Loss of symmetry of local environment of tin atoms in $Pb_{1-x}Sn_xTe$ crystal lattice

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Splitting of Mossbauer spectra of ^{119}Sn nuclei has been observed in the narrow-band semiconductors $Pb_{1-x}Sn_xTe$. This indicates that the tin atoms go over into a position with a lower than cubic symmetry of the local environment.

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The semiconductors $Pb_{1-x}Sn_xTe$ constitute a continuous series of solid solutions PbTe—SnTe, in which the width of the forbidden band varies with the composition x. In experiments on inelastic neutron scattering[1] and in measurements of the resistivity[2] of SnTe and compositions close to it, singularities were observed and can be ascribed to a restructuring of the phonon spectrum as a result of structural phase transitions. No such effects were investigated up to now in the ternary systems of the type $Pb_{1-x}Sn_xTe$, although phase transitions resulting from singularities of the electron spectrum at various points of the Brillouin zone have been predicted for them in theoretical papers.[3,4] We have therefore investigated the connection between the electron and phonon spectra of $Pb_{1-x}Sn_xTe$ crystals in a wide range of compositions at different temperatures.

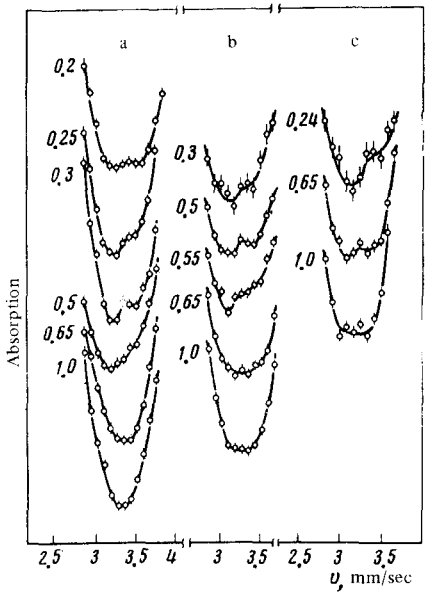

FIG. 1. Sections of Mössbauer spectra of ^{119}Sn nuclei in $Pb_{1-x}Sn_xTe$ near the resonant velocity. The number of counts per point in the spectra is $\sim 10^6$. a) $T = 78\,°K$, b) $T = 205\,°K$, c) $T = 300\,°K$. The numbers on the left of the spectra designate the tin content x.

Information on the changes in the structure of the crystal lattice and in the phonon spectrum can be obtained relatively simply from measurements of the probability f' of the Mössbauer effect. In particular, this method was used in[5] to detect an anomalous decrease of f' in the region of the zero-gap state. This fact was attributed to softening of the optical branches of the phonon spectrum.

In the present study we have carried out a detailed investigation of the form of the Mössbauer spectra of the nuclei ^{119}Sn in $Pb_{1-x}Sn_xTe$ for the purpose of observing the singularities of the behavior of the tin atoms in the crystal lattice. The idea of the experiment was the following: It is known that in crystals with cubic symmetry there is no quadrupole splitting of the energy levels of the Mössbauer nuclei, and the resonance spectrum takes the form of a single line (in the absence of hyperfine magnetic splitting). If for some reason the cubic symmetry of the environment of the Mössbauer atoms is distorted, then an electric-field gradient appears at the nuclei of these atoms, and produces a quadrupole splitting (in the case of ^{119}Sn, the result is a doublet Mössbauer spectrum). Thus, the shape of the spectrum yields information on the relative position of the Sn atoms in the unit cell.

The Mössbauer effect was measured in powdered absorbers. $Pb_{1-x}Sn_xTe$ crystals with compositions $0.13 \leq x \leq 1$ were prepared by the procedure described in[6]. The powdered samples were annealed at 450 °C (the observed regularities were less pronounced in samples that were not annealed). The standard procedure for measuring the Mössbauer effect in transmission geometry was used; the γ-ray source was tin dioxide at room temperature.

As already mentioned, a manifestation of quadrupole splitting is the doublet character of the resonance spectrum. We have therefore investigated thoroughly the sections of the spectra near the resonant velocity, where the expected splitting could manifest itself most pronouncedly. Fig. 1 shows

sections of the spectra of the samples with different compositions at temperatures 78, 205, and 300 °K. In these, a splitting ~ 0.3 mm/sec is observed at each temperature in a definite composition interval. We note that the splitting occurs at different values of x, depending on the temperature.

The simplest explanation, namely that the observed doublet is due to the existence of two phases, each of which yields a single line in accordance with a definite configuration of the nearest environment of the tin atoms, is not applicable. According to this explanation, the splitting should not depend on the temperature at a fixed composition, thus contradicting the experimental data. For example, the splitting decreases with decreasing temperature in the case of the composition with $x = 0.65$.

The observed splitting in the Mössbauer spectra is therefore evidence of a transition of the tin atoms to a position with a local-enviornment symmetry lower than cubic. There are two possibilities: either the crystal lattice of the semiconductor remains cubic and the tin atoms are only slightly shifted from the lattice sites into the interstices, or else the entire crystal experiences a phase transition into a state with noncubic symmetry.

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