental chemical composition was studied by the scanning electron microscopy (SEM) method on a JEOL JSM 6390 LA microscope coupled with a JED 2300 Energy Dispersive X-ray Analyzer. In addition, nanocrystalline silver sulfide was examined by transmission electron microscopy (TEM) method. The TEM images were recorded on a JEOL JEM-2010 transmission electron microscope with 0.14 nm (1.4 Å) lattice resolution.

The temperature and enthalpy of the acanthite – argentite phase transformation were determined by differential thermal differential thermal and thermogravimetric analyses (DTA-TGA) method on a Setaram SETSYS Evolution 1750 thermal analyzer. DTA and TGA experiments were carried out in argon Ar flow of 20 ml min^{-1} both during heating and during cooling in the temperature intervals 293-493 K and 493-333 K with a heating or cooling rate of 5 $K \cdot min^{-1}$.

The average particle size D in the synthesized silver sulfide powders was estimated by XRD method from the diffraction reflection broadening $\beta(2\theta)$,[37,38] from the specific surface S_{sp} value measured by the Brunauer-Emmett-Teller (BET) method, and from the scanning (SEM) and transmission (TEM) electron microscopy data (*see* ESI† for experimental details).

III. The effect of temperature and particle size on the structural characteristics and thermal expansion of acanthite α-Ag_2S

According to the BET and SEM data, the average particle size in coarse-crystalline silver sulfide powder is ~850 nm and the maximal size is ~1-2 μm (Fig. 1*a*).

The effect of temperature on the evolution of XRD patterns and on the unit cell parameters of coarse-crystalline and nanocrystalline silver sulfide is shown in Figs. 2-4.

The XRD patterns of coarse-crystalline silver sulfide recorded at 300, 400, 423, and 433 K (Fig. 2) contain a set of diffraction reflections of monoclinic (space group $P2_1/c$) stoichiometric acanthite α-Ag_2S (Table S1, ESI†). As the temperature increases, the positions and intensities of the diffraction reflections of acanthite gradually change. A polymorphous phase transformation of monoclinic acanthite α-Ag_2S into bcc argentite β-Ag_2S takes place at a temperature about 448-453 K.[16] Indeed, XRD pattern recorded at a temperature of 453 K contains a set of diffraction reflections of bcc (space group $Im\bar{3}m$) argentite β-Ag_2S.

Evolution of XRD patterns of nanocrystalline silver sulfide at heating from 295 to 443 K is shown in Fig. 3. The XRD patterns of nanocrystalline silver sulfide recorded at 295, 323, 348, 373, and 398 K contain the same set of broadened diffraction reflections. Qualitative analysis of the XRD patterns (Fig. S1, ESI†) and comparison with data[19] reveal that the observed set of diffraction reflections corresponds to nanocrystalline nonstoichiometric monoclinic (space group $P2_1/c$) acanthite α-$Ag_{1.93\text{-}1.96}S$ (Table S2, ESI†). The average size D of the coherent scattering regions was estimated

from the broadening of non-overlapping diffraction reflections (-1 0 2), (1 1 0), (-1 1 3), (-1 0 4), (0 3 1), and (0 1 4). According to these estimates, the average particle size *D* in the examined acanthite nanopowders is ~45-50 nm, in good agreement with the TEM data (Fig. 1*b*).

Nanocrystalline powder of silver sulfide is very hygroscopic and even upon drying it contains to ~2 wt.% adsorbed water. Heating of the nanopowder up to 433 K leads to its partial oxidation (*see* Fig. 3) by adsorbed water. The XRD patterns of the nanopowder recorded at ≥ 433 K contain the diffraction reflections of different oxide and oxide-sulfate phases of silver along with some reflections of cubic argentite β-Ag_2S.

The quantitative analysis of the XRD patterns showed that the rise in temperature leads to the variation of all unit cell parameters (*a*, *b*, *c*, β) of coarse-crystalline and nanocrystalline acanthite (Fig. 4) and to an increase in the unit cell volume *V*.

The volumetric thermal expansion coefficient is determined as

$$\beta_V(T) = \frac{1}{V_{300\mathrm{K}}}\frac{\Delta V}{\Delta T} = \frac{V(T) - V_{300\mathrm{K}}}{V_{300\mathrm{K}}(T - 300)}. \quad (1)$$

Analysis of the data on the unit cell volume of coarse-crystalline acanthite α-Ag_2S revealed that the temperature dependence of the volumetric thermal expansion coefficient β_V can be quantitatively described by the quadratic function

$$\beta_{V\mathrm{ac}}(T) = 34.81\times10^{-6} + 8.87\times10^{-8}T - 62.57\times10^{-12}T^2 \pm 2\times10^{-6}\ [\mathrm{K}^{-1}]. \quad (2)$$

In the first approximation, the isotropic (averaged in all directions) linear thermal expansion coefficient $\alpha_{\mathrm{ac\,isotr}}$ can be found through the volumetric expansion coefficient β_V as $\alpha_{\mathrm{ac\,isotr}} \cong \beta_{V\mathrm{ac}}/3$

$$\alpha_{\mathrm{ac\,isotr}}(T) = 11.6\times10^{-6} + 2.9\times10^{-8}T - 20.8\times10^{-12}T^2 \pm 1\times10^{-6}\ [\mathrm{K}^{-1}]. \quad (3)$$

In line with eqn (3), the value of the isotropic linear expansion coefficient $\alpha_{\mathrm{ac\,isotr}}$ of coarse-crystalline acanthite in the temperature region 300-433 K increases from ~18.4×10^{-6} to ~24.0×10^{-6} K^{-1}. As regards the value, this agrees with data,[30,31] according to which the linear expansion coefficient of bulk acanthite at a room temperature is equal to 20×10^{-6} K^{-1} or 16.8×10^{-6} K^{-1}, respectively.

As the temperature rises, the unit cell volume *V* of nanocrystalline acanthite increases. Note that the determination accuracy of the unit cell parameters *a*, *b*, *c*, and β of nanocrystalline acanthite is much smaller than for coarse-crystalline acanthite. Analysis of the data on the unit cell volume showed that the temperature dependence of the volumetric thermal expansion coefficient of nanocrystalline acanthite in the temperature range 300-400 K can be quantitatively described by the linear function

$$\beta_{V\mathrm{ac\text{-}nano}}(T) = 40.08\times10^{-6} + 8.21\times10^{-8}T \pm 4\times10^{-6}\ [\mathrm{K}^{-1}]. \quad (4)$$

In accordance with eqn (4), the isotropic (averaged in all crystallographic directions) linear thermal expansion coefficient $\alpha_{\text{ac-nano isotr}} \cong \beta_{V\text{ac-nano}}/3$ in the same temperature interval is equal to

$$\alpha_{\text{ac-nano isotr}}(T) = 13.4\times10^{-6} + 2.7\times10^{-8}T \pm 2\times10^{-6}\ [\text{K}^{-1}]. \quad (5)$$

The isotropic linear thermal expansion coefficient $\alpha_{\text{ac-nano isotr}}$ of nanocrystalline acanthite is by ~25 % larger than the analogous coefficient $\alpha_{\text{ac isotr}}$ of coarse-crystalline acanthite. The difference in the coefficients $\alpha_{\text{ac-nano isotr}}$ and $\alpha_{\text{ac isotr}}$ is due to the small particle size in nanocrystalline acanthite, which may induce variations of the phonon spectrum and its boundaries. Earlier, a similar difference in the linear thermal expansion coefficients of nanocrystalline film and coarse-grained sample was observed for lead sulfide PbS.[39-42]

The linear thermal expansion coefficient $\alpha(T)$ is related to specific heat capacity $C_{\text{sp}} = C_V/\nu_{\text{m}}$ per unit volume of substance, whose molecule contains n atoms, by the equation:[43]

$$\alpha(T) = n\gamma C_{\text{sp}}(T)/3B \equiv \frac{\gamma}{3B}\frac{C_V(T)}{\nu_{\text{m}}}, \quad (6)$$

where B is the bulk modulus, ν_{m} is the molar volume, and γ is the Grüneisen constant.

The main idea of the majority of models for modification of the phonon spectrum of small particles and/or nanostructured systems consists in the appearance of low-frequency modes in the phonon spectrum, which are absent in the spectrum of the bulk crystal. Indeed, the lattice vibration spectrum in small particles differs drastically from the bulk, as demonstrated by authors[44-46] and many others.

The phonon vibration spectrum of the perfect lattice of macroscopic crystal is distributed between the values of $\omega_{\text{min}} = 2\pi c_{\text{t}}/D$ (c_{t} is the transverse velocity of sound, and D is the size of the sample) and the Debye limit $\omega_{\text{maxD}} = \pi c_{\text{t}}/l$ (l is the characteristic interatomic distance). Reduction of the D values to the size of nanocrystals should result in the long-wave vibrations cutoff proportional to the value of D and in the corresponding rise of the lower frequency boundary ω_{min} of the phonon spectrum. For example, at the characteristic value $c_{\text{t}} \cong 10^3$ m s^{-1} for a nanocrystals with D = 10 nm, the frequency $\omega_{\text{min}} \cong 10^{12}$ s^{-1}. Therefore, waves can occur in the nanoparticles, whose length does not exceed the doubled maximum size of the particle D, i. e. $\lambda \le 2D$; so, on the side of low-frequency vibrations the phonon spectrum is limited by a certain minimal frequency $\omega_{\text{min}} \ge 2\pi\frac{c_{\text{t}}}{2D}$, where c_{t} is the velocity of propagation of transverse elastic vibrations (i. e. transverse velocity of sound).[37,47-49] In bulk crystals, there is no limitation like this. Besides, the phonon spectrum is limited on the side of high frequencies. Let us represent lattice heat capacity C_V through the average energy $\varepsilon(\omega,T) = (\hbar\omega/2)\text{cth}(\hbar\omega/2k_{\text{B}}T)$ of the linear oscillator and the frequency distribution function

$g(\omega)$, then, with allowance for the low- and high-frequency restrictions of the phonon spectrum, the thermal expansion coefficient of nanocrystalline substance is equal to

$$\alpha(T) = n\frac{\gamma}{3v_{\mathrm{m}}B}\int_{\omega_{\min}}^{\omega_{\max}}\frac{\partial\varepsilon(\omega,T)}{\partial T}g(\omega)d\omega. \qquad (7)$$

From eqn (7) it is clear that the temperature dependence of the thermal expansion coefficient depends directly on the spectral distribution of frequencies $g(\omega)$.

In studies,[40,41] taking into consideration the restrictions of the phonon spectrum of the small particles and using the approach[50] for the upper boundary $\omega_{\max}$ of the phonon spectrum of small particle, it was shown that thermal expansion coefficient of a nanocrystalline substance can be presented as

$$\alpha(T,D) = \alpha_{\mathrm{bulk}}(T) + n\frac{\gamma}{3B}\left(\frac{12k_1T}{D^2} + \frac{6k_2T^2}{D}\right), \qquad (8)$$

where $\alpha_{\mathrm{bulk}}(T)$ is the thermal expansion coefficient of bulk coarse-crystalline substance, γ is the Grüneisen constant, B is the bulk modulus, and D is the particle size. The values $k_1 = (k_{\mathrm{B}}^2 c_1^{-1}/8\pi\hbar)I_2$ and $k_2 = (k_{\mathrm{B}}^3 c_2^{-1}/2\pi\hbar^2)I_3$ are positive constants, $I_{\mathrm{m}} = (4m!/2^{m+1})\sum_{N=1}^{\infty}N^{-m} \equiv (4m!/2^{m+1})\zeta(m)$, $\zeta(m)$ is the Riemann zeta function (I_3 = 1.8031; $I_2 = \pi^2/6$), and c_1^{-1} and c_2^{-1} are effective propagation velocities of elastic vibrations determined through the velocities of longitudinal and transverse vibrations, c_ℓ and c_{t}: $c_1^{-1} = c_\ell^{-1} + 2c_t^{-1}$ and $c_2^{-1} = \dfrac{2c_t^4 - 3c_t^2c_\ell^2 + 3c_\ell^4}{c_t^2c_\ell^2(c_\ell^2 - c_t^2)}$.

The data on the propagation velocities of longitudinal and transverse elastic vibrations, c_ℓ and c_{t}, for acanthite are not available in the literature. Therefore the contribution of the particles with small size to the thermal expansion of acanthite cannot be estimated quantitatively. Nevertheless, from eqn (8) it is clear that the small particle size makes a positive contribution to the thermal expansion coefficient, which is experimentally observed in the comparison of nano- and coarse-crystalline acanthite α-Ag_2S.

In the general case, the thermal expansion coefficient $\alpha(T)$ is related to the coefficient of anharmonicity of atomic vibrations β_{anh} as $\alpha(T) = k_{\mathrm{B}}\beta_{\mathrm{anh}}/(A_h^2 a_{293\mathrm{K}})$, where A_h is a constant and $a_{293\,\mathrm{K}}$ is the lattice constant. In case of monoclinic acanthite, the value $V^{1/3}$, where V is the unit cell volume of acanthite, can be considered as the averaged lattice constant. Taking into account eqn (8), the dependence of the coefficient of anharmonicity of atomic vibrations on the particle size can be represented as

$$\beta_{\text{anh}}(T,D) = \frac{A_h^2 a_{293\text{K}}}{k_{\text{B}}}\left[\alpha_{\text{bulk}}(T) + n\frac{\gamma}{3\nu_{\text{m}}B}(k_1 L_\Sigma T + k_2 S_\Sigma T^2)\right]. \quad (9)$$

In accordance with eqn (9), the reduction of the particle size in silver sulfide should be accompanied by enhancement of the anharmonicity of atomic vibrations. This agrees with the conclusions[37,40,51] about an essential increase of the role of anharmonicity of thermal vibrations for nanomaterials as compared with microstructures.

The crystal lattice parameters and the averaged lattice constant $a_{293\text{ K}}$ of acanthite remain unchanged when its particle size decreases. If we assume that the coefficient A_h also remains constant when the particle size decreases, then the ratio of anharmonicity coefficients of nano- and coarse-crystalline acanthite α-Ag_2S is $\beta_{\text{nano}}/\beta = \alpha_{\text{ac-nano isotr}}/\alpha_{\text{ac isotr}}$, hence $\beta_{\text{nano}} = (\alpha_{\text{ac-nano isotr}}/\alpha_{\text{ac isotr}})\beta$. At 300 K, the coefficient $\alpha_{\text{ac isotr}}$ of coarse-crystalline acanthite is ~18.6×10^{-6} K^{-1}, while the thermal expansion coefficient of nanocrystalline acanthite is $\alpha_{\text{ac-nano isotr}} \cong 22.6\times10^{-6}$ K^{-1}. Therefore $\beta_{\text{nano}} \approx 1.2\beta$. Thus, the reduction of the particle size in silver sulfide is really accompanied by enhancement of the anharmonicity of atomic vibrations.

IV. Thermal expansion of argentite β-Ag_2S

Let us consider now the thermal expansion of argentite β-Ag_2S.

In order to refine the acanthite - argentite phase transition temperature, the powders of silver sulfide were studied by the DTA-TGA method both during heating and during cooling (Fig. 5). During heating, one endothermic peak is observed on the DTA curves at ~449-450 K, which corresponds to the α-Ag_2S (acanthite) - β-Ag_2S (argentite) phase transition. During cooling from 493 K to room temperature, the DTA dependences exhibit an exothermic peak corresponding to the argentite - acanthite phase transition, which is displaced into the region of temperatures lowered by ~20 K. The presence of a temperature hysteresis T_{trans} is indicative of the first order of reversible acanthite - argentite transformation. The phase transformation enthalpy ΔH_{trans} was found to be equal to ~3.7-3.9 $kJ\cdot mol^{-1}$. This is very close to the value $\Delta H_{\text{trans}} = 4.0\pm0.5$ $kJ\cdot mol^{-1}$ determined in works.[26,28,52] Observed small mass loss of the nanocrystalline powder and weak diffused endothermic effect at a temperature above 423 K (Fig. 5*b*) is due to partial evaporation of adsorbed water and partial oxidation of nanopowder by adsorbed water.

Heating of coarse-crystalline silver sulfide up to 453 K led to acanthite - argentite transformation.

The effect of temperature on the evolution of XRD patterns and on the unit cell parameters of cubic β-Ag_2S argentite is demonstrated in Figs. 6-8.

The X-ray diffraction patterns recorded during heating from 453 K and above contain a set of diffraction reflections of bcc (space group $Im\bar{3}m$) argentite β-Ag_2S (Fig. 6). The survey during temperature lowering made it possible to register a supercooled argentite phase at 443 K. The XRD patterns recorded at 443, 453, 463, and 473 K contain a trace of weak reflection $(100)_{mon}$ of monoclinic acanthite to the left of the (110) reflection. The rise of temperature leads to displacement of the cubic argentite reflections into the region of smaller 2θ angles (Fig. 6, inset), i. e. to gradual increase in the lattice constant a_{arg} of argentite.

The structure of the high-temperature phase of silver sulfide was determined using the XRD patterns recorded at 463 and 503 K. The structure of the high-temperature phase was refined with the use of model[20] having two modifications (completely statistical distribution of 4 Ag atoms in 42 positions 6(*b*), 12(*d*), and 24(*h*) and distribution with probabilities of occupation of 6(*b*), 12(*d*), and 24(*h*) positions by Ag atoms equal to 2/9, 1/9, and 1/18), as well as model.[22] The analysis of the experimental data showed that models[20,22,23] are not realistic. Improved data were obtained by additional consideration of disorder in the form of displacement of Ag atoms from the 12(*d*) positions into the 48(*j*) sites and by refining of the degree of occupation of the 6(*b*) and 48(*j*) positions (Fig. S2, ESI†). Thus, at temperatures above 433 K silver sulfide contains one phase with bcc (space group $Im\bar{3}m$) structure of β-Ag_2S argentite type, in which silver atoms are statistically distributed in 6(*b*) and 48(*j*) positions with occupation degrees 0.0978(7) and 0.0711(0) (Table S3, ESI†). The bcc structure of argentite β-Ag_2S is described in detail in work[27] and Crystallographic information file (CCDC reference number 1062400) attached thereto.

The dependence of the lattice constant a_{arg} of argentite β-Ag_2S on the temperature T is not linear (Fig. 7) and in the temperature interval from 443 to 623 K is described by polynomial

$$a_{arg}(T) = a_0 + a_1T + a_2T^2 , \quad (10)$$

with a_0 = 0.46747 nm, $a_1 = 5.6086\times10^{-5}$ nm·K^{-1}, and $a_2 = -3.3873\times10^{-8}$ nm·K^{-2}.

According to our experimental results obtained and data,[16,26-29,52] argentite β-Ag_2S exists at a temperature above ~443-445 K. The experimental linear thermal expansion coefficient α is determined as the average expansion coefficient in the temperature interval between the initial temperature 443 K and measured temperature T, i. e.

$$\alpha(T) = \frac{1}{a_{443K}}\frac{\Delta a}{\Delta T} = \frac{a(T) - a_{443K}}{a_{443K}(T - 443)} , \quad (11)$$

where $a(T)$ and $a_{443\,K}$ are the crystal lattice constants of argentite β-Ag_2S measured at temperature T and at the initial temperature 443 K, respectively.

Figure 8 shows the found temperature dependence of the thermal expansion coefficient $\alpha_{arg}(T)$. As the temperature rises from 443 to 623 K, the coefficient α_{arg} decreases from ~54×10^{-6} to

~43×10^{-6} K^{-1}. The dependence of the thermal expansion coefficient α_{arg} on the annealing temperature T in the range 443-623 K can be represented through the polynomial coefficients (10) as

$$\alpha_{arg}(T) = [a_1 + a_2(T + T_0)] / a_{443K} = 84.5\times10^{-6} - 6.9\times10^{-8}T \pm 3\times10^{-6} \ [K^{-1}]. \quad (12)$$

According to,[31] the thermal expansion coefficient α_{arg} of bulk argentite at 523 K is 45.8×10^{-6} K^{-1}. Also the thermal expansion coefficient α_{arg} can be estimated from scarce data on the temperature dependence of the argentite lattice constant. The lattice constant a_{arg} of argentite at 462 and 773 K is 0.4870 and 0.4926 nm.[26] From this it follows that the average thermal expansion coefficient of argentite is ~37×10^{-6} K^{-1}. According to the neutron diffraction data,[22] the lattice constant a_{arg} of argentite at 459, 473, 533, and 598 K is 0.4860, 0.4862, 0.4873, and 0.4889 nm, hence $\alpha_{arg} \approx 43\times10^{-6}$ K^{-1}. These data on α_{arg} coincide within the limits of measurement error with the values of α_{arg} found by us at temperatures from 443 to 623 K.

Although the linear thermal expansion coefficient α_{arg} of argentite with an increase in temperature from 443 to 623 K decreases from ~54×10^{-6} to ~43×10^{-6} K^{-1}, the lattice constant a of argentite increases from 0.4856 to 0.4894 nm (*see* Fig. 7). Apparently, the decrease in thermal expansion coefficient is caused by the peculiarities of crystal structure of argentite. At temperatures above 433 K silver sulfide contains one β-Ag_2S argentite phase with bcc (space group $Im\bar{3}m$) structure, in which silver atoms are statistically distributed in 6(*b*) and 48(*j*) positions with occupation degrees 0.0978 and 0.0711 (*see* Table S3, ESI†). The structure with such small occupancies can be stable only if the mobility of Ag atoms (ions) is very high. The amount of Ag^+ ions in argentite β-Ag_2S is much smaller than the number of sites of cation sublattice, therefore significant positional disorder in an arrangement of ions Ag^+ and gigantic (more than 92 %) concentration of vacant sites facilitate jumping of cations and provide superionic conductivity of β-Ag_2S phase. In the general case, metal sublattice of argentite β-Ag_2S can be thought of as anisotropic strongly interacting Coulomb liquid consisting of Ag^+ cations diffuses under the effective potential of the bcc anion sublattice. Owing to the absence of rigid metal sublattice and migration of silver cations, the thermal expansion coefficient of argentite lowers slightly with the temperature growth in the interval 443-623 K.

To compare the thermal expansion of different Ag_2S phases, we use the unit cell volumes of these phases relative to the number of formula units z of Ag_2S in the cell, i. e. reduced volumes $V_{rc} = V_{un.cell}/z$ (z = 4 for monoclinic acanthite α-Ag_2S and high-temperature face-centered cubic γ-Ag_2S phase, and z = 2 for bcc argentite β-Ag_2S). Increasing temperature in the region 443-623 K is accompanied by an increasing of reduced volume of argentite, which approaches to the reduced volume of γ-Ag_2S phase: At temperature of ~440 and 620 K the reduced volume of β-Ag_2S is equal

0.0573 and 0.0587 nm^3 (*see* Fig. 9 in manuscript), and according to,[53] the reduced volume of γ-Ag_2S at temperature of ~870 K is equal ~0.0616 nm^3.

As the temperature increases from 300 to 623 K, the reduced volume of silver sulfide grows, and at ~440 K the reduced volume exhibits a stepwise rise attributed to the acanthite - argentite transformation (Fig. 9*a*). The discontinuous change in the volume is in agreement with the conclusions of works[16,26-29] about the first order of the acanthite - argentite transformation.

For direct comparison of the thermal expansion of acanthite α-Ag_2S and argentite β-Ag_2S it is possible to use the isotropic linear thermal expansion coefficient of acanthite $\alpha_{\text{ac isotr}}$ and the linear thermal expansion coefficient of argentite α_{arg} (Fig. 9*b*). As is seen, the measured coefficient α_{arg} of argentite β-Ag_2S is much larger than $\alpha_{\text{ac isotr}}$ and $\alpha_{\text{ac-nano isotr}}$ of coarse-crystalline and nanocrystalline acanthite α-Ag_2S. The jump of the thermal expansion coefficient α of coarse-crystalline silver sulfide from ~24.0×10^{-6} to ~55×10^{-6} K^{-1} is observed at a temperature of ~433-443 K (Fig. 9), which is the acanthite - argentite phase transition temperature T_{trans}. The presence of the jump of the coefficient α at T_{trans} is a consequence of the stepwise change of the reduced volume and confirms the conclusions of calorimetric and thermochemical studies,[16,26,27,52] as well as our conclusions made on the basis of DTA measurements showing that the acanthite - argentite transformation takes place by the first-order phase transition mechanism.

V. Conclusion

As a result of our studies it was established that the isotropic linear thermal expansion coefficient $\alpha_{\text{ac-nano isotr}}$ of nanocrystalline acantitie α-Ag_2S at ~300-400 K is equal to $(22\text{-}24)\times10^{-6}$ K^{-1} and is approximately 1.2-1.3 times larger than $\alpha_{\text{ac isotr}}$ of coarse-crystalline acanthite. The observed difference in the coefficients α of acanthite is due to the small size of Ag_2S particles in the nanocrystalline phase, which leads to an increase in the anharmonicity of atomic vibrations. The linear thermal expansion coefficient α_{arg} of argentite in the temperature range 443-623 K changes from ~54×10^{-6} to ~43×10^{-6} K^{-1}. The stepwise increase in the thermal expansion coefficient of coarse-crystalline silver sulfide in more than 2 times during acanthite - argentite transformation is indicative of the first-order phase transition. According to the DTA data, the acanthite - argentite transformation takes place at ~449-450 K and the phase transformation enthalpy is equal to ~3.7-3.9 $kJ\cdot mol^{-1}$.

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Figure captions for the paper
"High-Temperature X-Ray Diffraction and Thermal Expansion of Nanocrystalline and Coarse-Crystalline Acanthite α-Ag_2S and Argentite β-Ag_2S" by S.I. Sadovnikov, A.I. Gusev, A.V. Chukin and A.A. Rempel

Fig. 1. Synthesized coarse-crystalline and nanocrystalline Ag_2S powders: (*a*) SEM image of coarse-crystalline Ag_2S powder prepared by hydrothermal synthesis from aqueous solutions of $AgNO_3$ and thiourea $(NH_2)_2CS$; powder contains a rounded irregular shape particles with a size about 1000 nm. (*b*) TEM image of nanocrystalline Ag_2S powder deposited from aqueous solutions of $AgNO_3$, Na_2S and $Na_3C_6H_5O_7$; nanopowder contains small particles with a size of ~45-50 nm.

Fig. 2. XRD patterns of coarse-crystalline silver sulfide with the average particle size of ~500-800 nm at heating from 300 to 453 K.

Fig. 3. Evolution of XRD patterns of nanocrystalline acanthite α-Ag_2S with the average particle size of ~45-50 nm at heating from 300 to 398 K. Nanopowder was oxidized at a temperature of 433 K, and its XRD pattern contains diffraction reflections of oxide and oxide-sulfate phases instead of silver sulfide reflections.

Fig. 4. The effect of temperature *T* on the unit cell parameters *a*, *b*, *c*, β, and volume *V*, and on the volumetric thermal expansion coefficient β_V of coarse- and nanocrystalline acanthite. The approximation of the experimental data by the solid line and the closed symbols (●), (▲), (▼), (×), (■), and (♦) correspond to coarse-crystalline acanthite and the approximation by the dotted line and the open symbols (○), (Δ), (∇), (+), (□), and (◊) correspond to nanocrystalline acanthite.

Fig. 5. The DTA and DTG curves measured during heating and cooling of (*a*) coarse-crystalline Ag_2S and (*b*) nanocrystalline $Ag_{1.93}S$ silver sulfide powders.

Fig. 6. Evolution of XRD patterns of coarse-crystalline argentite β-Ag_2S in the temperature range 446-623 K. The inset shows a systematic displacement of the (200) diffraction reflection of bcc argentite with increase of measuring temperature.

Fig. 7. Dependence of the lattice constant a_{arg} of argentite β-Ag_2S on the temperature *T*: (1) data of present work; (2), (3), and (4) data,[22,24,27] respectively. The approximations of measured lattice constant a_{arg} by the function (10) in the temperature range 440-660 K is shown by solid lines.

Fig. 8. Temperature dependence of linear thermal expansion coefficient α_{arg} of argentite β-Ag_2S and its approximation by the function (12).

Fig. 9. The temperature dependences of reduced volume $V_{un.cell}/z$ (*a*) and isotropic linear thermal expansion coefficient α (*b*) of silver sulfide in the range 300-623 K. At ~440 K, there take place jumps of the reduced volume and the thermal expansion coefficient α attributed to the first-order acanthite - argentite phase transformation. Isotropic linear thermal expansion coefficient $\alpha_{ac\text{-}nano\ isotr}$ of nanocrystalline acanthite α-Ag_2S is larger than $\alpha_{ac\ isotr}$ of coarse-crystalline acanthite.