INVESTIGATION OF THE KINETICS OF THE β-Sn → α-Sn TRANSFORMATION BY THE MÖSSBAUER EFFECT METHOD

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An investigation was made of the nucleation of the α modification in white tin and of the kinetics of the allotropic transformation β-Sn → α-Sn. This investigation was made using the Mössbauer effect method, which made it possible to determine the nature and dynamics of this phase transformation. It was established that crystallization centers appeared first on the surface of a sample. A value of 0.41×10^{-2} cm/h was obtained for the linear velocity of the boundary between the white and the gray tin. The temperature dependence of the probability of the Mössbauer effect was determined for the gray tin in the temperature range 80–300°K. A comparison of the widths Γ_{exp} of the spectra of the gray and the white tin yielded the quadrupole splitting ΔEQ for β-Sn, which was 0.18 ± 0.03 mm/sec.

INTRODUCTION

THE allotropic transformation β-Sn ⇄ α-Sn is a special transition in which not only the distribution of the atoms (crystal structure) but also the bonds between them are altered. This particular transformation has been investigated before by various methods[1-4] but no Mössbauer study has yet been made of the β-Sn → α-Sn transformation, in spite of the fact that tin is a widely used Mössbauer nuclide. White tin, which has a tetragonal lattice (space group D_{4h}^{19}-I4/amd), transforms at +13.2°C into gray tin, which has a cubic diamond-type lattice (space group T_d^2-$F\bar{4}3m$). White tin has a tendency to strong supercooling and the question of spontaneous nucleation of the α modification has not yet been resolved. The maximum rate of rise in the number of nuclei of the α modification has been observed at −50°C,[1] whereas the highest velocity of the α-phase boundary has been found at −30°C.[4] The transformation is influenced by the presence of impurities (even those introduced by the technological processes), some of which (Bi) enable white tin to remain in the supercooled state for months whereas others (Zn) promote a rapid transformation.[4] The absence of published data on Mössbauer studies of the β-Sn → α-Sn transformation is evidently due to methodological difficulties and the long times required in experiments due to the low linear velocity of the α-phase boundary.

EXPERIMENTAL METHOD AND RESULTS

The investigation was carried out using a Mössbauer spectrometer with an electrodynamic vibrator operating in the time mode. A solid solution of Sn^{119} in palladium was used as the source. An NaI(Tl) scintillation counter, 1 mm thick, was used to detect the 23.8 keV γ-ray quanta. All the measurements were carried out in a cryostat, in which a sample was subjected to combined cooling.[5] The investigated samples, consisting of 99.999% pure tin and tin containing 0.05–0.5 at.% Ge, were disks of 20 mm diameter, cut from rolled foil, 0.03–0.1 mm thick. Some of the samples were subjected to diffusion annealing in order to check their homogeneity.

The Mössbauer spectra of each of the samples were recorded at room temperature and at −50°C (each of these spectra consisted of a single symmetrical line). Next, each sample was placed in a cryostat kept at −50°C until gray tin "hillocks" appeared on the surface (this indicated the beginning of the transformation). The samples had to be kept at this temperature for 2–5 weeks (this was in good agreement with the results reported in[4]). As soon as the number of "hillocks" reached ~10 per cm², the sample was cooled to liquid nitrogen temperature. A still brush was used to remove the gray surface deposit in liquid nitrogen and the sample was returned to the cryostat. During all these operations, the temperature of the sample did not rise above −50°C.

After this treatment, the Mössbauer spectra were recorded again at −50°C. During the first two days, the spectra were symmetrical. After 60 h at −50°C, the Mössbauer line became asymmetrical and its center of gravity shifted because of the appearance of gray tin on the surface of the sample. This was observed for all the samples, irrespective of the heat treatment to which they were subjected and of the Ge impurity concentration. Repeated cleaning of the surface, which removed the freshly formed layer of α-Sn on the surface of β-Sn, demonstrated that α-Sn formed first on the surface. When α-Sn was removed from the surface of the sample, the Mössbauer line reverted to its initial shape. Thus, no submicroscopic inclusions of the α-Sn were found in white tin. The nucleation of the crystallization centers of the α modification was equiprobable over the whole surface of the sample.

The temperature dependences of the areas under the resonance curves of white tin were determined before the β → α transformation. It was found that the ratio of the areas obtained at 80 and 296°K was 6.51. This

ratio was proportional to the ratio of the Mössbauer effect probabilities f′ at the same temperatures (if the absorber was thin) and it agreed with the results reported in[6,7]. This was used later in an analysis of the experimental data obtained in the study of the β-Sn → α-Sn transformation.

When white tin was transformed to the gray modification, the temperature dependences of the areas under the resonance absorption curves were determined for gray tin. The ratio of the areas under the resonance absorption curves of white and gray tin was found at a given temperature and used to determine the value of f′ for gray tin and to plot the temperature dependence of f′ in the range 80—300°K. The characteristic temperature, calculated in the Debye approximation, was 162°K. The Mössbauer effect probability for α-Sn was 0.16 ± 0.03 at 296°K and 0.53 ± 0.06 at 80°K. Figure 1 shows our values of f′ for gray tin and the values of f′ for white tin taken from[7,8].

Since the absorption line of α-Sn had a natural width and since the gray and white tin absorbers had the same thickness for the resonating nucleus (n = const) throughout our experiments, a comparison of the experimental values of the line widths of white and gray tin should give the value of the quadrupole splitting ΔE_Q in β-Sn. Bearing in mind the change in the effective absorber thickness during the transition from the β to the α modification (which resulted in a change in the line half-width by less than 30% at T = 80°K for samples 0.03 mm thick), we compared the experimentally obtained spectrum with the spectra calculated for different values of ΔE_Q and found that $\Delta E_Q = 0.18 \pm 0.03$ mm/sec at T = 80°K. This value was in good agreement with the γ-γ correlation data.[8]

The kinetics of the β-Sn → α-Sn allotropic transformation was observed by contaminating a sample of white tin, kept at − 30°C, with powdered gray tin spread over an area of 1 mm² in the center of the sample. This contaminated sample was placed in a cryostat, in which the temperature was maintained at − 30 ± 0.02°C, and the Mössbauer spectrum was recorded. The initial spectrum consisted of a single symmetrical line (Fig. 2a), which represented pure white tin. Figures 2b-2g represent the spectra recorded for a sample 0.03 mm thick after 70, 124, 165, 205, 230, and 300 h at − 30°C. The spectrum recorded after 300 h represented pure gray tin and consisted of a single Lorentzian line, which was not affected by further exposure for 200 h at −30°C. The intermediate spectra were broadened lines with non-Lorentzian energy distributions. The centers of gravity of these

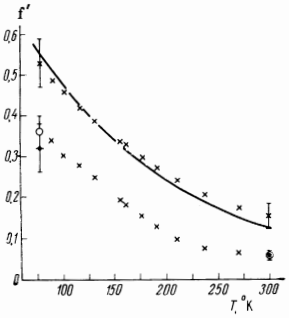

FIG. 1. Temperature dependence of the Mössbauer effect probability f′ for white and gray tin: ○) results reported in [7]; ●) results reported in [8]; ×) results of the present investigation (gray tin on top, white tin below). The continuous curve is the theoretical temperature dependence of f′ for gray tin with $\Theta_D = 162$°K.

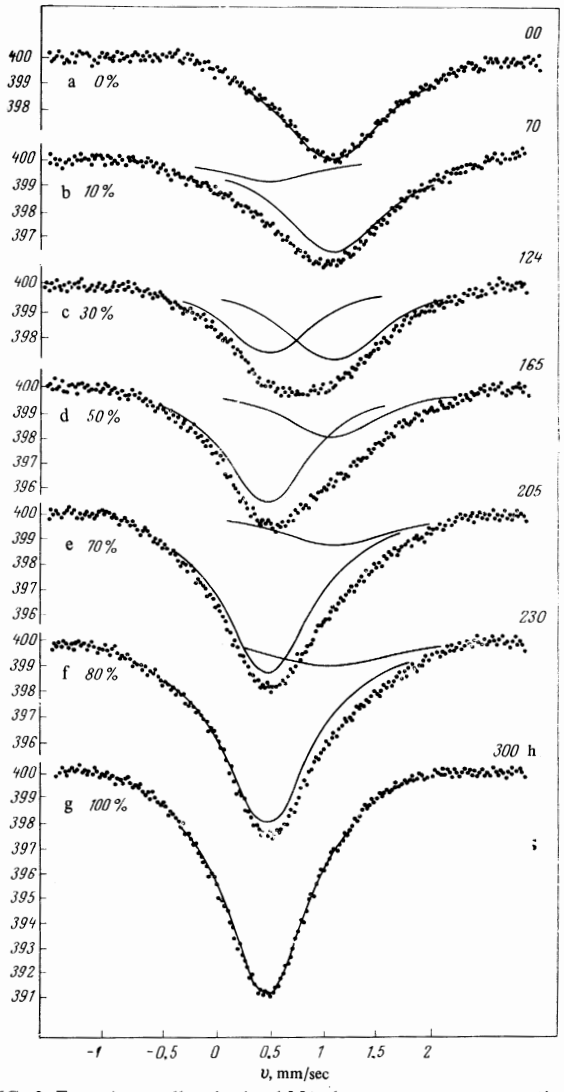

FIG. 2. Experimentally obtained Mössbauer spectra representing the extent of the β-Sn → α-Sn transformation after storage at a fixed temperature for various periods. The continuous curves are the results of the analysis of the spectra into the components representing white and gray tin. The concentration of gray tin is given in percent.

lines were located between the centers of gravity of the lines representing the pure white and pure gray modifications.

Figure 3 shows the dependence of the "normalized" area on the duration of exposure. The ordinate represents the quantity

$$A = \frac{S_k^{\alpha}}{S_k^{\alpha} + S_k^{\beta} S^{\alpha}/S^{\beta}}, \qquad (1)$$

where S^{α} and S_k^{α} are the areas under the Mössbauer lines of gray tin and of the k-th intermediate state representing the contribution of gray tin; S^{β} and S_k^{β} are the areas under the Mössbauer lines of white tin and of the k-th intermediate state representing the contribution of white tin.

A careful calculation was made of the quantity $S_k^{\alpha} + S_k^{\beta} S^{\alpha}/S^{\beta}$, which represented the total area for any ratio of the numbers of tin atoms in the α and β mod-

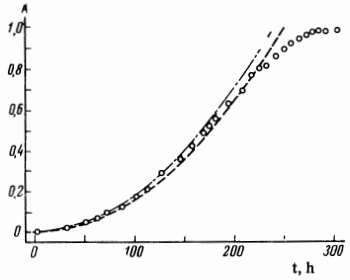

FIG. 3. Dependence of the "normalized" area under the Mössbauer line, representing the amount of gray tin, on the duration t of storage at a fixed temperature. The dashed and chain curves represent calculated parabolas $A = v_{av}^2 t^2$ for v_{av} equal to 0.40×10^{-2} and 0.42×10^{-2} cm/h.

ifications. Within the limits of the experimental error, this quantity remained constant throughout the transformation.

According to[9], the area under the experimentally determined curve, calculated in the thin-absorber approximation, is

$$S_e = \frac{\varkappa}{2} \pi n \sigma_0 f f', \qquad (2)$$

where κ is the fraction of the resonant γ quanta; n is the number of resonating atoms; σ_0 is the resonance absorption cross section; f is the Mössbauer effect amplitude for the source material; f′ is the Mössbauer effect amplitude for the absorber material. The error introduced by the use of Eq. (2) does not exceed 3% for a sample 0.03 mm thick. Then, Eq. (1) modified by Eq. (2) becomes

$$A = n_\alpha / (n_\alpha + n_\beta),$$

i.e., it gives the ratio of the number of atoms of gray tin n_α to the total number of atoms of gray and white tin $n_\alpha + n_\beta$.

Thus, the experimental values in Fig. 3 represent the fraction of atoms, transformed into gray tin, as a function of time. The dependence shown in Fig. 3 can be interpreted satisfactorily on the assumption that the contaminated gray-tin region expands in the shape of concentric circles at a constant radial velocity. It follows that the amount of gray tin increases with time in proportion to the square of the radius whose absolute value represents the displacement of the gray-tin boundary per unit time. It follows that, during the first two-thirds of the experiment, the time dependence can be described by a parabolic curve $A = 0.17 \times 10^{-4} t^2$, where t is the duration of the experiment in hours. Using this parabolic dependence, which describes the growth of the α phase, we can determine the average radial velocity of the phase boundary in the β-Sn → α-Sn transformation. The value of A can be represented as the ratio L/L_0 of the area $L = \pi r_{av}^2 = \pi (v_{av} t)^2$ occupied by gray tin to the total area of the sample $L = \pi R^2$. Here, r_{av} is the average radius of the circle occupied by gray tin; v_{av} is the average velocity of the boundary of the α phase; R is the radius of the sample. If the radius of the sample is 1 cm and the area on which the transformation has been completed is proportional to the fraction A of gray tin atoms, the value of the square of the velocity is found to be the coefficient of t^2.

Figure 3 shows theoretical parabolas corresponding to the velocities of 0.40×10^{-2} and 0.42×10^{-2} cm/h. A comparison of these parabolas with the experimental dependences shows that the average velocity of the new phase boundary lies within the limits $(0.41 \pm 0.01) \times 10^{-2}$ cm/h. This value is in agreement with the results reported in[4]. The deviation of the experimental points from the theoretical curves, observed in Fig. 3 just before the end of the β-Sn → α-Sn transformation, may be attributed to the influence of the edge effects. This is because the boundary of the α phase does not reach the boundary of the sample at the same time at all points and the formation of gray tin may continue at some places.

It is known that the nucleation of a new phase may be a heterogeneous process at the phase boundary, or it may be a homogeneous (spontaneous) process inside the old phase. Thermodynamic calculations[10] show that the heterogeneous nucleation process is favored by the energy considerations. Our investigation of the nucleation of gray tin in the white modification, carried out using the Mössbauer effect, shows that only the heterogeneous nucleation of the α phase is observed on the surface of white tin.

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