

The phase transition of small tin particles under pressure

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The change in the stability region of dispersed condensed phases, when the particles are commensurate with the dimensions of the defect-free regions of the lattice of bulk crystals, is due to the increase in the contribution of the surface part of the thermodynamic potential under equilibrium conditions, and to the heightening of the elastic barrier for nucleation near the initial formations of the new structural modification. A Mössbauer study has been carried out of a polydisperse system of isolated tin particles (with mean diameter $D = 45$ nm), and a considerable increase in the equilibrium pressure P has been established for the β -Sn–SnII transformation with increasing dispersion. The dependence $P(D^{-1})$ is linear with a coefficient 3.3–4.3 mbar·nm. Values of the interphase surface energy $\Delta\sigma$, the magnitudes of the heats of this transformation and the slopes of the equilibrium line for monodisperse tin systems with $D < 90$ nm were obtained from an analysis of the pressure dependences of the parameters of the Mössbauer spectrum of small particles. For $D = 90$ nm, the equilibrium pressure $P \approx 150$ kbar, $\Delta\sigma \approx 850$ erg·cm⁻². The structure and forces of interaction between tin atoms in the highly dispersed state agree with the macrophase characteristics. The surface sheath of the nucleus of tin particles which is responsible for the size effects consists of $\approx 12\%$ of the total number of atoms for the polydisperse system studied, and is surrounded by two monolayers of dioxide.

INTRODUCTION

The essential conditions of formation of the new phase for the occurrence of a structural rearrangement, taking account of the surface states, is expressed by the inequality

$$(\mu_{02} - \mu_{01}) + (\mu_{s2} - \mu_{s1}) < 0, \quad (1)$$

where μ_0 and μ_s are the bulk and surface parts of the chemical potential of the new (2) and original (1) phases. The dependence of the phase equilibrium conditions on the dispersion, which determines the contribution of the surface term, follows from the inequality. For small tin particles with radius 2.3–3 nm, an analysis of the surface as a separate part of the system determining the size effects and its influence, proportional to the change in area, within the framework of a thermodynamic approach, describes the experimental results of Koverda *et al.*¹ satisfactorily. The results of this investigation show that the representation of highly dispersed particles as a heterophase system, consisting of a nucleus and a surface layer, is valid experimentally for tin particles with radius up to 3 nm. The influence of dispersion on the melting temperature was studied.

In 1971 Tananaev formulated a general approach to a physicochemical analysis.^{2,3} An additional degree of freedom appears on the introduction of dispersion: the size of the particles entering into the ensemble and an additional coordinate for the phase diagram. As the results of calculation show, the surface term is small for cylindrical carbon particles with base radius $r \geq 100$ nm, and the graphite-diamond equilibrium condition is similar to that for the bulk phase. With a reduction in radius, $r \leq 10$ nm, the phase equilibrium surface in pressure-temperature-dispersion coordinates de-

parts in the directions of small pressures, and for $r \approx 1$ nm diamond is stable at atmospheric pressure up to 2000 K.^{4,5} The stability under ordinary conditions of high-temperature, non-equilibrium or of phases in general not observed before, has been reported for small particles in a number of works.^{6–9}

The chemical potential of the surface atoms of the initial phase can differ appreciably from the value characteristic of the bulk phase and from the surface potential of the newly formed phase. According to the inequality of Eq. (1), one would expect a shift in the equilibrium value of the driving parameter of the transformation for a system with a strongly developed surface. The main reason for this is the changes in the regions of phase stability over which reaction by directional means is possible. Existing methods provide the opportunity of obtaining many materials in a wide range of dispersion down to a few nanometers.^{10–13}

On the other hand, because of the volume defect accompanying a structural phase transformation in solids, the initial formation of regions of the new phase will be accompanied by expenditures on elastic energy. This energy is added to the surface energy of the interphase boundary and increases the region of metastability of the initial phase. The contribution of elastic energy will depend on the degree to which diffusion or plastic deformation achieves relaxation of the volume changes and of the shape of the regions undergoing transformation. Relaxation of elastic strains in small particles ($r \sim 1$ –10 nm) by the mechanism of plastic flow is made difficult because of the absence of dislocation sources (of the Frank-Read type) in such small volumes. One would expect large elastic strains accompanying a phase transformation with a volume defect in small particles of a material

and the absence of their relaxation. This is the basis for the second reason for dispersion being able to change the region of stable existence of a given or newly formed phase.

The conditions for phase stability for a strongly dispersed material can thus be appreciably changed. The character of the evolution of the system would then be determined only by the nucleation and growth of regions of the new phase in the absence of processes for defects to arise or move. In this work, experimental results on the behavior of a system of isolated small tin particles, over a pressure range which encompasses the region of the known structural phase transition for the macrophase, ($P > 92$ kbar, 20°C) is analyzed within the framework of present physical ideas.

THE EXPERIMENTS

A histogram of the size distribution of the spherical tin particles studied is shown in Fig. 1, constructed from the results of an electron-microscope analysis. The maximum in the distribution occurs near 45 nm. The large width of the distribution characterizes the polydisperse state of the system studied.

An x-ray diffraction study revealed no other phases or compounds other than β -Sn in the small tin particles. However, as can be seen in Fig. 2, the Mössbauer spectrum of the freely dispersed system of small particles contains a tin dioxide, SnO_2 , absorption line with zero isomer shift relative to the source. It was established by the method of a model absorber that the amount of tin dioxide on the surface of the particles was not more than 3 wt%, which corresponds to two monolayers for a sphere of diameter 45 nm.

According to our results, the parameters of the Mössbauer spectrum of the polydisperse system of particles studied is the same as for bulk tin crystals. A similar result was established in a Mössbauer investigation of particles with mean diameter 4.5 nm (1300 atoms per particle), obtained in an oxygen atmosphere.¹⁴ The authors determined the number of oxide layers and their thickness by electron-microscope (diffraction) and Mössbauer methods. It appeared that with such a production regime, six layers of mixed oxide ($\text{SiO} + \text{SiO}_2$) are formed on the surface; the thickness of each layer is 0.2 nm, and the size of the nucleus of the β -Sn phase is not more than 2 nm. The valuable conclusion was drawn by Akselrod *et al.*¹⁴ about the absence of bonding

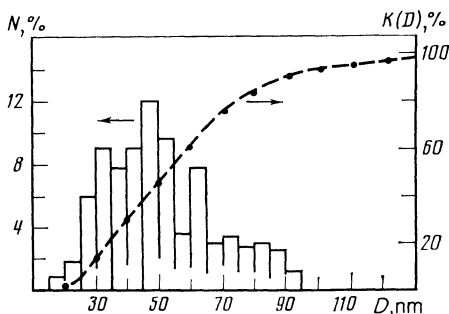


FIG. 1. The size distribution of tin particles: N is the number of particles, $K(D)$ is the number of particles with diameter less than D .

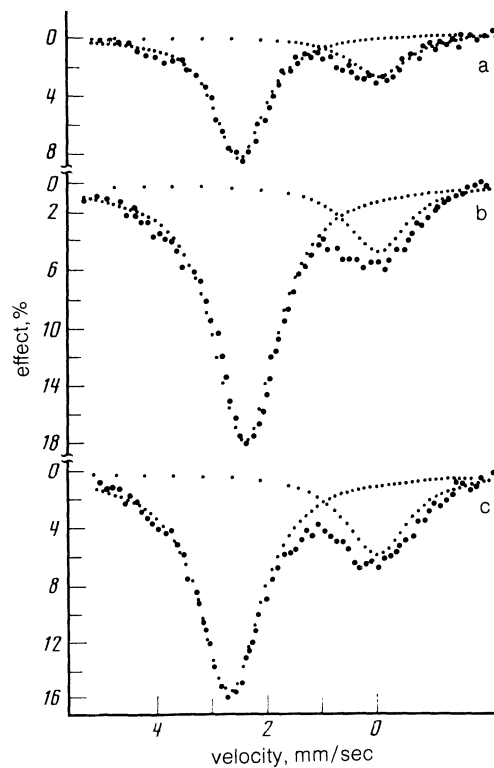


FIG. 2. Mössbauer spectra of a polydisperse system for different pressures: a) 1 atm, b) 154 kbar, c) 198 kbar. The source was $\text{Ca}^{119\text{m}}\text{SnO}_3$.

between the metallic nucleus of the β -Sn phase with the sheath of oxide surrounding it. In what follows, based on these results, we ignore the influence of the oxide sheath on the results obtained.

The specimens studied were discs of diameter 1.3 nm and thickness 0.3 nm of compacted small tin particles, isolated from one another by an oxide sheath. The specimens were compressed by fluid in a high-pressure chamber, in which Mössbauer studies could be carried out in the range up to 200 kbar with fixed geometry and constant monitoring of the value of the pressure near the specimen-absorber being studied.¹⁵ Communicating porosity of the specimens was guaranteed by hydrostatic compression of each particle.

RESULTS

1. The size dependence of the transition pressure for small β -Sn particles

The Mössbauer spectra of the specimens (Fig. 2) consisted of two lines: the line of high intensity corresponds to resonance absorption in the β -Sn phase, and the second to the oxide sheath. The intense line at $P = 198$ kbar reflects absorption in the high-pressure SnII phase. Its position E and probability F agree with the extrapolated values of the same quantities for macrophase specimens, see Fig. 3.

For thin absorbers, the relative values of F/F_0 , where F_0 is the probability of the effect at atmospheric pressure, is proportional to the relative area of the absorption curves. In this way the changes with pressure of the probability of the

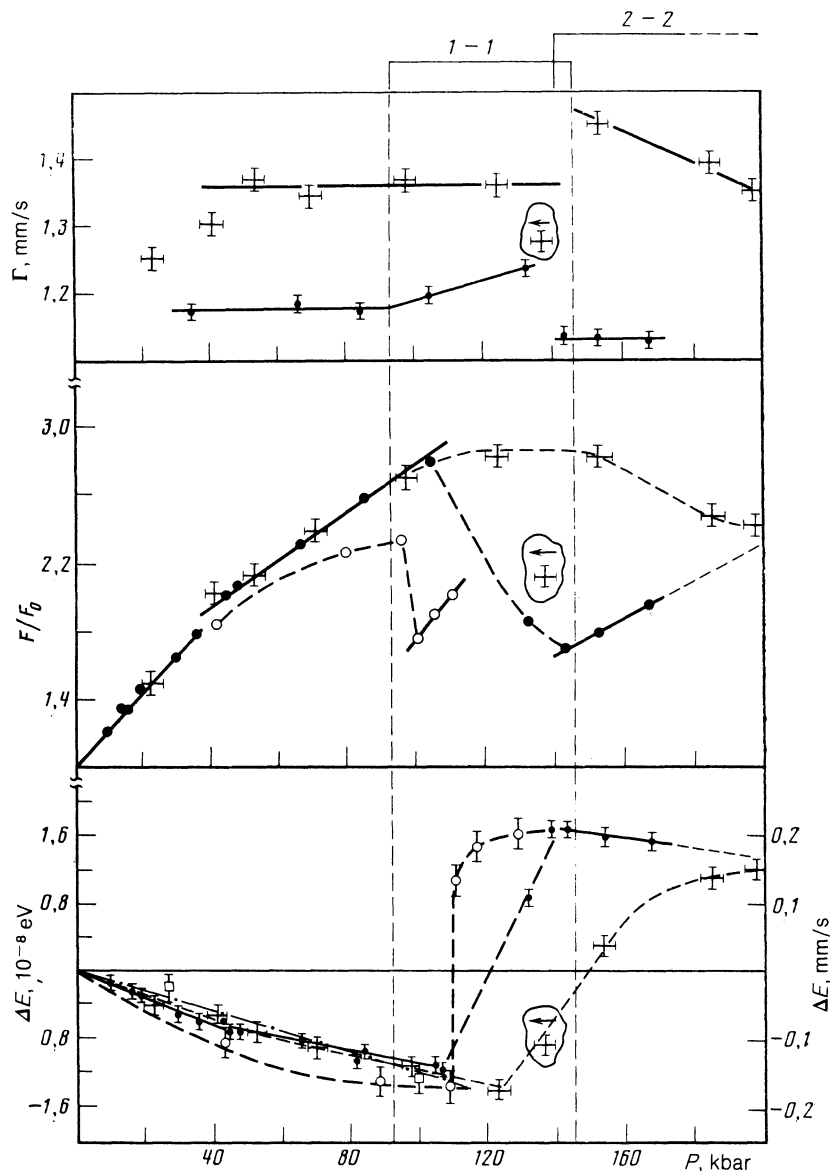


FIG. 3. The variations of the width Γ , relative probability of the Mössbauer effect F/F_0 and the relative position of the center of gravity $\Delta E = E(P) - E_0$ of spectra of macrophase (dark circles) and highly disperse (crosses) specimens, obtained under hydrostatic conditions. The open circles and the squares are the results of studying macrophase specimens under non-hydrostatic conditions.^{19,20} The encircled crosses with arrows are the results obtained on reversing the pressure change. 1-1 is the two-phase region for the transformation of macrophase specimens; 2-2 is the region for the successive transformation of an assembly of particles with dimensions less than the characteristic $D_{\text{char}} = 90$ nm. The parameters of the Mössbauer spectrum of macrophase and disperse specimens undergo a change of slope near 40 kbar: F/F_0 with a positive and ΔE with a negative jump.

effect for the low and high pressure phases of Mg_2Sn and SnTe ,^{16,17} for the present system of small particles and for the macrophase of tin were studied.¹⁸ We show in Fig. 3 all the existing data on the influence of different conditions of compression on F/F_0 , ΔE (the change in the position of the center of gravity of the absorption line) and its width for the β -Sn and SnII phases. The crosses are the results of the present investigation, and the dark circles are for the macrophase of tin.¹⁸ The compression conditions were hydrostatic for the small particles and for the bulk crystals. The open circles¹⁹ and squares²⁰ are nonequilibrium compression of macrophase specimens (these results are not analyzed).

The F/F_0 and $\Delta E(P)$ curves coincide for a system of small particles and for macrophase specimens (tin foil) for hydrostatic compression up to $P \approx 100$ kbar. At large pressures the parameters of the Mössbauer spectrum of bulk crystals start to depart appreciably from the linear depen-

dence due to the start of the β -Sn-SnII transformation. There is a flat section on the F/F_0 pressure dependence curve above 100 kbar. Such a form for the change in probability can be explained by the polydisperse nature of the specimen. Nucleation and growth of the SnII phase in large particles takes place under conditions similar to those in bulk crystals: the equilibrium pressure is 92 kbar and the two-phase region is up to ≈ 140 kbar. The conditions for stable growth are different for particles of smaller dimensions. The 15% reduction in F/F_0 for a system of small particles in the pressure range 150–185 kbar reflects the step by step transformation of particles with dimensions less than 90 nm. A similar conclusion can be reached by analysing the change in the line width $\Gamma(P)$. The characteristic dimension of 90 nm is obtained from a combined analysis of the granulometric structure of the extrapolated F/F_0 dependences on P for β -Sn and SnII in the two-phase region, and of known values of the

change in F/F_0 as a result of the transformation of bulk crystals and of small particles. The spectral line consists of two Lorentz curves in the transition region ($P > 92$ kbar) from the β -Sn phase and from the SnII phase. Their intensities are proportional to the amount of the corresponding phases:

$$B_1 = \eta A_1, \quad B_2 = (1 - \eta) A_2. \quad (2)$$

If the distance Δ between the centers of gravity of the lines from the phases is less than the half-width $\Gamma/2$, then the position of the resulting line is

$$E_p = (B_1 E_1 + B_2 E_2) / (B_1 + B_2). \quad (3)$$

It follows from Eqs. (2) and (3) that

$$\eta = A_2 (E_2 - E_p) / [A_1 (E_p - E_1) + A_2 (E_2 - E_p)]. \quad (4)$$

The position E and the intensity of each line changes linearly with pressure:

$$E_1 = (-0.32 \pm 0.01) - (0.8 \pm 0.1) \cdot 10^{-2} P, \quad (5)$$

$$E_2 = (2.50 \pm 0.01) - (0.6 \pm 0.1) \cdot 10^{-2} P, \\ B_1(P)/B_0 = (1.36 \pm 0.02) + (1.44 \pm 0.02) \cdot 10^{-2} P, \quad (6)$$

$$B_2(P)/B_0 = (0.10 \pm 0.02) + (1.16 \pm 0.02) \cdot 10^{-2} P.$$

Here P is in kbar and E in $\text{eV} \cdot 10^{-8}$. Equation (6) approximates the experimentally determined $F(P)/F_0$ dependence. From these results, the $\eta(P)$ dependence, the volume fraction of particles in the β -Sn phase, is obtained. The $\xi(D)$ dependence, the volume fraction of β -Sn particles with dimensions less than D , is determined by using the analytical dependence for the logarithmic normal size distribution curve for aerosol particles:

$$N(D) = [(2\pi)^{1/2} \ln \sigma_g]^{-1} \exp \left[- \frac{\ln^2(D/D_g)}{2 \ln^2 \sigma_g} \right], \quad (7)$$

where D is the diameter of the particles, D_g is the geometrical mean diameter and σ_g is the standard geometrical deviation:

$$\ln \sigma_g = \left[\frac{\sum n_i \ln^2 \frac{D}{D_g}}{\sum n_i} \right]^{1/2},$$

$$\ln D_g = \frac{\sum (n_i D_i)}{\sum n_i}.$$

The distribution for the polydisperse system of Fig. 1 can be described to good accuracy by Eq. (7) for

$$D_g = 45 \pm 3 \text{ nm} \quad \sigma_g = 1.38 \pm 0.05.$$

If the increase in the amount of SnII phase is determined by the successive transformation of particles, starting with the largest for which the transition pressure is ≈ 92 kbar, and ending with the smallest with an equilibrium pressure ≈ 200 kbar, then within the framework of such a model, i.e., on the assumption of a unique $P \leftrightarrow D$ correspondence,

$$\eta(P) = \eta[P(D)] = \xi(D). \quad (8)$$

This equation was solved graphically by a comparison of ordinates in Fig. 4. The size dependence of the pressure sought for the observed start of the transformation is con-

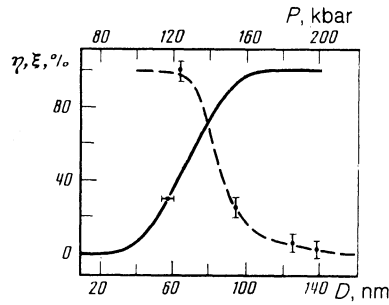


FIG. 4. $\eta(P)$, the mass fraction in the β -phase (dashed curve) and $\xi(D)$, the fraction of particles with dimensions less than D (full curve).

structed in Fig. 5. The $P(1/D)$ dependence is also shown there, approaching 92 kbar linearly as D is increased, the pressure for the start of the transformation for the macro-phase. The slope is $k = 3.3\text{--}4.3$ Mbar \cdot nm. The combined analysis of the granulometric composition of the system of particles and the temperature variation of the integral intensity reflected from the crystalline structure was carried out earlier for investigating the influence of dispersion on the melting temperature of tin.¹ The size dependence obtained, $T_m(D)$, described well the results of other work, which is evidence in favor of the correctness of such a method for determining size dependences of physical parameters.

The $P(D)$ dependence constructed in Fig. 5, the observed pressure for the β -Sn-SnII transformation for particles with diameter D , was determined without any assumptions about the reasons for the change in transformation pressure for small particles. Such other equilibrium conditions can lead to a change in the pressure for a phase transition as an increase in the energy barrier separating the phase states. The magnitude of this barrier is determined by the surface energy at the interface of the phases and by a contribution from elastic energy, accompanying a phase transition in a solid with a volume defect. The overcoming of the ener-

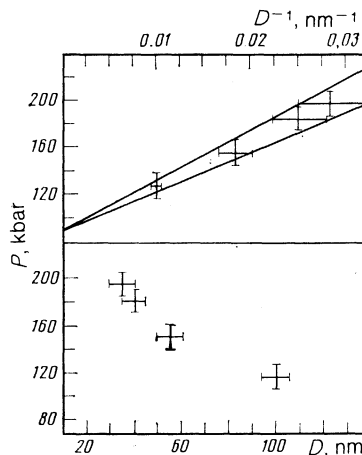


FIG. 5. The size dependence of the pressure for the phase transformation, $P(1/D)$ and $P(D)$.

gy barrier by means of an excess difference of chemical potentials would lead to hysteresis. Only one Mössbauer spectrum was recorded on reversing the pressure change at 137 kbar (circled crosses with arrows in Fig. 3). Its parameters indicate that the specimen already contains an appreciable amount of β -Sn phase. The narrowness of the hysteresis loop provides a basis for drawing a conclusion about the change in equilibrium conditions for small tin particles. If the observed transition region (from 100 to 200 kbar) for the polydisperse system of small particles were a result of metastabilization of the β -Sn phase, as a result of high energy barriers for nucleation and growth or of kinetic features, then on the return journey the metastable region of the SnII phase would extend down to atmospheric pressure. However, the Mössbauer spectra recorded after reducing the pressure in the chamber to normal agreed completely with the β -Sn phase.

If the dimensions of the particles are appreciably greater than the range of action of intermolecular interaction, as in our case, then the departure of the energy from additive is taken into account by introducing a specific surface energy. The interphase surface energy $\Delta\sigma = \sigma_{\beta\text{-Sn}} - \sigma_{\text{SnII}}$ will then depend on the diameter D , the difference in equilibrium pressures for the transformation $\Delta(P) = P(D) - P(D_\infty)$ for small particles, $P(D)$, and for the macrophase, $P(D_\infty)$, and for spherical particles is determined by an expression²¹

$$\Delta\sigma = \Delta PD\delta/12. \quad (9)$$

The change in volume for the β -Sn-SnII transformation is $\delta = 10^{-2}$ (Ref. 22). Substituting into Eq. (9) the experimentally determined size dependence $\Delta PD = 3.3\text{--}4.3$ Mbar·nm (see Fig. 5) and the relative volume change δ , we obtain the range of values $\Delta\sigma \approx 280\text{--}360$ erg·cm⁻². If we compare these values with the surface energy of small β -Sn particles, $\sigma_s \approx 850$ erg·cm⁻², then the estimated value obtained appears reasonable.

2. The role of the elastic energy of the transformation

A phase transition with a volume defect in small particles can lead to an appreciable expense of the supersaturation ($\mu_1\text{-}\mu_2$) through the elastic energy Δg_e , due to the absence of relaxation of the strains by the dislocation mechanism. For estimating the elastic energy and the difference of pressure on a particle with dimensions 45 nm and nucleus of the SnII phase, a model of a spherical nucleus of radius r arising in a particle of radius R was considered, in the approximation of the sphere having a non-coincident dimension.²³ If the lattices of the nucleus and of the matrix are considered coherent, and the elastic constants of the corresponding phases in the small particles are the same and equal to the elastic constants of the macrophase, then the difference of pressure in the nucleus and in the matrix is

$$\Delta P = 4\mu_1 C_6 \frac{v_2 - v_1}{3v_2} \left(1 - \frac{r^3}{R^3} \right),$$

and the elastic energy per atom is

$$\Delta g_v = 2\mu_1 C_6 \frac{(v_2 - v_1)^2}{3v_2} \left(1 - \frac{r^3}{R^3} \right).$$

The calculation gives for the maximum elastic energy stored in a particle on the formation of a single nucleus, the value ≈ 4 J·mole⁻¹ and correspondingly $\Delta P \sim 1$ kbar.

Comparison of the results of the forward and backward (the encircled crosses with arrows in Fig. 3) β -Sn-SnII transformation on the Mössbauer spectra of the polydisperse system of particles provides evidence for the negligible hysteresis, and gives a value for the starting pressure for the transition into the SnII phase for the main mass of particles near 150 kbar. The estimates carried out indicate a small (≈ 1 kbar) contribution of elastic energy to hysteresis for the present transformation, even for the case of the absence of strain relaxation, which is in agreement with experiment.

3. The P-T phase diagram of tin and a section of the equilibrium line for a polydisperse system of small particles

A calculation of the heat of transformation and of the slope of the equilibrium lines for β -Sn-SnII was carried out on the basis of the results obtained, for tin particles with dimensions less than 90 nm. For such particles, as follows from an analysis of the results of this work, the equilibrium pressure for the direct transformation at room temperature lies in the range above 150 kbar. It is known that the heat of the phase transformation Q can be expressed through the ratio of the Debye temperatures of the initial (β -Sn) and new (SnII) phases by the following relation:²⁴

$$Q = \ln \left(\frac{\Theta_{\beta\text{-Sn}}}{\Theta_{\text{SnII}}} \right)_{P=150 \text{ kbar}} 3RT = 280 \pm 30 \text{ cal}\cdot\text{mole}^{-1} \\ \left(\frac{\Theta_{\beta\text{-Sn}}}{\Theta_{\text{SnII}}} \right)_{P=150 \text{ kbar}} = \left(\frac{\ln F_{\text{SnII}}}{\ln F_{\beta\text{-Sn}}} \right)_{P=150 \text{ kbar}}^{1/2} = 0.16,$$

where $\Theta_{\beta\text{-Sn}}$ and Θ_{SnII} are the Debye temperatures of the initial and new phases, determined from $F(P)/F_0$.

Using the known specific volume difference of the phases $\Delta V/V = 1.1 \pm 0.2\%$ (Ref. 22), the slope of the equilibrium line near 150 kbar was calculated on the basis of the Clausius-Clapeyron equation for particles with $D \approx 90$ nm: $dP/dT = 220$ atm·deg⁻¹. Similar calculations were carried out for macrophase specimens using the results of Kapitánov and Yakovlev:¹⁸ $Q = 260$ cal·mole⁻¹, $dP/dT = 200$ atm·deg⁻¹ near the equilibrium pressure $P = 92$ kbar. The slope of the β -Sn-SnII equilibrium line for a tin bulk crystal near 92 kbar was determined by using an x-ray structural analysis as 170 atm·deg⁻¹. A value of the heat of transformation is also given there,²² $Q = 225 \pm 45$ cal·mole⁻¹, which, within the accuracy in the determination, agrees with the value obtained by us from Mössbauer results for the macrophase.

The anomalous change in the probability of the Mössbauer effect and of the electron density near 40 kbar, first found for macrophase specimens,¹⁸ reflects the special nature of the interaction between tin atoms in the doubly tetragonal body-centered β -Sn lattice. The existence of such anomalies in the analogous dependences for small particles indicates the conservation of the interaction force and of the structural arrangement of the atoms, characteristic for bulk crystals, in the highly disperse tin of the present granulometric composition.

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