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Temperature investigations of the ferroelectric crystals $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ by means of ^{119}Sn Mössbauer spectroscopy

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Abstract. Mössbauer spectra of $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ proper uniaxial ferroelectrics were investigated over a wide temperature region including phase transition points with the aim of studying the dynamics of ferroactive tin ions used as a Mössbauer isotope (^{119}Sn). The characteristics of the gamma-resonance lines (isomer shift, effect probability, etc) and the parameters calculated from the measured spectra in the Debye approximation (mean square displacement, Debye–Waller factor, Debye temperature, etc) were analysed in comparison with the available structural and thermodynamical data. The data obtained support the assumption of a two-well local potential of the tin atoms in addition to the displacement of their time-averaged position below the phase transition points. It was concluded that displacement and ordering occur in the same Sn sublattice, and that the variation in long-range forces leads to lattice instability.

1. Introduction

Investigations by means of Mössbauer spectroscopy (nuclear gamma resonance) provide information about the local dynamics and the character of the electron-density distribution of a particular sort of atom in the solid matrix. The data are of great importance especially in the cases of phase transitions including a ferroelectric one, but the scope for realizing such studies is limited. In order to apply the Mössbauer effect most efficiently, the following are necessary:

- (a) the Mössbauer isotope (^{119}Sn , ^{57}Fe , ^{151}Eu) must be a natural constituent of the material (not introduced artificially by doping or implantation);
- (b) the Mössbauer atom must itself be ferroactive.

Therefore the ferroelectrics from the thio(seleno)-hypodiphosphates group $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ are of great interest as regards such studies.

These compounds are proper uniaxial ferroelectrics, exhibiting the change of symmetry $P2_1/c \rightarrow P_c$ at the transition from a paraelectric phase to a ferroelectric one [1]. The second-order phase transition occurs at $T_0 = 337$ K in $\text{Sn}_2\text{P}_2\text{S}_6$. In the $\text{Sn}_2\text{P}_2\text{Se}_6$ crystal an intermediate incommensurate phase exists and two phase transitions are observed: the second-order transition from the paraelectric phase to the ferroelectric one at $T_i = 220$ K and the lock-in phase transition of first order from the incommensurate phase to the ferroelectric one at $T_c = 193$ K. In the solid-solution system $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$, at $x = 0.28$ there exists a

Lifshitz point that separates paraelectric, ferroelectric, and incommensurate phases [2, 3]. For the mixed crystals $(\text{Pb}_y\text{Sn}_{1-y})_2\text{P}_2\text{S}_6$, the temperature of the phase transition decreases with increase in the Pb content without there being any change in the transition character [4].

The crystals mentioned above are representatives of a wider compound system $\text{M}_2\text{P}_2\text{S}_6$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cd}, \text{Zn}, \text{Hg}, \dots$), exhibiting a great variety of structural types and phase transitions. The possibility of changing the phase transition type by chemical substitution and the sensitivity to external influences make these compounds useful models for studying the interrelation between the character of the phase transitions and structural peculiarities, the lattice dynamics, electron–phonon interaction, etc.

In a previous paper devoted to the investigation of the compounds $\text{Sn}(\text{Pb})_2\text{P}_2\text{S}$ and $\text{Sn}(\text{Pb})_2\text{P}_2\text{Se}_6$ by means of ^{119}Sn Mössbauer spectroscopy [5, 6], the main focus of attention was the changes in spectral parameters, and changing the composition of the solid solutions by substituting lead for tin or selenium for sulphur. Recently, advanced studies of compounds of a specified type by nuclear gamma-resonance spectroscopy have been presented, particularly for the solid solutions $(\text{Eu}_y\text{Sn}_{1-y})_2\text{P}_2\text{S}_6$ and $(\text{Sr}_y\text{Sn}_{1-y})_2\text{P}_2\text{S}_6$ using both ^{119}Sn and ^{151}Eu nuclei [7]. Our previous studies [5, 6] have enabled us to define the character of the crystal-field changes in the vicinity of Sn ferroactive atoms upon isovalent substitution at two temperatures (room temperature and 80 K). Comparison of our results with data from thermodynamical studies has enabled us to explain the form of the temperature–composition phase diagram of $\text{Sn}(\text{Pb})_2\text{P}_2\text{S}_6$ and $\text{Sn}(\text{Pb})_2\text{P}_2\text{Se}_6$ mixed crystals. However, as the concentration relations of the Mössbauer spectrum parameters are determined by the combined influence of several factors, the analysis of the critical dynamics of the ferroactive atoms is complicated when the phase transitions are induced by the changes in the concentrations (at morphotropic phase transitions).

In different experiments, features characteristic of transitions of displacive type and of order–disorder ones were observed. This led to controversial conclusions about the character of the phase transitions. According to the data obtained from Raman scattering [8] and dielectric spectroscopy [9], the soft optical mode is observed clearly in the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals, confirming a displacive-type phase transition. A higher degree of relaxational character of the critical dynamics manifests itself in $\text{Sn}_2\text{P}_2\text{Se}_6$ [10]. Meanwhile, the soft-mode peak in the Raman spectra of $\text{Sn}_2\text{P}_2\text{S}_6$ exhibited an asymmetrical non-Lorentzian shape, and was approximated well using the model of a mixed oscillator and relaxator [11]. The mode softening was observed no lower than $12\text{--}15\text{ cm}^{-1}$ [8–12], whereas the ‘pure’ displacive soft-mode behaviour presupposes a zero value at a phase transition point. The measured values of the entropy of the phase transitions in $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ are quite high ($8.6\text{ J K}^{-1}\text{ mol}^{-1}$ and $10.0\text{ J K}^{-1}\text{ mol}^{-1}$, respectively [13]), which is more typical for order–disorder transitions. At the same time the Curie–Weiss constant values are sufficiently high ($C \sim 10^5\text{ K}^{-1}$ for $\text{Sn}_2\text{P}_2\text{S}_6$ [14]) to be typical of displacive transitions.

The first structural data to be obtained by x-ray diffraction [15–17] show the shifting of ferroactive tin ions from centrosymmetrical positions below the phase transition point. The most recently obtained refined x-ray data [18] demonstrate that the structure of the paraelectric phases of $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ can be described more adequately using a double-well position of Sn, and the centre of this twinned (doubled) position is shifted in the ferroelectric phase relative to the sites in the paraelectric phase. It seems that the phase transitions in $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ crystals cannot be attributed entirely to one of the two models, which is fairly typical for ferroelectric crystals. So, more detailed investigations of the dynamics of the phase transitions in the ferroelectrics studied, including the re-examination of previously obtained data, are important, and the $\text{Sn}_2\text{P}_2\text{S}_6$ crystal family can itself be considered as a model system for investigations on the variety of the critical static and dynamic behaviours. The aim of the

present work is to reveal the dynamics of ferroactive atoms by investigating the temperature dependences of the ^{119}Sn Mössbauer line parameters of $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ crystals in the vicinities of the phase transitions.

2. Experimental procedure

The $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ single crystals were grown by the vapour transport method using iodine as a transport agent. The absorbers were prepared from single crystals by means of crumbling. The effective sample thickness was 0.5 mg cm^{-2} in terms of the ^{119}Sn isotope. The CaSnO_3 compound at ambient temperature served as a gamma quantum source and the measured isomer shifts are quoted relative to it. Between the source and the absorber a $60 \mu\text{m}$ thick palladium foil filter was placed. To calibrate the energy scale, a $^{57}\text{CoPd}$ source and iron foil absorber were used at room temperature. The magnitude of the effect α , the linewidth Γ , and the shift of the line centre δ were calculated by the least-squares method. The area A below the Mössbauer spectrum line was calculated using the formula

$$A = \frac{\pi \alpha \Gamma}{2}. \quad (1)$$

In the case of a single Lorentz line the area under the absorption line is expressed as [19]

$$A = \chi \pi f t_a \exp\left(-\frac{t_a}{2}\right) \left[I_0\left(\frac{t_a}{2}\right) + I_1\left(\frac{t_a}{2}\right) \right] \quad (2)$$

where χ is the relative contribution of the resonance gamma quanta to the total counting rate, f is the probability of recoilless emission of the gamma quanta, $t_a = \sigma_0 f' n_a$ is the effective thickness of the absorber, σ_0 is the maximum cross-section of resonance absorption, f' is the recoilless emission probability (to be determined), n_a is the number of atoms of the isotope under study per area unit of the absorber, and I_0 and I_1 are the Bessel functions of zeroth and first order, respectively.

The constant $C = \chi \pi f$ was determined by using an absorber with a known probability f' . A β -Sn foil of thickness 1.46 mg cm^{-2} of ^{119}Sn was used as the absorber. The probability for β -Sn foil at room temperature $f' = 0.039$ [20]. Using the probability values, the Debye–Waller factor $2W$ has been calculated ($f' = \exp(-2W)$); this depends on the thermal vibrations of the atoms. In the isotropic case and within the harmonic approximation, the mean square of the thermal displacements of the atoms $\langle u^2 \rangle$ can be calculated:

$$f = \exp(-2W) = \exp\left(-\frac{1}{3} k^2 \langle u^2 \rangle\right) \quad (3)$$

where k is the wave vector of γ -quanta.

In the Debye approximation the index $2W$ is given by the Debye temperature:

$$2W = \frac{6R}{k_B \Theta} \left[\frac{1}{4} + \int_0^{\Theta/T} \frac{x \, dx}{e^x - 1} \right] \quad (4)$$

where R is the recoil energy, k_B is the Boltzmann constant, and T is the temperature of the absorber. Although the Debye model is not strictly applicable for our system, it is useful for comparing the samples.

3. Results and discussion

The Mössbauer spectra of the compound $\text{Sn}_2\text{P}_2\text{Se}_6$ measured at 143 K and at 223 K are shown in figure 1. These lines prove that all tin ions are in the Sn^{2+} state. The temperature variation

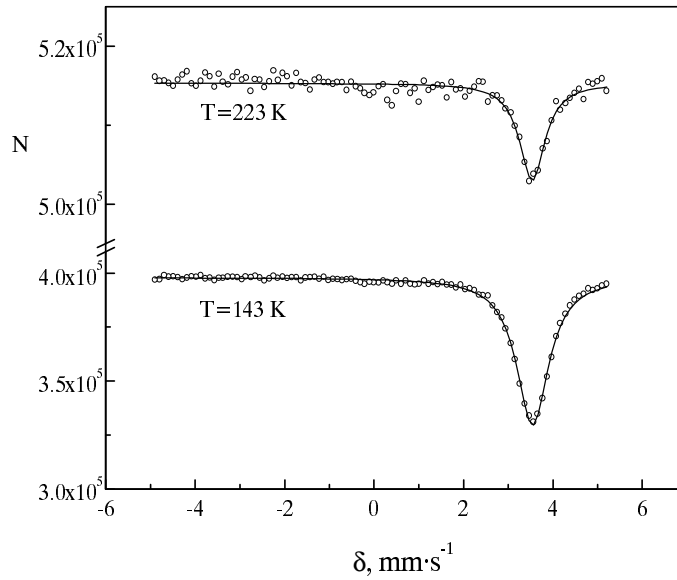


Figure 1. The Mössbauer spectra of ^{119}Sn in $\text{Sn}_2\text{P}_2\text{Se}_6$ at 143 K and 223 K. The velocity scale is relative to that of CaSnO_3 at room temperature.

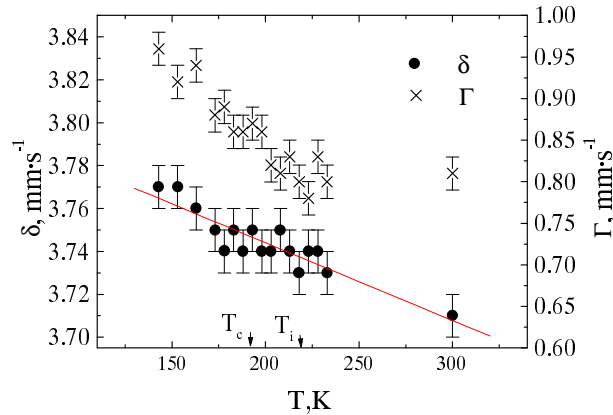


Figure 2. The temperature variations of the Mössbauer linewidth Γ and line shift δ for the compound $\text{Sn}_2\text{P}_2\text{Se}_6$. The linear fit for δ gives $\partial\delta^{\text{SOD}}/\partial T = -(3.6 \pm 0.4) \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$. T_c corresponds to the first-order phase transition and T_i to the second-order one.

of the Mössbauer linewidth Γ and the line shift δ for the $\text{Sn}_2\text{P}_2\text{Se}_6$ are shown in figure 2. The temperature changes in the gamma-resonance spectral parameters may be caused by the electron-density redistribution and changes in the character of the motion of the nuclei. Typically, the first factor influences the isomer shift value mainly. Another factor, in this case influencing the location of the Mössbauer line peak, is the second-order Doppler shift, which is a consequence of atom vibration, and is determined by the mean square velocity of the thermal motion of the atoms. So, the measured line shift δ is the sum of the second-order Doppler shift δ^{SOD} and the isomer shift δ^{I} :

$$\delta = \delta^{\text{SOD}} + \delta^{\text{I}}. \quad (5)$$

As in previous studies [5–7], the values of the line shift δ demonstrate the usual temperature dependence over the entire range of investigation and change from $3.77 \pm 0.01 \text{ mm s}^{-1}$ (140 K) to $3.73 \pm 0.01 \text{ mm s}^{-1}$ (230 K) for $\text{Sn}_2\text{P}_2\text{Se}_6$ (see figure 1) and from $3.83 \pm 0.01 \text{ mm s}^{-1}$ to $3.79 \pm 0.01 \text{ mm s}^{-1}$ for $\text{Sn}_2\text{P}_2\text{S}_6$. It is known that at high temperatures ($T > \theta_D$) δ^{SOD} is independent of Θ_D , and for ^{119}Sn it has a temperature derivative [21]

$$\partial\delta^{\text{SOD}}/\partial T = -3.5 \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}.$$

This value, within the experimental error, is the same as our experimental results: $-(3.6 \pm 0.4) \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ (see figure 2). This means that the temperature changes in the line shift δ result only from δ^{SOD} , and are not caused by changes in the electron density. The ionicity of the bond, estimated in the same way as in [22], makes up 0.7 for $\text{Sn}_2\text{P}_2\text{S}_6$ and 0.6 for $\text{Sn}_2\text{P}_2\text{Se}_6$, and so is much higher than those observed for other chalcogenide compounds of tin. Moreover, in [7] the ionicity was found to increase to 0.93 and 0.92, respectively, when strontium and europium replaced tin atoms. In particular, this attests to the model of rigid ions used in [23] being applicable for the lattice dynamics calculations. Even quantitative agreement may be found: in the calculations [23] the effective charge of tin, which was evaluated in such a way as to give the best agreement with experimentally observed phonon frequencies, was considered to be equal to +1.2 (in units of the elementary charge) rather than +2 as in the case of 100% ionicity of ‘tin–chalcogen’ bonds.

Usually the line area A , which characterizes the strength of the chemical bonding by which atoms are bound in the lattice, is the parameter of the Mössbauer spectrum that is the most sensitive to the phase transition. For the crystals in which the phase transition of displacive type occurs, a sudden decrease in the A -value is expected to be observed in the vicinity of the phase transition point. The lowering of the soft-mode frequency and decreasing of the probability of the effect cause such an anomaly. In contrast, at the order–disorder transition the anomaly can be weak or even absent in the case in which the period of the frustration of the ordered nuclei is large in comparison with the Mössbauer level half-life.

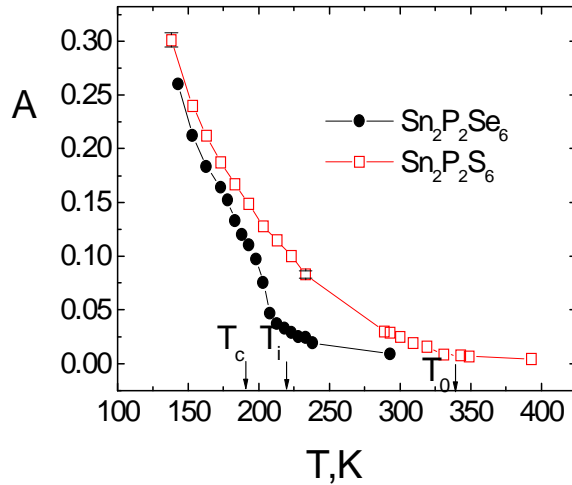


Figure 3. Temperature dependences of the $^{119}\text{Sn}^{2+}$ Mössbauer line area A .

Similar temperature changes in the Mössbauer line area A are observed for the crystals $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ (figure 3). It is seen from this figure that at the second-order PT point T_0 for $\text{Sn}_2\text{P}_2\text{S}_6$, as well as at the T_i - and T_c -points for $\text{Sn}_2\text{P}_2\text{Se}_6$, the dependence $A(T)$ does not manifest any significant anomalies, but only a slow break.

The temperature dependence of the inter-planar distances (i.e., the dimensions of the unit cell) shows a large break for $\text{Sn}_2\text{P}_2\text{Se}_6$, according to the data from x-ray diffraction studies [16]. The absence of a substantial anomaly in the relation $A(T)$ at this temperature confirms the decisive role of the short-range interaction of Sn^{2+} ions with just the nearest chalcogen atoms. This correlates with structural analysis [18], where the $\text{P-S(Se)-Sn-S(Se)-P}\cdots$ chains formed by the shortest Sn-S(Se) bonds (mainly along [001] directions) were represented as a structural skeleton for both phases, and the tin ions shifted in the perpendicular direction below T_0 .

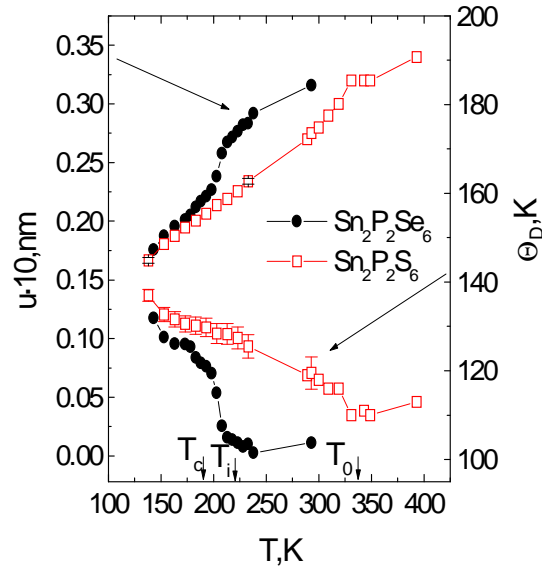


Figure 4. Temperature dependences of the mean square displacement u and the effective Debye temperatures Θ_D for $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ crystals, obtained by means of the ^{119}Sn Mössbauer spectroscopy.

The observed temperature dependence of the effective Debye temperature Θ_D may be related to the transformation of the phonon spectrum in the vicinity of the phase transition (figure 4). The lowering of this temperature in the vicinity of the phase transition may be related to the decrease in the elastic modulus. It may also be pointed out that our estimates of Θ_D correlate with the calculations based on the data for the heat capacity of the crystals investigated in [24], where the following magnitudes were obtained: 80 K for $\text{Sn}_2\text{P}_2\text{Se}_6$ and 100 K for $\text{Sn}_2\text{P}_2\text{S}_6$. The difference between these magnitudes coincides with the results of our measurements, and the extrapolation of the temperature dependences $\Theta_D(T)$ toward the high-temperature region (figure 4) provides adequately close absolute values of the effective Debye temperatures, in particular for $\text{Sn}_2\text{P}_2\text{S}_6$. The temperature of the phase transition in $\text{Sn}_2\text{P}_2\text{Se}_6$ is close to double the Debye temperature, while for $\text{Sn}_2\text{P}_2\text{S}_6$, $T_0 \geq 3\Theta_D$.

Discussion of the character of the motion of the tin ions and their temperature behaviour is most transparent in terms of the Debye–Waller factor $2W$ (figure 5) and mean square thermal displacements u (figure 4). The estimated values of u in the temperature range investigated change for both crystals approximately from 0.17 Å to 0.34 Å. These values are sufficiently high in comparison with the shift of Sn^{2+} ions from their centrosymmetrical positions as a result of the transition to the ferroelectric phase (0.26–0.32 Å) [15–18]. They exceed the estimates of mean square displacements obtained in the first x-ray diffraction experiments [15–17] and

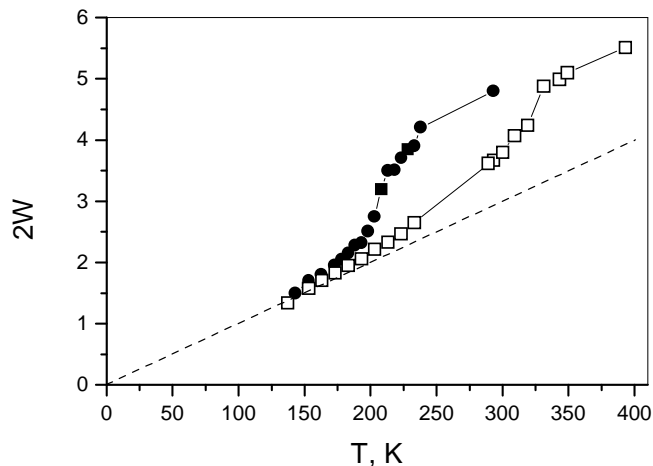


Figure 5. Temperature dependences of the Debye–Waller factor $2W$. The definitions are the same as for figure 4.

calculated from the thermodynamic data [24]. Let us note that the u -value for a paraelectric phase coincides with the distance between Sn positions (0.34 \AA) calculated in the two-site model [18].

According to the results of our analysis, the u -values are higher for $\text{Sn}_2\text{P}_2\text{Se}_6$ (figure 4), and are in good agreement with the refined x-ray data [18]. In previous studies it was reported [25] that these values were similar in magnitude and that the mean square displacement was higher for $\text{Sn}_2\text{P}_2\text{S}_6$ ($0.14\text{--}0.18 \text{ \AA}$) than that for $\text{Sn}_2\text{P}_2\text{Se}_6$ ($0.12\text{--}0.15 \text{ \AA}$). At the same time, the volume of the coordination polyhedron (at room temperature) for atoms of tin formed by the chalcogen atoms varies from 190 \AA^3 to 250 \AA^3 when sulphur is replaced by selenium [26]. Thus, our results are more readily explainable from the crystallochemical point of view. In fact, the mean square displacement obtained from the gamma-resonance spectra corresponds to motion of nuclei, whereas similar x-ray diffraction data are produced by the electron-density thermal fluctuation. So, we can conclude that the u -values obtained in our experiments are determined by inter-well jumps and that the frequency of this motion in a paraelectric phase and near the transition point exceeds the Mössbauer level half-life.

It may be pointed out that, in the ferroelectric phase, tin has two pairs of inequivalent positions—seven- and eight-coordinated ones—while, in the centrosymmetric paraelectric phase, all four positions are equivalent and the coordinate number becomes equal to eight [15, 16]. However, such a change is not manifested clearly in the temperature dependences of the Mössbauer spectra that are obtained. This difference in Sn^{2+} coordination can give an additional contribution to the parameters A (and Γ) below T_0 , but this influence seems to be fairly small.

The Debye–Waller factor, proportional to u^2/ω^2 ($\sim k_B T$), where ω is the phonon frequency, reflects the energy of the thermal vibration. In the case of usual temperature behaviour, $2W \sim T$, and deviation from this linearity can be interpreted as an increase of anharmonicity. As is seen in figure 5, the $2W(T)$ curves deviate from linearity for both crystals studied in a ferroelectric phase over a large temperature interval far from the phase transition points. This dependence can be analysed more carefully in the case of $\text{Sn}_2\text{P}_2\text{S}_6$, for which a second-order phase transition takes place. The temperature variation of the anomalous part of $2W$ calculated as a difference between measured values and the linear extrapolation

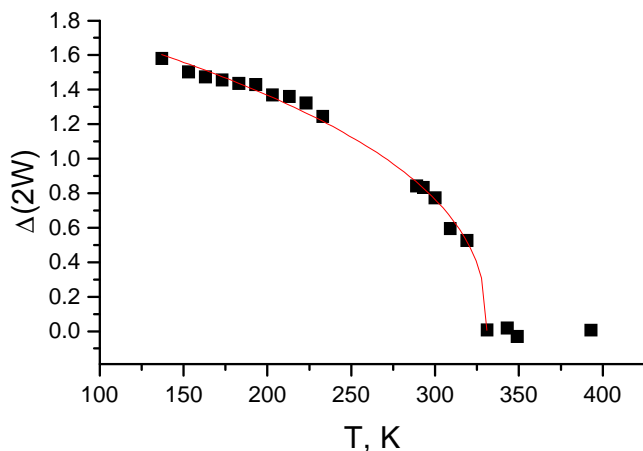


Figure 6. The anomalous part of the $2W(T)$ dependence of $\text{Sn}_2\text{P}_2\text{S}_6$ determined as a difference between measured values and ones linearly extrapolated from the paraelectric phase. The solid curve corresponds to a fitting with the power function $2W \approx (T_0 - T)^b$, with $b = 0.4$ and $T_0 = 331$ K.

from the paraelectric phase is described well by a power function:

$$\Delta(2W) \sim (T_0 - T)^{0.4}$$

(figure 6). The similar power value was calculated for the anomalous part of the entropy ΔS as a function of temperature [13], as well as for the birefringence [3, 27]. As is known from thermodynamical analysis [28], ΔS is always proportional to the square of the local value of the order parameter. The temperature dependences for ΔS reported in [13] and $2W$ for $\text{Sn}_2\text{P}_2\text{Se}_6$ (figure 5) also are very similar in shape. So, the Debye–Waller factor measured using the gamma-resonance technique is proportional to the square of the order parameter over a wide temperature region. We believe that the lowering of the phonon soft-mode frequency observed in Raman spectra does not play the leading role in the $2W(T)$ variation, and reflects only the dynamics of inter-well motion, and the spectrum of the order parameter fluctuation includes a considerable relaxational part. As was shown previously, the soft mode can make a contribution of several per cent to the static value of the dielectric susceptibility at T_0 [9].

From figure 5 it is seen that the Debye–Waller factors extrapolated from the paraelectric phase to zero temperature give non-zero values (~ 1.5) for the both crystals. This can be considered as an indirect confirmation of the disordered two-site positions of tin in the paraelectric phase.

Taking into account the above-mentioned absence of an anomaly in the temperature dependence of the isomer shift, it may be assumed that the temperature transformation of Mössbauer spectra is related to the change in the character of the atom motion—from disordered to partially ordered at non-centrosymmetrical positions and down to the single-well potential at $T < 100$ K, without significant electron-density redistribution in the Sn–S and Sn–Se bonds, i.e. at the expense of long-range forces.

So, the correctness of the modelling of the lattice instability in the paraelectric phase in terms of the change in the effective charges (i.e., long-range forces) is confirmed indirectly. This modelling takes into consideration the effective variation of the Coulomb interaction. It is evident as well that the quasi-harmonic approximation used in the rigid-ion model is too rough for the description of the lattice dynamics in crystals of the $\text{Sn}_2\text{P}_2\text{S}_6$ type near the points at which phase transitions occur.

It should be pointed out that the conclusions drawn have gone beyond the framework of the assumptions—the basis of the usual analysis procedure of Mössbauer spectral parameters. So both additional studies, including methods alternative to the local dynamics investigation, and progress as regards the method of analysis used for the anisotropic and anharmonic crystals are needed. Therefore subsequent studies will be of interest—in particular, the investigation of a specimen enriched with ^{119}Sn , as well as single-crystal oriented samples, with the aim of increasing the sensitivity and accuracy of the measurements.

4. Conclusions

The dynamics of the ferroactive tin atoms in the proper isostructural ferroelectrics $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ was investigated using Mössbauer spectroscopy near the phase transitions. The temperature dependence of the measured and calculated parameters agrees well with the assumption of a two-well local potential of Sn ions. It can be concluded that both displacement and ordering occur in the same Sn sublattice, and that the variation in the long-range forces leads to lattice instability.

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