CONCENTRATION DEPENDENCE OF THE PROBABILITY OF THE MOSSBAUER EFFECT IN ALLOYING OF SEMICONDUCTORS

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We investigated the dependence of the Mossbauer-effect probability f' on the Te^{125} nuclei in PbTe on the degree of doping with indium and lanthanum in the concentration range from zero to 1% (by weight). The radiation source was Te^{125m} (gamma-transition energy 35.6 keV) in the compound TeO_3 [1]. In all the measurements, the source was at room temperature and the absorbers at 77°K. We used polycrystalline samples synthesized with natural tellurium [2] with component purity: Pb - 99.999, Te - 99.999, In - 99.9995, and La - 99.93. The sample thickness in terms of Te was the same in all measurements - 30 mg/cm^2. The experiments were performed with a spectrometer of the electrodynamic type with uniformly-accelerated motion of the radiation source and a scintillation system for recording the pulses.

Experimental Results and Discussion

The Mossbauer spectra of all samples consisted of a single line with the same value of the isomer shift, $\delta = 0.12 \pm 0.04$ cm/sec. Figure 1 shows $\ln(f'/f'_0)$ vs. the concentration of In and La (f' - probability of Mossbauer effect for doped PbTe samples, f_0 - for undoped sample), and Fig. 2 shows the experimental line width Γ_e vs. the concentration of In and La in PbTe.

The experimental results can be explained in the following manner. It is known that crystals always contain a certain number of defects, including Schottky vacancies. Electrophysical measurements have shown that in the investigated undoped PbTe sample the excess of the Pb vacancies over the Te vacancies is 1.9×10^{18} cm^{-3}, which agrees also with the results of [3]. In the concentration region 0 - C_1 (for curve 1, Fig. 1) the lattice defects are Schottky vacancies, and their filling with impurity atoms, in this case, In) naturally leads to a decrease of the lattice potential energy, thereby increasing f', inasmuch as the rms

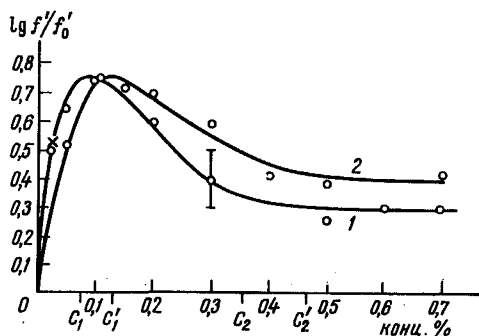

Fig. 1. Mossbauer-effect probability vs. the concentration of the In and La impurity atoms in the semiconductor PbTe: 1 - doped, 2 - undoped.

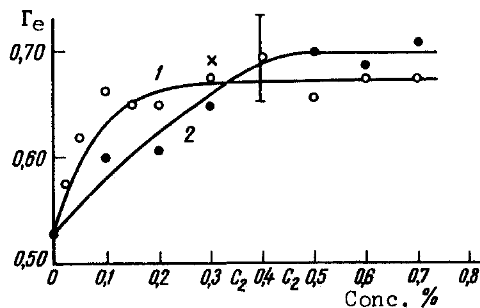

Fig. 2. Line width Γ_e as a function of the concentration of the impurity atoms In and La in doped PbTe.

displacements of the Te atoms are increased thereby. We note in this connection that such an effect should influence also the temperature shift of the Mossbauer line. The expected value of this change in the section $0 - C_1$ amounts to several fraction of a mm/sec when the temperature ranges from 20 to 80°K. After all the vacancies are filled (in this case, apparently, first the Pb and then the Te vacancies), the impurity atoms begin to crowd out the Pb atoms into the interstices, i.e., further increase of the concentration (interval $C_1 - C_2$ for curve 1 of Fig. 1) leads already to an increase of the number of defects of the Frenkel type. These defects perturb the vibrational spectrum of the lattice, increasing the mean-square displacements of the atoms, leading to a decrease of f'. At large impurity concentrations ($C > C_1$ for curve 1 of Fig. 1), the In atoms may also fall into the interstices and a second phase may be produced, and this should lead to the appearance of dislocations connected with the impurity and to the formation of a highly dispersed phase [4, 5]. This circumstance can also lead to a decrease of f' [6].

Upon annealing, the impurities should be more uniformly distributed, and f' may increase again. A certain confirmation of this assumption may be the fact that after annealing a PbTe sample doped with 0.3% In for 60 hours at T = 750°C the value of f' increased 20% (compared with the value prior to annealing), and for a PbTe sample with concentration 0.05% In the value of f' following a similar annealing remained practically unchanged.

Since the line width of an undoped PbTe sample (see Fig. 2) is close to double the natural width ($2\Gamma_e = 0.49$ cm/sec, $\Gamma_e = 0.52 \pm 0.05$ cm/sec, it can be assumed that in PbTe the electric field of the ions located in the first coordination sphere of the tellurium has spherical symmetry. Introduction of the impurity produces a nonzer electric-field gradient (owing to the difference between the In-Te, La-Te, and Pb-Te valence bonds),and this leads to a broadening of the Mossbauer line. If it is assumed that beyond a concentration C > (0.3 - 0.4)% all the impurities accumulate in definite sections of the crystal, then the additional broadening connected with the electric hyperfine interaction amounts to approximately 0.2 cm/sec.

A similar qualitative reasoning can be presented also for PbTe samples doped with lanthanum (curve 2, Fig.1).

Using the results of [7], we can show that for the case when $TR \gg b\theta$ we can write for the value of f'/f'_0

$$\frac{f'}{f'_0} = \exp -\left\{\frac{A(T/\theta)(b/\lambda)^2}{R^2}\right\},$$

where T is the crystal temperature, θ the characteristic temperature, analogous to the Debye temperature, b a characteristic length on the order of the dimensions of the unit cell, and R the distance from the nucleus under consideration to the defect (it is assumed that $R \gg b$).

This expression describes qualitatively the observed dependence of f'/f'_0 on the concentration of the defects.

Assuming that the maximum of f' corresponds to the filling of all the vacancies, we find that the Pb vacancy concentration in the initial PbTe amounts to 2.23×10^{19} cm^{-3} (the number of Te vacancies is 2.04×10^{19} cm^{-3}). The total concentration of all the vacancies corresponds to apparently to 0.1 wt. % for In doping (curve 1) and 0.12 wt. % for La doping (curve 2), which corresponds to the ratio of their atomic weights.

It is evident from Fig. 1 that the probability of the Mossbauer effect at the maximum increases by $e^{0.8} \approx 2.1$ times compared with the undoped PbTe. From this we easily get the estimate $\bar{L}_0^2 >> \bar{L}_{dop}^2 \approx 2.3 \times 10^{-19}$ cm^2, and for the initial PbTe the rms displacement of the tellurium atom, averaged over the sample, is $\bar{L}^2 \geq 2.1 \times 10^{-19}$ cm^2.

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[1] V. A. Lebedev, R. A. Lebedev, A. M. Babeshkin, A. N. Nesmeyanov, Vestnik, Moscow State Univ., Chem. Series, 4, 18 (1968).
[2] W. Zachariasen, Z. Phys. Chem. 124, 273 (1929).
[3] Masatomo Fujemoto, Jasuo Sato, Japanese J. Appl. Phys. 5, 12 (1966).
[4] E. Miller, K. Komaren, and J. Kadoff, J. Appl. Phys. 32, 11 (1961).
[5] V. I. Fistul', Fiz. Tverd. Tela 6, 3738 (1964) [Sov.Phys. Solid State 6, 2999 (1965)].
[6] I. P. Suzdalev, M. Ya. Gen, V. I. Gol'danskii, and E. F. Makarov, Zh. Eksp. Teor. Fiz. 51, 118 (1966) [Sov. Phys.-JETP 24, 79 (1967)].
[7] V. I. Peresada, ibid. 38, 1140 (1960) [11, 825 (1960)].

EXPERIMENTAL OBSERVATION OF OSCILLATORY EFFECTS UPON TUNNELING OF ELECTRONS IN $Al-Al_2O_3-Bi_{1-x}Sb_x$ FILM JUNCTIONS AT VARIOUS PRESSURES

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The tunnel junctions were obtained by vacuum sputtering of the $Bi_{1-x}Sb_x$ alloys on a previously oxidized aluminum film deposited on glass. During the sputtering of the alloy, the substrate was maintained at room temperature. The alloy was deposited by the "flash" method [1] from an incandescent tantalum vessel. The thickness of the $Bi_{1-x}Sb_x$ layer was several thousand Å. The hydrostatic pressure was applied to the sample by a procedure described in [2]. The $Al-Al_2O_3-Bi_{1-x}Sb_x$ tunnel junction was connected to the measurement circuit in such a way that when the bias voltage, picked off a slide-wire resistor, was positive the potential of the alloy film was positive relative to the aluminum electrodes. The plots of the conductivity dI/dU of the junction were recorded with an x-y plotter as functions of the voltage U applied to the sample.

Figure 1a shows a typical plot of di/dU(U) for the junctions with concentration x of the antimony in the $Bi_{1-x}Sb_x$ alloy up to $x \leq 0.5$. The plot is a W-shaped curve. At room temperature there is either no maximum at all on the dI/dU (U) curve, or is weakly pronounced. When the temperature is lowered to 4.3°K, three distinct extrema are observed on the W-curve, and the distances L_1 and L_2 between the extrema change quite noticeably with the alloy composition (see Fig. 1b), and are practically independent of the temperature. When the temperature is lowered from 300 to 77°K the value of L_1 increases about 10%. The parameters L_1