Anomalous behavior of the Mössbauer-effect probability in tin-based alloys

N. B. Brandt, R. N. Kuz'min, and V. G. Snigirev

Moscow State University
(Submitted June 7, 1974)
ZhETF Pis. Red. **20**, 104–108 (July 20, 1974)

We have investigated the dependence of the probability f' of the Mössbauer effect in solid solutions based on tin at temperatures 293 and 77 °K. We have observed that for a number of alloys, in the region of small impurity concentrations, a minimum appears on the concentration dependence of f'. We propose an explanation for the minimum and estimate the quasilocal oscillations with SnBi alloys as an example.

1. We investigated the probability f' of the Mössbauer effect on the matrix atoms Sn^{119} in binary alloys SnZ (Z = Zn, Ga, Cd, In, Sb, Tl, Pb, and Bi) in the solid-solution region, as a function of the concentration of the second component at temperatures 293 and 77 °K. The alloys were prepared from tin of special high purity (OVCh brand, 99.995%), and the purity of the component Z was not less than 99.99%. The alloys were subjected to a homogenizing annealing at 175 °C for two weeks. The samples were obtained from the ingots by rolling, following by annealing to remove the stresses, and constituted disks of 25 mm diameter and 20–180 μ thickness, corresponding to contents 1–11.5 mg/cm^2 of the isotope Sn^{119} per unit surface. To prevent the possible decay of certain solid solutions with large impurity contents, the samples were stored in liquid nitrogen. The single-phase character of the alloys was monitored by x-ray diffraction and by measuring the residual resistivity at 4.2 °K.

The measurements were performed with a Mössbauer spectrometer in the constant-acceleration mode, using a multichannel NTA-512 analyzer. The γ quanta were detected with an NaI(Tl) scintillator coupled with a photomultiplier with low intrinsic-noise level, or with a resonant counter.

The sources of resonant 23.8-meV γ quanta were $Sn^{119m}O_2$ and $BaSn^{119m}O_3$. The measurements at 77 °K were made in a special cryostat that excluded the possibility of the exposure of the liquid nitrogen to the γ-quantum beam, thereby ensuring equal attenuation of the beam at room and nitrogen temperatures.

To plot the Mössbauer absorption spectra, we accumulated 60 000–100 000 counts per channel, resulting in an error 0.3–0.4%.

The areas S under the absorption lines were determined graphically with accuracy ~0.7%. To determine the normalized area S_{alloy}/S_{Sn} (S_{Sn} is the area under absorption curve for pure Sn), we took into account the difference between the number of the resonant Sn^{119} nuclei per unit surface of the sample. The error in the determination of S_{alloy}/S_{Sn} was ±1.4% for thick samples and reached 3–4% for thin ones. At small concentrations of the component Z (on the order of 1–2%), the change of the possibility f'_{alloy} of the Mössbauer effect in the alloys was $f'_{alloy} = f'_{Sn}(S_{alloy}/S_{Sn})$, since in this case the nonresonant absorption values are given by $S_{alloy} \approx S_{Sn}$.

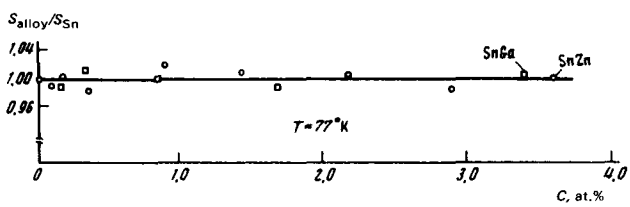

FIG. 1.

2. Figure 1 shows the results of the measurements of S_{alloy}/S_{Sn} for SnZn and SnGa at 77 °K. We see that within the limits of the measurement accuracy the probability of the Mössbauer effect remains constant at all the investigated concentrations c of the components Z.

The plots of S_{alloy}/S_{Sn} against c are entirely different for the solid solutions SnCd, SnIn, SnSb, SnTl, SnPb, and SnBi. The most typical curves for the samples are shown in Fig. 2. The main feature of these curves is the presence of a clearly pronounced minimum, which is located, for the different alloys, in the Z-component concentration region from 0.15 to 0.3 at.%. To the right of the minimum, the value of S_{alloy}/S_{Sn} decreases monotonically. When the temperature changes from 293

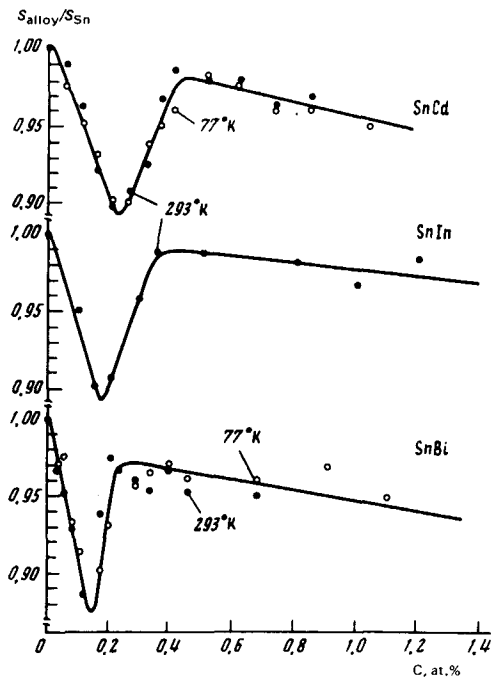

FIG. 2.

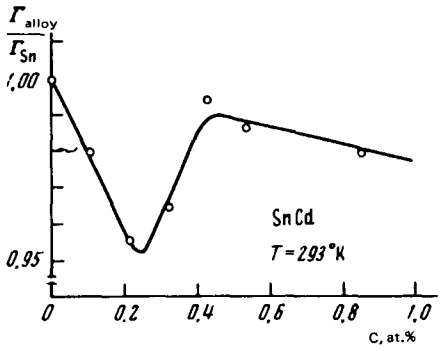

FIG. 3.

to 77 °K, the depth, position, and width of the minimum remain unchanged within the limits of the measurement accuracy.

Careful special investigations have shown that the appearance of a minimum of the $S_{alloy}/S_{Sn}=f(c)$ curves is not the consequence of a possible internal oxidation of the impurity atoms, of the heat-treatment conditions, and of the texture of the samples. Nor is the minimum the result of a possible error in the determination of S_{alloy}, inasmuch as in the region of the minimum the width Γ of the absorption line does not increase (Fig. 3), and the ratio $\Gamma_{alloy}/\Gamma_{Sn}$ is independent of the sample thickness.

3. An analysis of the obtained data shows that the appearance of the minimum is not connected with the dimensions of the impurity atoms, with the character of the change of the lattice parameters (increase or decrease) under the influence of the impurities, with the difference between the valences of the matrix and of the impurity, or with the possibility of cluster formation.

The only parameter that determines the appearance of a minimum on the $S_{alloy}/S_{Sn}=f(c)$ curves is apparently the ratio of the masses M of the impurity end of the matrix element. The minimum appears at $M_{imp}/M_{Sn} \geqslant 0.9$ (for the SnZn and SnGa alloys the mass ratio is 0.55 and 0.58 respectively, and there is no minimum), and consequently characterizes the changes in the vibrational spectrum of the Sn lattice (for light impurity atoms, the local oscillation frequency is larger than ω_{max} for the Sn lattice).

We can propose the following model to explain the appearance of the minimum. The impurity atoms weaken the force constants in the impurity—matrix system, causing the impurity atoms to execute oscillations at quasilocal frequencies (even in the case of comparable masses of the impurity atoms and matrix atoms). Regions with a perturbed phonon spectrum are produced in the lattice near the impurity atoms, and in these regions the atomoscillations amplitudes increase. Within such a region, the oscillation amplitude is maximal at the center (at the impurity atom) and falls off to zero at the boundary of the region. This leads to the appearance of a gradient in the matrix-atom oscillation amplitudes. The decrease of S_{alloy}/S_{Sn} at low impurity concentrations is due to the increase in the number of the perturbed regions in the crystal. At an impurity concentration C_{cr} corresponding to the minimum the perturbed regions begin to come in contact, and the alloy becomes maximally inhomogeneous from the point of view of the oscillations amplitudes. An increase of the overlap with further increase of C is accompanied by an equalization of the oscillation-amplitude gradient in the lattice, which apparently terminates almost completely when the overlap becomes large enough (at $C \approx 2C_{cr}$). The equalization of the amplitude gradient is accompanied by a growth in the Mössbauer-effect probability to almost the initial value. Further monotonic decrease with increasing concentration is typical of the case when the force constants become weaker in the impurity—matrix system.

Simultaneously, starting with the instant when the perturbed regions come in contact, an indirect phonon interaction (via the matrix atoms) sets in between the impurity atoms, and leads to the formation of a low-frequency peak of the quasilocal oscillations (QLO) in the phonon spectrum of tin.

The considered model allows us to make the following estimates for the quasilocal oscillations in the alloys. For example, for SnBi we have $C_{cr}=1.5\times10^{-3}$, dimension of the perturbed region $R \approx 25$ Å, $\omega_{QLO} \approx 4 \times 10^{12}$ sec^{-1}, width of the QLO peak $\Gamma_{QLO} \approx 9\times10^{11}$ sec^{-1}, QLO excitation temperature $\Theta_{QLO} \approx 32$ °C, and the amplitude of the Bi impurity atom oscillations at $T=293$ °K is ~6% of the averaged lattice parameter and exceeds by a factor 1.6 the amplitude of the tin-atom vibrations in the unperturbed matrix. The role of the QLO increases as the temperature decreases to $T \sim \Theta_{QLO}$. At $T=\Theta_{QLO}$ the QLO are quenched and the minima on the concentration dependences of S_{alloy}/S_{Sn} should vanish.