SOVIET PHYSICS JETP VOLUME 19, NUMBER 6 DECEMBER, 1964

THE MÖSSBAUER EFFECT IN BINARY TIN COMPOUNDS

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Submitted to JETP editor January 17, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) **46**, 1996-2002 (June, 1964)

Resonance absorption of γ radiation by Sn^{119} nuclei in the binary compounds SnAs, SnSb, SnTe, and SnPt is investigated within a broad temperature range. For all four compounds the probability f′ of recoil-free absorption and its temperature dependence cannot be described by only a single parameter in the Debye approximation. This result is attributed to the influence of the optical branches of the phonon spectrum. The measurements of f′ are interpreted qualitatively using a simple phonon spectrum model constructed by superposing the Debye and Einstein spectra. The measurements of absorption line widths, quadrupole interactions, and chemical isomeric shifts are used to analyze properties of the chemical bonds and structures of the investigated compounds.

THE present work investigates the characteristics of the Mössbauer effect (the probability of the effect and its temperature dependence, isomeric shifts, and line widths) in certain binary tin compounds having crystal lattices of the NaCl or closely similar types. A more definite interpretation of the characteristics of the effect can be expected for these compounds than for more complex structures. Binary compounds are of particular interest for determining how the Mössbauer effect is influenced by the optical branches of the phonon spectrum.[1] The probability of the effect in cubic lattices has been calculated in [2], with optical vibrations taken into account. A direct comparison between theory and experiment requires knowledge of the force constants (or other equivalent characteristics), which are usually unknown. In analyzing experimental data one is therefore compelled to follow the artificial procedure of characterizing the probability of the Mössbauer effect by an "effective Debye temperature" Θ, which is calculated from the Debye approximation formula using the experimental probability f′ of recoil-free photon absorption. The temperature dependence of Θ is regarded as indicating an essential difference between the phonon and Debye spectra, specifically the presence of optical branches.

It is obvious, however, that the effective temperature obtained in the foregoing manner cannot generally be used directly to obtain a more definite interpretation of the results. We recall that with decreasing temperature both the increase of Θ (in magnesium stannide[3]) and its decrease (in metal oxides [4,5]) have been observed. Our explanation[3] of the increase of Θ with decreasing temperature is probably correct, but a decrease of Θ at lower temperatures cannot be interpreted in as simple a manner. In the next section we shall therefore consider the probability of the Mössbauer effect for a simple model of the phonon spectrum. Quantitative agreement with experiment cannot be expected because of the elementary character of the model, which does, however, furnish a simple means of relating certain properties of the phonon spectrum to the effective temperature Θ, giving the latter a great deal of physical meaning.

PROBABILITY OF THE MÖSSBAUER EFFECT FOR A SIMPLE MODEL OF THE PHONON SPECTRUM

Let us consider a simple model of the phonon spectrum of a crystal, formed by superimposing the Debye and Einstein spectra with the characteristic temperatures Θ_D and Θ_E. This model is sometimes used to approximate real spectra, as in calculating specific heats. In our case the Einstein frequency represents in some measure the existence of optical frequencies in the real spectrum. The spectral density of the vibrational frequencies in an absorbing atom, normalized to unity, can be represented by

$$\psi(\omega) = \mu\delta(\omega - \omega_E) + (1 - \mu)3\omega^2 / \omega^3_D,$$

where μ is the relative contribution of the Einstein frequency ($0 \leq \mu \leq 1$). Writing the probability of the Mössbauer effect in the customary form f′

$= e^{-Z}$, we easily find that in the present case $Z = \mu Z_E + (1-\mu)Z_D$, where*

$$Z_D = \frac{12R}{k\Theta_D}\left(\frac{T}{\Theta_D}\right)^2 \int\limits_0^{\Theta_D/2T} x \operatorname{cth} x dx,$$

$$Z_E = \frac{R}{k\Theta_E} \operatorname{cth}\left(\frac{\Theta_E}{2T}\right)$$

(R is the recoil energy for a free atom). These formulas were obtained by calculating the temperature-dependent rms atomic displacement, which is easily obtained by using Kagan's results,[6] for example.

The foregoing expressions show that the probability depends on the three parameters μ, Θ_D, and $\lambda = \Theta_D/\Theta_E$. The probability and its temperature dependence can now be calculated for different values of these parameters. By comparing the values obtained for f′ with the Debye approximation formula we can now obtain the "effective Debye temperature" Θ and determine its dependence on μ, Θ_D, λ, and temperature. Some results that are important for our purposes can be obtained analytically; omitting the simple but somewhat tedious calculations, we present the main results.

1. For any values of the parameters μ and λ at temperatures $T > \Theta_D, \Theta_E$, the probability of the Mössbauer effect and its temperature dependence can be described using only a single parameter in the Debye approximation when the effective temperature is given by

$$\Theta = \Theta_\infty = \Theta_D\{3/(3-\mu[3-\lambda^2])\}^{1/2}. \quad (1)$$

It is here seen that $\Theta_\infty > \Theta_D$ when $\lambda < \sqrt{3}$.

2. At low temperatures Θ can be either higher or lower than Θ_∞. When T = 0 the effective temperature is

$$\Theta = \Theta_0 = \Theta_D / (1 - \mu + {}^2/_3(\mu\lambda)). \quad (2)$$

A comparison of (1) and (2) shows that $\Theta_0 > \Theta_\infty$ when

$$\mu < \frac{9+3\lambda^2-12\lambda}{9+4\lambda^2-12\lambda}. \quad (3)$$

If the optical frequencies do not greatly exceed the frequency limit of the quasi-continuous spectrum, the result $\Theta_0 < \Theta_\infty$ indicates a large amplitude of Mössbauer-atom optical vibrations. We note that for some values of μ and λ the temperature dependence of f′ can be represented using a single parameter within the entire temperature range, despite the great difference between the phonon and Debye spectra.

EXPERIMENT

We have investigated the compounds SnAs, SnSb, SnTe, and SnPt, which were prepared by alloying natural tin with suitable amounts of each of the other components. The alloys were homogenized, crushed to a powder, and annealed for several hours in a vacuum at 300°C. The structure and parameters of each lattice were determined by x-ray analysis.

SnAs and SnTe belong to the NaCl type with the lattice constants a = 5.72 Å and 6.30 Å, respectively. SnSb has a rhombohedrally distorted NaCl structure with the lattice parameters a = 6.23 Å and $\alpha = 89.4°$. SnPt has a hexagonal lattice with a = 4.11 Å and c = 5.44 Å (the NiAs structure). These results of the x-ray analysis agree with the literature.

The resonance absorption spectra were measured using a Sn^{119m} source in the compound Mg_2Sn; the emission line width of this source is very close to the natural line width.[3] The source was kept at liquid nitrogen temperature; the measurements and treatment of the data were performed as in our earlier work.[6,7] The absorption spectrum of each compound was measured with absorbers of different thicknesses in a broad temperature range. In each case we determined the magnitude of the Mössbauer effect, the line width and the shift of the absorption line relative to the emission line.

EXPERIMENTAL RESULTS AND DISCUSSION

The principal characteristics of the Mössbauer effect in SnAs, SnSb, SnTe, and SnPt at 77° and 290°K are given in the accompanying table.

Compound	Γ_a, mm/sec	δ, mm/sec		f′		Θ, °K	
		77° K	290° K	77° K	290° K	77	290
SnAs	0.34±0.02	0.67±0.03	0.62±0.02	0.50±0.05	0.20±0.02	145±15	180±10
SnSb	0.42±0.04	0.80±0.03	0.76±0.03	0.31±0.03	0.084±0.005	110±6	144±3
SnTe	0.36±0.03	1.51±0.02	1.43±0.03	0.37±0.03	0.070±0.006	120±5	139±3
SnPt	—	−0.22±0.02	−0.30±0.02	0.50±0.06	0.30±0.04	145±15	210±10

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*cth = coth.

1. Line widths. For SnAs and SnTe the absorption line width Γ_a equals, within experimental error, the natural line width 23.8 keV of an excited Sn^{119} state, thus indicating cubic lattices for these compounds. For SnSb the width Γ_a somewhat exceeds the natural width. It is reasonable to assume that rhombohedral distortion of the SnSb lattice creates a small electric field gradient in tin atoms of this compound, thus broadening the line.

In the case of SnPt, using thin absorbers (less than 10 mg/cm^2) a doublet structure of the absorption spectrum (quadrupole splitting) was observed. Figure 1 shows one of the spectra; the separation of the hfs components indicates the velocity 0.75 ± 0.10 mm/sec. In no case was Γ_a observed to depend on the temperature of the absorber.

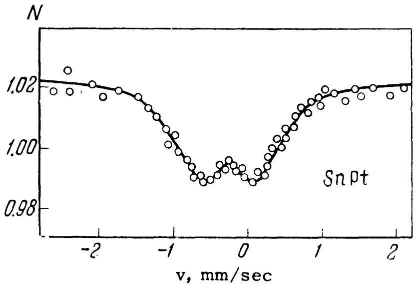
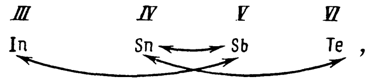


FIG. 1. Resonance absorption spectrum of SnPt sample 9 mg/cm^2 thick at room temperature. Abscissa – absorber velocity.

2. Chemical isomeric shifts. We write the symbols for a row of elements, as shown here, under the group numbers representing the num-



bers of valence electrons; the arrows indicate type AB compounds. The combinations In-Sb and Sn-Te with even total numbers of electrons form structures with electron-pair hybrid bonds. The compound InSb has the ZnS structure with sp^3 hybridization and four nearest neighbors for each atom. The Sn-Te combination leads to the NaCl structure with p^2 bonds. For SnSb and SnAs we can reasonably expect an intermediate chemical bond retaining the bond elements that characterize SnTe.

The chemical isomeric shift observed for SnTe is characteristic of divalent tin compounds, and indicates that the chemical bond in SnTe is formed by p electrons. This bond is based on 90° valence angles, in agreement with the structure of the compound. By considering the possible valence schemes for SnSb and SnAs, the formation of mixed sp and p^2 bonds can be established. In SnSb these bonds differ in length, producing a rhombohedral distortion of the NaCl structure, whereas in SnAs the bonds are of equal length (As atoms having smaller geometrical size than Sb atoms); this again leads to a NaCl structure but with a somewhat different valence scheme than for SnTe. The effective numbers of tin atom electrons in the 5s state are estimated to be 1.33 and 1.5 for SnAs and SnSb, respectively. The formation of sp bonds results in a reduced electron density for the tin atom and therefore to a reduced isomeric shift. A linear extrapolation from SnTe (p^2 bond) to α Sn (sp^3 bond) yields effective numbers of s electrons in the tin atom for SnAs and SnSb that agree with the foregoing calculated values. It is thus indicated that such effects as the perturbation of the electron wave functions of filled shells by valence electrons are practically identical for the given compounds.

The shift for SnPt is characteristic of tin compounds and alloys with transition metals. A considerable reduction of electron density in tin atoms is evidently associated with the presence of unfilled shells in transition elements.

The similarity or difference in the chemical nature of the compounds is associated to a considerable degree with their ability to form solid solutions. We attempted to produce the quasi-binary solid solutions SnTe-SnAs, SnTe-SnSb, and SnAs-SnSb. In the first two cases an x-ray examination did not reveal the formation of solid solutions. After 700-hour anneals at 330°C solid solutions of SnAs-SnSb based on the rhombohedral SnSb lattice were observed for a broad range of concentrations (at least to molecular 70% SnAs). We note that the isomeric shifts for SnAs and SnSb resembled each other closely but differed considerably from the shift for SnTe. Thus, shifts that are very close in magnitude, reflecting the chemical similarity of compounds, indicate that such compounds can form solid solutions.

3. Probability of Mössbauer effect. Figure 2

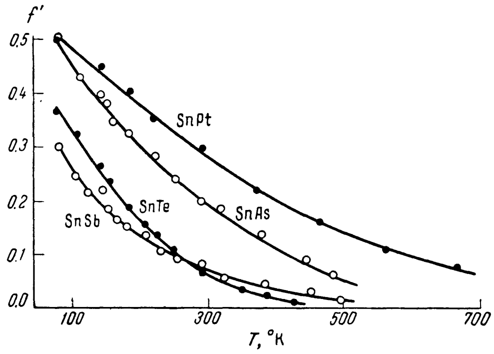


FIG. 2. Probability f' of recoil-free absorption versus temperature in SnAs, SnSb, SnTe, and SnPt.

shows the temperature dependence of the recoil-free photon absorption probability f′ for SnAs, SnSb, SnTe, and SnPt. In no case can the probability of the effect and its temperature dependence be described by only a single parameter in the Debye approximation. The table shows that the effective temperature Θ is not identical for 77° and 290°K.

The influence of the optical branches of the phonon spectrum on f′ is especially clear in the case of SnPt. The large difference between the atomic masses in the crystal induces optical vibrations in the high-frequency region of the phonon spectrum. Tin atoms must have large vibrational amplitudes in the optical branches (corresponding to a large value of μ), because they are the lighter of the two kinds of atoms comprising the crystal. Accordingly, f′ decreases very slowly with a rising temperature, remaining of considerable magnitude at high temperatures. High-frequency optical vibrations can also be expected in SnAs. In this case, however, tin is the heavier atom; therefore its vibrational amplitude in the optical branches will not be as large as in SnPt, and there should be a sharper temperature dependence of f′, other conditions being equal. These results are in qualitative agreement with the theoretical conclusions in [1,2].

Because of the approximately equal atomic masses in SnSb and SnTe we cannot assume the existence of high-frequency optical vibrations in the phonon spectrum. Nevertheless, the optical branches can result in a considerable deviation from the Debye spectrum. Figure 2 shows the very similar temperature dependences of f′ for these two compounds, despite the very marked difference between other properties of these crystals such as the melting point, which is 790°C for SnTe and 420°C for SnSb.

The data in Fig. 2 were used to calculate the temperature dependences of the effective Debye temperatures Θ shown in Fig. 3; for all four compounds Θ is smaller at low temperatures than at high temperatures, and remains constant above a certain temperature (150–250°K for the different compounds). The constancy of Θ at sufficiently high temperatures indicates the transition to the so-called classical limit.

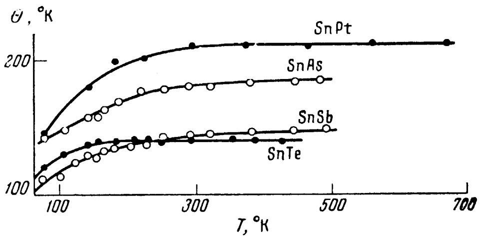


FIG. 3. Temperature dependence of the effective Debye temperature Θ for SnAs, SnSb, SnTe, and SnPt.

For SnTe the Debye temperature was determined[8] (by a specific heat measurement) to be 130°, which is very close to our value $\Theta_\infty = 139 \pm 3°$. This result agrees naturally with the foregoing hypothesis that the vibrational spectrum of SnTe does not contain optical branches having frequencies appreciably exceeding the frequency limit of the quasi-continuous spectrum.

The reduction of Θ at low temperatures in accordance with the considered model of the phonon spectrum can occur within broad ranges of the parameters μ and λ [see Eq. (3)]. The observed dependences $\Theta(T)$ agree qualitatively with the considered model if it is assumed that for SnTe, SnSb, and SnAs the respective values of Θ_E and Θ_D are close, and that for SnPt there is a high value of μ. We note, however, that there is no quantitative agreement; the observed temperature dependences of Θ exceed predictions based on the considered model of the phonon spectrum.

The authors wish to thank A. I. Firov for his assistance.

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Translated by I. Emin
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