

Singularities of lattice dynamics in tin-lead alloy

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Measurements were made of the low-temperature heat capacity, resistivity, thermal gamma expansion, and nuclear δ resonance of alloys of tin with small amounts of lead. Hardening of the vibrational spectrum in the course of the decay of the solid solution is observed. It is established on the basis of the experimental measurements that the spectral density of the vibrations increases abruptly at low temperature prior to the decay of the investigated alloys, and decreases after the decay. The kinetics of variation of the spectral density of the vibrations in the course of the decay is studied.

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1. INTRODUCTION

The influence of heavy substitutional impurities in a weak solution on the vibrational spectrum of a crystal is the subject of a large number of experimental^[1-5] and theoretical^[6,7] studies. Allowance was made for the change of the force constants and the real form of the vibrational spectrum,^[6,7] as well as for a more complicated model of the impurity atom, in which changes take place not only in the bonds of the impurity atom with its nearest neighbors, but also in the bonds between the atoms and the matrix and the nearest environment of the impurity atom.^[8]

In this paper we have investigated experimentally how "clusters" of impurity atoms that produce in a crystal strong internal stress fields, as well as their dimensions, influence the vibrational spectrum of the crystal. The indicated situation is compared with the case of dissolved impurities. In addition, we have examined the effect exerted on the Grüneisen coefficient by the restructuring of the vibrational spectrum.

2. EXPERIMENTAL PROCEDURE

Alloys of tin with 0.36, 0.72, and 1.1 at.% lead were smelted in an atmosphere of argon with excess pressure. The samples for the measurements were subjected to a prolonged homogenizing annealing at temperatures close to the melting point, followed by quenching in water. Table I shows the values of $R_{300\text{ K}}/R_{4.2\text{ K}}$ of the samples prepared in this manner.

The heat capacity of the alloys was measured in a vacuum adiabatic calorimeter, in the range 1.5-40 K, accurate to less than 1%.

The thermal expansion was registered with an automatic dilatometer with sensitivity $\Delta l/l \sim 10^{-6}$, and we registered in the experiment the difference between the elongations of two samples placed alongside each other. The measurement accuracy was within 5%.

The Mössbauer effect probability was measured with an Sn^{119} source in the form of the compound SnO_2 . The thickness of the investigated samples was $\sim 30\ \mu\text{m}$, thereby excluding the effect of self-absorption of the γ

rays.

3. RESULTS AND DISCUSSION

Heat capacity. Figure 1a shows the temperature dependences of the heat capacity C in the temperature interval 2.24-5.5 K (i.e., in the region where a singularity is observed in the change of the relative phonon heat capacity) for the investigated tin-lead alloys.

It is seen that addition of 0.36 and 0.72 at.% of lead to the tin increases the heat capacity, while addition of 1.1 at.% lead decreases the heat capacity, but the electronic heat capacity C_{el} remains practically unchanged. Thus, $\gamma(0)$ of tin and its alloys has a value $\sim 1.4\ \text{mJ/mole-K}^2$, and the Debye temperature $\Theta(0)$ of Sn according to the heat-capacity data (Fig. 1) is $\sim 185\ \text{K}$, while for Sn with Pb added the values of $\gamma(0)$ vary, but lie within the limits of the experimental error. It can therefore be assumed that the influence of the impurity atoms on the heat capacity C is due to a restructuring of the vibrational spectrum and manifests itself most clearly in the temperature dependence of the relative change of the lattice heat capacity. When $C_p(T)$ for tin is separated, the temperature dependence of the lattice heat capacity can be extrapolated into the region of temperatures below T_{cr} , inasmuch as the lattice component of the heat capacity remains unchanged on going into the superconducting state.

The upper insert of Fig. 1a shows the temperature dependence of the relative change of the lattice heat capacity $\Delta C_{ph}/\eta C_{ph}(0)$, where $\Delta C = C_{ph}(\eta) - C_{ph}(0)$; $C_{ph}(0)$ is the lattice component of the heat capacity of pure tin, and η is the impurity concentration. The presence of a narrow maximum on the plots of $\Delta C_{ph}/\eta C_{ph}(0)$ at 4.5 K for Sn+0.36 at.% Pb and 4.7 K for Sn+0.72 at.% Pb at-

TABLE I.

Material	$R_{300\text{ K}}/R_{4.2\text{ K}}$
Sn	1762
Sn + 0.36 at.% Pb	99
Sn + 0.72 at.% Pb	62
Sn + 1.1 at.% Pb	98

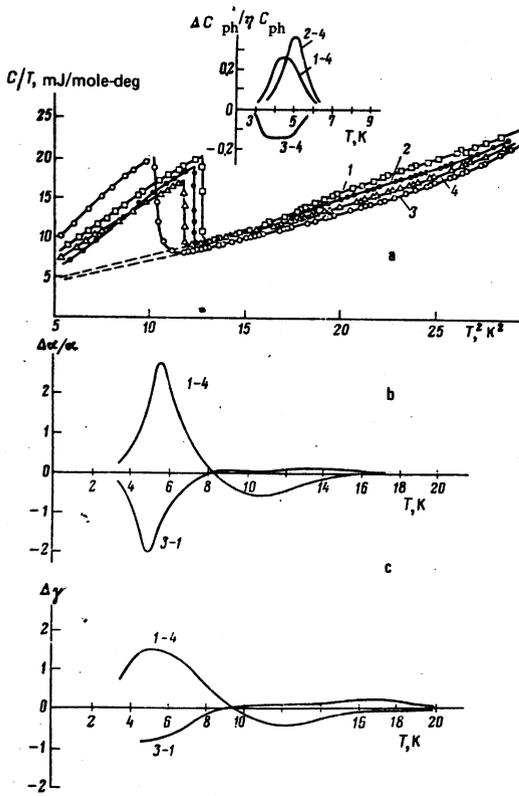


FIG. 1. Temperature dependences of the measured heat capacity (a), of the relative change of the thermal-expansion coefficient (b), and of the deviation from the Grüneisen parameter of pure tin (c). The insert shows the temperature dependences of the relative change of the lattice heat capacity normalized to the impurity concentration. 1—Sn+0.72 at.% Pb; 2—Sn+0.36 at.% Pb; 3—Sn+1.1 at.% Pb; 4—Sn. The indices 1-4, 2-4, 3-4, and 3-1 designate for ΔC , $\Delta\alpha$ and $\Delta\gamma$, respectively: $\Delta C_{1-4} = C(\text{Sn}+0.72 \text{ at.}\% \text{ Pb}) - C(\text{Sn})$, $\Delta C_{2-4} = C(\text{Sn}+0.36 \text{ at.}\% \text{ Pb}) - C(\text{Sn})$, $\Delta C_{3-4} = C(\text{Sn}+1.1 \text{ at.}\% \text{ Pb}) - C(\text{Sn})$, $\Delta\alpha_{1-4} = \alpha(\text{Sn}+0.72 \text{ at.}\% \text{ Pb}) - \alpha(\text{Sn})$, $\Delta\alpha_{3-4} = \alpha(\text{Sn}+1.1 \text{ at.}\% \text{ Pb}) - \alpha(\text{Sn}+0.72 \text{ at.}\% \text{ Pb})$, $\Delta\gamma_{1-4} = \gamma(\text{Sn}+0.72 \text{ at.}\% \text{ Pb}) - \gamma(\text{Sn})$, $\Delta\gamma_{3-4} = \gamma(\text{Sn}+1.1 \text{ at.}\% \text{ Pb}) - \gamma(\text{Sn})$.

tests to the appearance of a quasilocal mode in the vibrational spectra of these systems.^[6,7] An increase of the superconducting-transition temperature is observed (the values of T_{cr} coincide for the heat capacity, Fig. 1a, and for the resistivity, Fig. 2). It should be noted that according to Ref. 5 the change of the temperature of the superconducting transition in dilute solid solutions can be represented in the form $\delta T_{cr} = A_1 + A_2 + A_3$, where A_1 , A_2 , and A_3 are determined, when impurity atoms are introduced into the system, by the changes of the following: the density of the electronic states on the Fermi surface, the amplitudes $\langle v^2 \rangle$ of scattering by the ions, the effective force constants γ' , and the spectral density $g(\omega)$. In this case, when lead is added to tin, $A_1 \sim 0$, so that C_{cr} remains unchanged; $A_3 < 0$ because of the anomalous increase of the spectral density of the oscillations (Fig. 1a) in the low-frequency region^[5] (pseudopotentials: $\langle v_{Sn}^2 \rangle \sim \langle v_{Pb}^2 \rangle$, Ref. 9). Then the inequality $\delta T_{cr} > 0$ follows when the conditions $A_4 > 0$ and $A_2 > A_3$ are satisfied, i.e., according to Ref. 5 it is necessary that the ratio of the force constants be $\gamma'_{Sn-Sn} / \gamma'_{Sn-Pb} < 1$. This conclusion can follow also from the fact

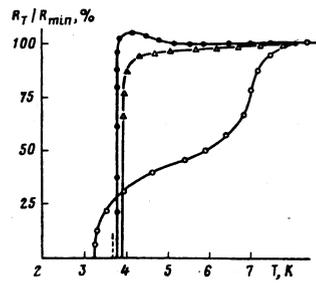


FIG. 2. Temperature dependence of the relative change of the electric resistance: ●—Sn+0.36 at.% Pb, △—Sn+0.72 at.% Pb, ○—Sn+1.1 at.% Pb.

that in Sn-Pb almost pure lead is segregated upon decay (Ref. 10) (this is evidenced also by the partial superconducting transition (Fig. 2) typical of pure lead), and therefore $\gamma'_{Sn-Sn} > \gamma'_{Sn-Pb}$ and $\gamma_{Pb-Pb} > \gamma'_{Sn-Pb}$.

The minimum of $\Delta C_{ph}/\eta C_p(0)$ is evidence of the hardening of the lattice-frequency spectrum. It is accompanied by a decrease of T_{cr} of tin and by a partial superconducting transition at 7.2 K (Fig. 2), a fact that indicates that pure lead particles are segregated.

Thus, prior to the decay, the relative change of the heat capacity has a resonant burst. After the decay, i.e. when the lead particles are formed, the converse is observed—a resonant decrease of the relative change of the lattice heat capacity. Taking into account, Ref. 11, the formula for the lattice heat capacity.

$$C_{ph}(T) = 3Nk_B \int_0^\infty d\omega g(\omega) \frac{(\hbar\omega/2k_B T)^2}{\text{sh}^2(\hbar\omega/2k_B T)} \quad (1)$$

(T is the temperature, N is the number of atoms in the crystal, k_B is the Boltzmann constant, ω is the lattice vibration frequency, and $g(\omega)$ is the lattice state density), the results on the temperature dependence of the heat capacity should be regarded as a manifestation of a resonant burst and a decrease of the low-frequency oscillation density $g(\omega)$ of the Sn-Pb solid solution before and after the decay, respectively.

In the general case we can obtain from the theory of dynamic lattices for the oscillation density $g(\omega)$ the relation

$$g(\omega_{ph}) = g_0(\omega_{ph}) + B_2 g_0^2(\omega_{ph}) + B_1 g_0(\omega_{ph}) + B_0, \quad (2)$$

where the coefficients B_0 , B_1 , and B_2 are complicated functions of $g(\omega)$. From the proposed condition for the positive and negative signs of the correction to the oscillation density at the resonant frequencies in the asymptotic limits, respectively, of small $g_0(\omega) \rightarrow 0$ and large values of the function $g_0(\omega_{ph})$ it follows that $B_2 < 0$ and $B_0 > 0$. It can therefore be concluded that the resonant decrease of the oscillation density $g(\omega_{ph})$ of the solid solution implies rather large values of the oscillation density $g_0(\omega_{ph})$ for the solvent lattice. It appears that these values should not exceed a certain critical value at which, owing to the large damping, the peak smears out to zero.

The resonant decrease of the function $g(\omega)$, which is

revealed by measurement of the temperature dependence of the heat capacity of the Sn-Pb solid solution, agrees with the condition established above that $g_0(\omega_{ph})$ of tin be large in the low-frequency region of the oscillation spectrum.

It should be noted that the appearance of the resonant decrease of the low-frequency oscillation density of the solution correlates with the experimentally established fact that it decays.

Since the decrease of $g(\omega)$ is accompanied at lower temperatures by a resonant burst,^[12] it follows that in the system considered by us, where the resonant decrease is observed at 4 K, it can be assumed a possibility exists of experimentally observing quasilocal oscillations at temperatures close to 0 K.

It should be noted in addition that the minimum of $\Delta C_{ph}/\eta C_{ph}(0)$ can be due in part also to singularities of the heat capacity of the segregated lead particles C_{PbP} . This follows from the fact that according to the theoretical and experimental results,^[13-15] in the region of 5 K and lower, compression of ultradisperse particles can lead to a decrease of the heat capacity all the way to zero. In the present case there is a strong compression of the lead phase, since the volume of the unit cell of pure lead is 19% larger than that of tin. If the heat capacity C of the alloy is expressed in the form $C_{Sn} + C_{PbP}$, then the contribution of C_{PbP} to the experimentally observed minimum of the ratio $\Delta C_{ph}/\eta C_{ph}(0)$, which amounts to ~12%, does not exceed 1%. Therefore the entire effect on the whole is determined by $C_{ph}(0)$ of tin.

Mössbauer effect. Qualitative information on the singularities of the frequency spectrum of tin in the Sn-Pb alloy was obtained by us by the nuclear gamma resonance (NGR) method. For our system this is a selective method, because the lead segregations contain ~10⁻³ at. % of Sn¹¹⁹ and their contribution to the NGR spectrum is negligibly small.

Figure 3 shows the measured γ -line intensity in the Mössbauer effect on Sn¹¹⁹ in the solid solution Sn+0.36 at. % Pb in the course of annealing at 300 K. Since the investigated alloys decay by diffusion, the radius of the segregated particle as a function of the decay time τ can be represented in the form $R \sim (D\tau)^{1/2}$, where D is the coefficient of diffusion of lead in tin. The presented estimates yield $R_{max} \sim 40 \text{ \AA}$. Since the width of the in-

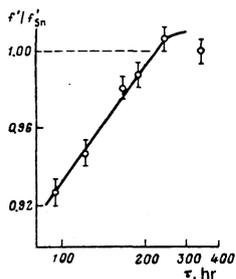


FIG. 3. Change of probability of the Mössbauer effect of Sn + 0.36 at. % Pb in the course of heat treatment at 300 K.

terphase boundaries is of the same order, ~30–40 Å (Ref. 16), one can speak in this case of coherent segregations or "clusters."

The observed increase of the relative intensity of the Mössbauer-effect γ lines with increasing dimensions of the lead clusters is due to the hardening of the spectrum of the oscillations of the crystal lattice of the solution in the course of the decay.

In fact, according to the theory of the Mössbauer effect,^[17] in the general case the intensity I of the γ absorption can be represented in the harmonic approximation in the form

$$I \sim \exp \left\{ -2 \int_0^{\infty} \left\langle \left(\frac{\hbar}{2M_{i,k}\omega} \right) (x e_w(l, k))^2 \right\rangle (2n(\omega) + 1) g(\omega) d\omega \right\}. \quad (3)$$

where $n(\omega)$ is the Planck function, the symbol $\langle \dots \rangle$ denotes thermodynamic averaging over the states of the system and averaging over the impurity configurations, and x is the wave vector of the γ quantum. Taking into account the rapid decrease of the function $n(\omega)$ with increasing temperature, we can conclude from (3) that when the center of gravity of the function $g(\omega)$ shifts to the high-frequency region, i.e., when the spectrum of the crystal-lattice vibrations becomes harder, the intensity of the γ absorption by the Mössbauer nucleus increases.

There is every reason for assuming that the hardening of the frequency spectrum of tin upon segregation of the lead clusters is the result of coexistence of regions with different interatomic distances. Since the interatomic distance in the lead clusters is larger than in tin, local static compressions of the Sn lattice take place, the mean squared thermal displacement $\langle x_T^2 \rangle$ decreases, and accordingly $g(\omega)$ becomes harder.

Taking into account the relation $R \sim (D\tau)^{1/2}$ and the experimentally established relation

$$I/I_{Sn} = 0.2 \ln \tau + 0.9, \quad (4)$$

we obtain

$$R = 1.04 D^{1/2} \exp(0.1(I/I_{Sn} - 0.9)), \quad (5)$$

i.e., the relation that connects the hardening of the vibrational spectrum of tin in the Sn+0.36 at. % Pb system with the increase of the lead clusters.

The softening of the spectrum of the tin oscillations in the case of the Sn-Pb solid solution and its hardening upon decay follow also from measurements of the γ -absorption intensity ratios I_{80K}/I_{300K} . Since there are no magnetic or structural transitions of noticeable rate in Sn-Pb at temperatures 80–300 K, the change of the ratio I_{80K}/I_{300K} can serve as a criterion for the estimate of the vibrational spectrum.^[18] This ratio increases relative to pure tin at the low-frequency burst of $g(\omega)$, and decreases with resonant decrease of $g(\omega)$. The Mössbauer-investigation results are given in Table II.

Thermal expansion. That the vibrational spectrum in the investigated system becomes restructured in the course of its decay is attested also by measurements of the thermal expansion (Fig. 1b). Here, just as in the

TABLE II.

Material	Half-width		Isomeric shift		$f_{80\text{K}}/f_{300\text{K}}$ *
	300 K	80 K	300 K	80 K	
Sn	53	64	105	107	6.15±0.05
Sn + 0.72 at. % Pb	52.5	63	105.5	107.2	6.27±0.05
Sn + 1.1at. % Pb	54.5	62.5	106	107.2	5.69±0.05

* $f_{80\text{K}}/f_{300\text{K}} = 6.26 \pm 0.05$ for the alloy Sn+ 0.36 at. % Pb.

case of the heat capacity, the maximum and minimum of the relative thermal expansion correspond respectively to a resonant burst and to a decrease of the decrease of the density of the vibrational spectrum in the low-temperature region. Indeed, if we represent the temperature expansion as the mean value of the displacement vector u of all the atoms, then, introducing the frequency distribution function $g(\omega)$, we can write

$$\Delta l_T = B^*(\omega, T) g(\omega). \quad (6)$$

The function $B^*(\omega, T)$ is not very sensitive to perturbations of the crystal lattice and decreases rapidly with increasing temperature and frequency. Thus, when (6) is taken into account, it follows that the observed resonant increase of the relative temperature expansion of the Sn-Pb alloy prior to the decay in the low temperature region is connected with the corresponding burst relative to the pure tin of the function $g(\omega)$, which describes the density of the frequency spectrum. On the contrary, the resonant decrease of the relative temperature expansion of the Sn-Pb alloy after the decay is due to the corresponding resonant decrease of the density of the frequency spectrum relative to the pure tin.

Notice should also be taken of the fact that the data on the thermal expansion (Fig. 1b) indicate that the resonant bursts are accompanied by small effects of opposite sign at frequencies higher than the resonant frequency. A phenomenon of this kind was observed by a direct method in a V-Ta alloy.^[19]

The Grüneisen law. A study was also made of the influence of the restructuring of the vibrational spectrum on the low-temperature dependence of the Grüneisen factor

$$\gamma = \alpha V / KC_v, \quad (7)$$

where V is the volume of the system, α is the coefficient of volume expansion, C_v is the heat capacity, and $K = V^{-1}(\partial V / \partial P)_T$ is the compressibility coefficient. Figure 1c shows the change of γ relative to the Grüneisen parameter of pure lead. To estimate γ , the data on C_v and α were taken from the results obtained in the present paper, and the values of V and K were taken from Ref. 20, since they depend little on the temperature. It is seen that the Grüneisen factor has at low temperatures singularities similar to the singularities of the heat capacity and of the coefficient of linear expansion. If account is taken of the previously obtained expressions

for Δl_T and C_v (formulas (1) and (6)), then (7) can be written in the form

$$\gamma = l_0^{-3} \int_0^{\infty} \frac{\partial B(\omega)}{\partial T} g(\omega) d\omega \left(\int_0^{\infty} \frac{\partial B(\omega)}{\partial P} g(\omega) d\omega \right)^{-1} \times \left\{ \int_0^{\infty} \left(\frac{\omega}{2k_B T} \right)^2 \text{sh}^{-2} \left(\frac{\omega}{2k_B T} \right) g(\omega) d\omega \right\}^{-1}. \quad (8)$$

The experimentally observed low-temperature singularities of the behavior of the Grüneisen coefficient can then be unequivocally interpreted on the basis of formulas (8) as the result of corresponding singularities of the spectral density, if it is assumed that the numerator is a function that depends more strongly than the denominator on the perturbation of the crystal lattice. This agrees with the singularities of expression (8) in the limiting case of low temperatures.^[21]

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