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Dynamics of Tin Impurity Oscillations in Lead

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The concentration dependences of the Mössbauer effect probability f′ for tin impurities in lead (the impurity content in lead varied from 1 to 8 atomic %) are investigated at 4.2 and 78°K, and the concentration dependences of the velocity of propagation of longitudinal ultrasound oscillations in Pb-Sn and Pb-In alloys containing respectively from 1 to 15 atomic % of Sn and from 1 to 26 atomic % of In are investigated at 300 and 78°K. A minimum in f′ is observed in the 1–3 atomic % Sn range, and after that the value of f′ increases monotonically with increasing tin content. The nonmonotonic dependence of f′ on composition in Pb-Sn alloys can be explained by assuming that a transition occurs from infinitely dilute alloys to concentrated ones. The values of f′ at 4.2°K enable us to conclude that the tin impurity, as well as the indium impurity, oscillates in a localized frequency band a little higher than the upper edge of the lead phonon spectrum. This can lead to an increase in the superconducting transition temperature for the alloy via the electron-phonon interaction.

THE effect of an impurity on the superconducting transition temperature T_S of a metal is realized via the change in its electron and phonon properties which are related by the electron-phonon interaction. The case is of interest when the impurity oscillates in the high frequency part of the phonon spectrum, noticeably increasing here the density of states and changing the electron-photon interaction constant, since the growth of these factors aids the growth of T_S.

According to experiments on superconducting tunneling, the phonon spectrum of lead consists of two peaks. The low frequency peak (for phonons with transverse polarization) has a maximum in the range of 4.4×10^{-3} eV, the maximum of the high-frequency peak (for phonons with longitudinal polarization) is situated near 8.5×10^{-3} eV. The high frequency edge of the distribution function for the oscillation frequencies is situated in the range $(9-10) \times 10^{-3}$ eV.[1] Since the high frequency edge of the phonon spectrum of white tin extends to 17.7×10^{-3} eV, and for indium up to 14×10^{-3} eV,[1] then for a lead matrix among the polyvalent metals the most favorable are the conditions for the appearance of local oscillations of impurity atoms both from the point of view of a lower maximum phonon frequency, and also from the point of view of greater mass of the matrix atoms. Experiment has shown[2] that the impurity atoms of indium in lead oscillate in a localized frequency band situated somewhat higher than the peak of the longitudinal oscillations of the lead phonon spectrum and situated in the energy domain of 9.5×10^{-3} eV (the content of In in Pb varied from 1 to 6 atomic %). An analogous result was obtained for Pb-In alloys containing 3.12 and 26 atomic % of In.[3] The ratios of the masses of atoms of indium and lead, and also of tin and lead are almost equal, and therefore it is not excluded that a tin impurity in lead also oscillates at local frequencies. Calculations[4] show that frequencies of local oscillations of impurity atoms of In, Sn, and Sb in Pb must be practically the same on the assumption that the impurities are isotopic.

As the composition of the alloy is varied not only does the frequency of local oscillations change, but so do the electronic properties and the intensity of electron-phonon interaction, and therefore in order to obtain a conclusion as to the degree of importance of one or another factor in determining the value of T_S of the alloy one needs detailed information on its electron and phonon characteristics. So far as we know, at the present time no detailed investigations have been carried out of the special features of oscillations of impurity atoms in superconducting metals, and in particular in lead, on the basis of which one might draw conclusions with regard to the role played by the high frequency oscillations of the impurity in the change of T_S of a particular alloy. In the present paper we have carried out a measurement of the probability of the Mössbauer effect probability f′ for nuclei of Sn^{119} impurity atoms of tin in lead at temperatures of 4.2 and 78°K. The alloys contained from 1 to 8 atomic % of Sn. Simultaneously with the Mössbauer measurements a determination was made at 300 and 78°K of the velocity of propagation of transverse ultrasound oscillations of 1 MHz frequency in Pb-Sn alloys containing from 1 to 15 atomic % of Sn, and in alloys of Pb-In containing from 1 to 26 atomic % of In.

From the values of f′ at 4.2 and 78°K characteristic temperatures were calculated for a tin impurity $\Theta(-1)$ and $\Theta(-2)$ which correspond to the minus first and the minus second moments of the phonon spectrum of the impurity related by well known expressions[5] with the values for the probability of the Mössbauer effect f′ in the low temperature limit which is attained practically at helium temperatures, and the value of f′ in the range of linear temperature dependence of the probability of the effect within the limits of which in the case of Pb-Sn alloys the liquid nitrogen temperature is situated (cf., the table).

The velocity of propagation of ultrasound oscillations in Pb-Sn and Pb-In alloys was determined to serve as a qualitative control on the change in the Debye temperature of the alloy Θ_D. As is well known,[6]

$$\Theta_D = \frac{\hbar}{k}\left(\frac{9N}{4\pi V}\right)^{1/3}\frac{v_l v_t}{(v_l^3 + 2v_l^3)^{1/3}},$$

c, at. %	f' (4,2° K)	f' (78° K)	Θ (—1) °K	Θ (—2) °K	$\hbar\omega_0$ (4,2 °K), 10^{-3} eV	f' (78 °K) calc.
1	0,79		189		10.6	
1,14	0.81	0.33	212	111	11.9	0,65
1,43	0.77		168		9.4	
1.53	0.69		120		6,7	
1.74	0.81		216		12.1	
2.1	0,65		104		5.82	
2,19	0.66	0.23	106	97	6.03	0.37
2.34	0.68		115		6,43	
2.46	0.71	0,25	129	100	7,31	0.50
2.48	0.75	0,25	152	100	8,5	0.59
3	0.80	0,28	206	104	11,6	0.73
4	0,78		180		10.1	
5	0.82		224		12.6	
6	0.80		197		11.2	
7	0,83		232		13.1	
8	0,85		276		15.4	

where N is the Avogadro number, V is the average volume per atom in the alloy, v_l and v_t are the velocities of propagation of ultrasound oscillations with longitudinal and transverse polarizations (V, v_l and v_t are determined for T = 0), k is the Boltzmann constant. Since v_l and v_t do not differ in order of magnitude for a polycrystalline solid and have the same nature of concentration dependences for an isotropic medium, then the Debye temperature varies with concentration as an average between the dependences for v_l and v_t. The formula quoted above is valid only for T = 0, but qualitatively the dependence of the velocity of propagation of ultrasound on the composition of the alloy does not change in going over to a finite temperature.

The Pb-Sn alloys for Mössbauer measurements were prepared from lead of purity 99.999 and tin enriched in the stable Sn^{119} isotope up to 85.2%. The components were alloyed in glass ampoules in vacuum in a high frequency furnace, being maintained in the molten state for 15 min. Then the ingot was rolled out into a foil of thickness of approximately 50 μ which was then annealed at a temperature of 180°C during 48 hours. A number of alloys of Pb-Sn containing from 1 to 3 atomic % of tin was maintained in the liquid state in the course of a day in a resistance furnace in order to obtain a more complete guarantee of uniform distribution of the impurity. Alloys for ultrasound investigations were prepared from lead of purity 99.999, from tin of brand OVCh-000 and from indium of brand In-00 utilizing the same method, only instead of rolling out, the butt ends of samples in the form of cylinders of length 30 mm and of diameter 25 mm were subjected to mechanical treatment for attachment of quartz plates. In order to eliminate error in the velocity of propagation of ultrasound due to the possible texture of alloys the velocity was also determined in a direction perpendicular to the axis of the cylindrical sample, and for this the side surface of the ingots was subjected to appropriate mechanical treatment. In the predominant majority of cases the values of the velocities of propagation of ultrasound along the axis of the ingot and in a perpendicular direction agreed with an accuracy up to 10 m/sec and in subsequent discussion the average values of the velocities were utilized. The composition of the alloys was controlled by means of chemical analysis.

The limiting solubility of tin in lead at room temperature amounts to 3.2 atomic %, and therefore Pb-Sn alloys with a higher concentration of tin were maintained in the furnace at a temperature of 180°C and were placed in the cryostat immediately before measurement. Evidence concerning the negligibly small decomposition of solid solutions of Pb-Sn in the course of a measurement was obtained on the basis of the values of isomeric shifts for tin impurity in lead, which corresponded to the state of a solid solution in all cases during the time required for the measurement of the velocity of propagation of ultrasound and of the probability of the Mössbauer effect.

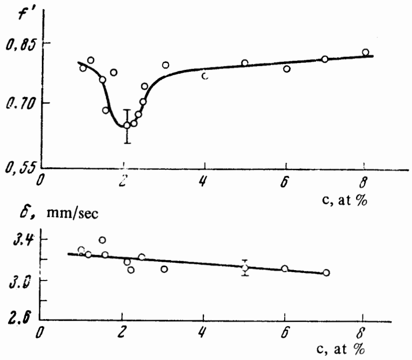

FIG. 1. Dependence of f′ and δ on the composition of the alloy.

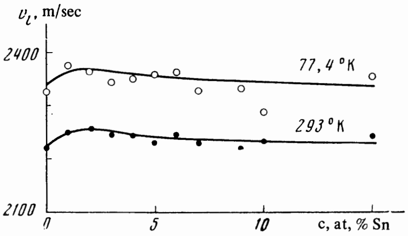

FIG. 2. Concentration dependences of v_l in Pb-Sn alloys.

Absolute values of the probability of the Mössbauer effect were determined from the area bounded by the resonance peak utilizing β-Sn foils as standard absorbers with a known value of f′. The Mössbauer absorption spectra consisted of singlet lines. $BaSnO_3$ at room temperature served as a source of resonance γ quanta. The error in determining the area of the resonance peak does not exceed 1%, and the accuracy of measuring the value of f′ essentially depends on the error in determining the number of resonance nuclei per 1 cm^2 of absorber area. The effective thickness of the absorber was determined by weighing the foils of Pb-Sn alloys on analytical balances utilizing the value of the tin content determined by means of chemical analysis. The relative error of the chemical analysis amounts to ±5%, and this essentially determined the relative error in the measurement of the value of f′, which turned out, in accordance with repeated determinations of the probability of the Mössbauer effect for alloys of a single initial composition to be equal to ±7%.

The velocity of propagation of ultrasound was determined by means of a method described by Bezuglyĭ.[7]

Figure 1 shows the concentration dependences of f′ and of the position of the absorption line δ at 4.2°K, and Figs. 2 and 3 show the corresponding dependences of v_l at 78 and 300°K for Pb-Sn and Pb-In alloys. First of all our attention is drawn to the minimum at 4.2°K in the domain of low concentrations of tin impurity which reminds us of an analogous behavior in the probability of the Mössbauer effect for tin impurity in indium.[8] The

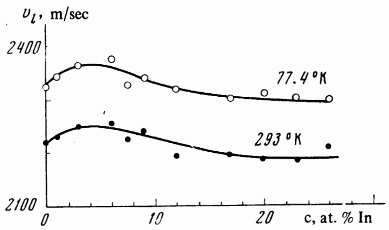

FIG. 3. Concentration dependences of v_l in Pb-In alloys.

variation in the value of f′ in the concentration range from 1 to 2.1 atomic % amounts only to approximately 0.15, while the absolute error in the determination of f′ amounts to ±0.05. From this it follows that the change in the probability of the Mössbauer effect in this region exceeds experimental error by a factor of three.

If the tin impurity in lead would behave as an isotopic impurity, then in accordance with the often used expression $\Theta_D' = \Theta_D (M/M')^{1/2}$ obtained for an isotopic impurity interacting in a cubic lattice only with the nearest neighbors (Θ_D' and M′ are the Debye temperature and the mass of the impurity atom, Θ_D and M are the same quantities respectively for the matrix), taking for Θ_D for lead at 4.2°K a value equal to 98°K,[9] we obtain $\Theta_D' = 129°K$ and f′ = 0.71. Experiment gives a higher value of f′ at a concentration of the tin impurity outside the minimum of f′ in Fig. 1, and this indicates the establishment of more rigid couplings of the impurity with the matrix atoms in the model of only nearest neighbor interaction.

The minimum in the probability of the Mössbauer effect in the range of 1–3 atomic % of Sn is related to either a change in the force constants for the alloy or in the range of interaction of the impurity with the matrix atoms surrounding it, or to both causes simultaneously. We assume that such a change can be brought about by transition from single impurities noninteracting with each other to interacting ones, or, in other words, by a transition from very dilute solid solutions to concentrated alloys when overlapping occurs of regions of perturbed electron density which screen the impurity atoms. In such a transition it is possible for a change to occur in the interaction of the impurity with its neighbors and for new force constants to become established. One can assume the presence of quite long range interactions in lead, taking into account the results of calculations of the phonon spectrum of Pb, which turned out to be quite different from the actual situation, if one utilizes the model of force constants which takes into account the interaction of eight nearest neighbors.[10]

As can be seen from Fig. 1, the position of the absorption line δ for a tin impurity in lead is almost independent of the composition decreasing slightly with increasing content of tin in the alloy. Owing to the value of the experimental error in the determination of δ equal to ±0.02 mm/sec we cannot draw a definite conclusion concerning the presence or absence of specific features of the concentration dependence of δ in the neighborhood of the minimum in f′.

The variation of the velocity of propagation of ultrasound v_l in Pb-Sn and Pb-In alloys with their composition is qualitatively the same and represents for the greater part of the alloys a monotonically falling dependence. In the region of low concentrations of the impurity a smeared out maximum in v_l is noticeable which for the Pb-Sn alloys is displaced in the direction of smaller concentrations. This can be related to the fact that an atom of tin is a stronger perturbation compared to an atom of indium in a lead matrix.

We are unaware of any results of determining Θ_D for Pb-Sn alloys by means of ultrasound or calorimetric methods. But there exists data in the literature concerning Θ_D for Pb-In, Pb-Bi and Pb-Tl alloys according to which Θ_D falls off approximately linearly with increasing impurity concentration[11-14] independently of the sign of the difference in the valences of an impurity and the matrix and of the change in the parameters of the crystalline lattice (a Bi impurity increases, while In, Tl and Sn impurities decrease the lattice constant for lead).[15] From these data and also from the analogy in the behavior of v_l for Pb-Sn and Pb-In alloys (Figs. 2 and 3) one can assume that Θ_D for Pb-Sn alloys will also decrease with increasing concentration of tin at least for concentrations beyond the maximum in v_l.

As can be seen from Fig. 1, the values of f′ show a tendency towards increase with increasing concentration of tin above 3 atomic % in contrast to the presumed behavior of the Debye temperature for the alloy, and this can be related to the oscillations of impurity atoms in a localized frequency band. In this case the impurity atoms either increase the probability of oscillations at local frequencies at the expense of oscillations in the continuous spectrum with increasing tin concentration, or the position of the localized band is shifted in the direction of higher frequencies.

The probability of the Mössbauer effect for an atom oscillating at local frequencies with a distribution of oscillations in the form of an Einstein peak with the value of ω_0 for the position of the maximum in the δ-function is determined by the expression[16]

$$f' = \exp\left[-\frac{E_R}{\hbar\omega_0}\,\mathrm{cth}\left(\frac{\hbar\omega_0}{2kT}\right)\right],$$

where E_R is the recoil energy, and k is the Boltzmann constant. In the table are listed values of $\hbar\omega_0$ for atoms of tin in Pb at 4.2°K calculated with the aid of this expression on the assumption that the tin atoms do not oscillate in the continuous spectrum. As can be seen from the table, the values of the energies of local phonons for compositions of alloys which do not lie in the region of the minimum in f′ turn out to be close to the value of 9.5×10^{-3} eV obtained for the maximum in the distribution of local frequencies of indium impurity in lead[2] and above the upper edge of the phonon spectrum of pure lead. It should be noted that the small values of the probability of the Mössbauer effect f′, and correspondingly of the frequencies of oscillations of tin impurity atoms in the neighborhood of the minimum in f′, can be related not with a downward shift of the localized frequency band along the energy scale, but with an increasing probability of oscillations of the impurity in the continuous spectrum (the value of f′ in the general case is a product of probabilities corresponding to oscillations of the impurity at local frequencies and in the continuous spectrum). Of future interest are direct measurements of phonon spectra of Pb-Sn alloys in the region of compositions investigated here in order to obtain more definite information concerning the oscillation spectrum of the tin impurity.

The function $\alpha^2(\omega)$ which characterizes the intensity of the electron-phonon interaction for phonons of frequency ω in the case of lead turns out to be approximately by a factor of two greater in the region of the high frequency peak in the phonon spectrum compared to the region of the low frequency peak.[17,18] As a result of this the presence of high frequency impurity oscillations in Pb-Sn alloys can in principle affect the value of T_S through a change in the function $\alpha^2(\omega)$. The superconducting transition temperature for Pb-Sn alloys increases according to a concave curve with increasing tin content,[19] and in the concentration region up to 2–3 atomic % one observes a considerable scatter of points. In other papers[20,21] where measurements of T_S for Pb-Sn alloys were also carried out the composition of alloys was varied by large steps in concentration, and therefore at the present time there is no possibility to carry out a comparison of the dependences of f' and T_S. In this connection it is desirable to have a more thorough, than in [19–21], determination of T_S by small steps in the concentrations of these alloys in the neighborhood of the minimum in f' where possibility of a change in the electronic properties exists and characteristic features occur in the nature of the oscillations of the impurity atoms.

An analysis of the data available in the literature on the values of T_S of alloys based on lead[19–21] leads to the conclusion that a change in the electronic properties exerts a great influence on the values of T_S. Thus impurities with a valence lower than that of lead (Hg, Cd, In, Tl) diminish T_S while those with a greater valence (Sb, Bi) or equal valence (Sn) increase this temperature. Calorimetric measurements and results obtained by means of determining critical magnetic fields show that the density of states at the Fermi level of lead decreases on introduction of indium[11,1] and thallium[13,22] and increases on introduction of bismuth[13,22] approximately linearly with the impurity concentration. At the same time the electron-phonon interaction constant increases as a result of introducing bismuth and diminishes as a result of introducing thallium. As a result of this the presence of high frequency oscillations of an indium impurity in lead is masked by other factors. Nevertheless, the effect of high frequency oscillations of a light impurity cannot be excluded, since in accordance with the data of [21] a Tl impurity having the same valence as In diminishes the T_S of lead more strongly than an In impurity, while a Sb impurity increases it considerably more than a Bi impurity.

A hypothesis concerning a relation between the minimum of the Mössbauer effect probability at 4.2°K for Sn^{119} nuclei in Pb-Sn alloys (Fig. 1) with a change in the nature of the screening of impurity atoms can in principle be checked by means of an NMR Knight shift for Sn^{119} and Pb^{207} nuclei if this readjustment is to a large extent connected with states at the Fermi level. The data available in the literature on the Knight shift for Pb^{207} nuclei in alloys based on lead with polyvalent impurities (tin among them) do not demonstrate the presence of any kind of anomaly in the region of low impurity concentrations. This, in particular, may be associated with too large steps in the variation of the composition of the alloy.[23]

The value of f' at 4.2°K for alloys in the neighborhood of the minimum is relatively small and therefore it is reasonable to check the possibility of a low temperature anharmonism of oscillations of impurity atoms. In [24], an inequality is obtained for two values of f' determined at different temperatures T and T_0 which should be valid in the harmonic approximation. In this case the phonon spectrum of the compound is represented by an Einstein distribution and the inequality has the form

$$\frac{1}{\omega(T)}\,\mathrm{cth}\,\frac{\hbar\omega(T)}{2kT} < \frac{1}{\omega(T_0)}\,\mathrm{cth}\,\frac{\hbar\omega(T_0)}{2kT} \qquad (T \leqslant T_0).$$

Utilizing for the comparison values of f' the values determined at 4.2°K as the most accurate ones a calculation was made with the aid of this inequality of the limiting values of f' at 78°K which cannot be exceeded if the oscillations of atoms in Pb-Sn alloys can be described by the harmonic approximation. The results of the calculation and of the measurements of f' at 78°K are shown in the table from which it can be seen that low temperature anharmonism is not manifested.

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