Long-term relaxation processes induced by a quantizing magnetic field in the metallic phase of $Pb_{1-x}Sn_xTe(In)$ alloys

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The kinetics of long-term charge carrier transfer processes between band and impurity localized states in a quantizing magnetic field have been investigated in single crystal $Pb_{1-x}Sn_xTe(In)$ alloys with $x \approx 0.20$ (metallic phase with n-type conductivity) and $x \approx 0.30$ (p-type metallic phase) at temperatures between 1.4 and 25 K, and pressures up to 16 kbar. The coefficients $\partial \varepsilon_F / \partial T$ which determine the linear shift of the stabilized Fermi level with increase in T have been calculated. It was established that the nonexponential nature of the relaxation is determined by the strong displacement of the system from the equilibrium state, which is comparable with the height of the barrier ($W \sim 25$ meV) between the band and impurity states. The results are analyzed within the framework of the model of metastable electron states in $Pb_{1-x}Sn_xTe(In)$ alloys.

1. INTRODUCTION

New trends associated with the study of deep localized and quasilocalized levels and the existence of metastable electron states caused by them, have been intensely developed recently in the physics of the A^4B^6 group (see Akimov *et al.*[1] and the references quoted there). Deep levels can be formed both within the forbidden band and on the background of allowed energies. As was shown by Volkov and Pankratov,[2] band and strongly localized impurity states are separated by a barrier W in configurational space (see also Kagan and Kikoin[3]). This barrier gives rise to the existence of long-term relaxation (LR) processes at low temperatures on disturbing the system from the equilibrium state.

The most interesting material for studying impurity states was and remains the series of alloys $Pb_{1-x}Sn_xTe(In)$. This is mainly due to the fact that thanks to the high solubility of In in $Pb_{1-x}Sn_xTe$, the crystals synthesized are sufficiently uniform.[1] The introduction of a number of other impurities (for example, Ga, Cd) in an amount necessary for the formation of (quasi) localized levels is, in general, accompanied by the occurrence of segregations, which turn out to be the determining influence on the kinetics of relaxation processes.[4] It is also important that $Pb_{1-x}Sn_xTe(In)$ is the only system in which both the metallic and dielectric phases are realized by varying the composition (x) of the alloy.[5]

LR processes in $Pb_{1-x}Sn_xTe(In)$ are found in the temperature range $T \lesssim 20$ K on disturbing the system from the equilibrium state by a quantizing magnetic field,[6] by IR irradiation[7,8] and by a strong electric field.[9] The investigations of LR processes and the determination of their quantitative characteristics for the last two parameters are associated with considerable experimental difficulties, since nonequilibrium states are induced by IR irradiation and by an electric field, which change not only with time but also are distributed nonuniformly within the volume of the specimen. A quantizing magnetic field, as a parameter disturbing the system from a state of equilibrium, has the advantage that the excitation arising is uniform over the whole of a massive specimen. The influence of contact phenomena and surface effects on the nature of the physical processes in the crystal are then practically completely eliminated.

The aim of the present work was a detailed study of the kinetics of the long-term processes found earlier[6] for the flow of current carriers between band and localized states in a quantizing magnetic field for $Pb_{1-x}Sn_xTe(In)$. The investigation of the kinetics of LR processes is carried out on the basis of analyzing the temperature dependences of the concentration of charge carriers in weak and strong magnetic fields.

2. EXPERIMENTAL METHOD. SPECIMENS

Measurements of the specific resistivity ρ and Hall coefficient R at normal pressure were carried out by using a closed metal chamber filled with pentane and practically totally shielding the specimen from external radiation. The design of the high-pressure chamber with 4.5 mm diameter channel was standard. The dimensions of the specimens studied were $2.5 \times 0.4 \times 0.4$ mm. When cutting the specimens by a spark erosion machine, special narrow bulges were made for the Hall contacts, placed opposite one another to a high degree of accuracy, so that the contribution of the magnetoresistance $\rho(H)$ to the Hall potential difference U_x could be almost completely eliminated. For all measurements, the vector **H** was directed along a ⟨100⟩ type crystallographic direction.

Single-crystal $Pb_{1-x}Sn_xTe(In)$ alloys were studied for which the transformation of the energy spectrum, in the space of the parameters composition, pressure, and magnetic field, has been established.[5,10,11] The specimens were grown by the Czochralski method. Indium at a concentration ~ 0.5 at.% is introduced into the crystal in the process of prolonged heating in InTe vapor. According to Hall effect results, the electron concentration $n_0 = 1/ecR$ in the alloy $Pb_{0.80}Sn_{0.20}Te(In)$ at $P = 1$ bar was 9×10^{15} cm^{-3}; the hole concentration $p_0 = 1/ecR$ in $Pb_{0.70}Sn_{0.30}Te(In)$ was 2.2×10^{16} cm^{-3}. The magnetic field strength corresponding

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to the ultraquantum limit H_{uql} was determined from the position of the last extremum of Shubnikov–de Haas oscillations. The alloy composition $x \approx 0.20$ ($x \approx 0.30$) was chosen by starting from the condition that in the gapless state at the maximum energy overlap of the quasilocalized level ε_t with the conduction band (valence band), the field H_{uql} should not exceed 60 kOe. For studying the kinetics of nonequilibrium processes, the chamber with the specimen was placed for a time $t < 10$ s in a superconducting solenoid in which the required current had already been flowing. In the range 4.2–25 K, the temperature was maintained to an accuracy of ~ 0.1 K. The recording apparatus enabled measurements of the values of ρ and U_x with a time constant of the order of a second, to be carried out with an accuracy $\sim 0.1\%$.

3. TEMPERATURE DEPENDENCES OF CONCENTRATION AND OF THE KINETICS OF FLOW OF CURRENT CARRIERS BETWEEN LOCALIZED AND BAND STATES

In a magnetic field $H > H_{uql}$, long-term processes of current carrier flow from a quasilocalized level ε_t to the 0^- Landau subband are observed in $Pb_{1-x}Sn_xTe$(In) alloys.[6] The "direct" flow process arises as a result of the growth in the number of states under the stabilized Fermi level for $H > H_{uql}$.[11] The ratio of the electron (or hole) concentration $n_{uql}(H)$ for $H > H_{uql}$ to the value n_0 for $H = 0$ is[11]

$$\frac{n_{uql}(H)}{n_0} = \frac{3m_0\mu_B H\varepsilon_g(\varepsilon_F^2-\varepsilon_g^2/4)^{1/2}}{2m_c[(\varepsilon_F^0)^2-\varepsilon_g^2/4]^{3/2}}\left[1-\frac{\mu_B H\varepsilon_g\Delta}{\varepsilon_F^2-\varepsilon_g^2/4}\right]^{1/2}, \quad (1)$$

where $\Delta = (m_0/m_c)(1-\tilde{g}/2)$, $\tilde{g} = gm_c/m_0$ is the effective g factor, m_c is the cyclotron mass at the bottom of the band, μ_B is the Bohr magneton, ε_F is the Fermi energy, ε_g is the width of the forbidden band. In the equilibrium state $\varepsilon_F = \varepsilon_F^0 = \text{const}$. Because of the existence of a barrier W between the impurity and band states, the flow process is slowed down and the value of ε_F is a function of time and field. In this case the order of carrying out the measurement is extremely important. The specimens studied were initially cooled to 4.2 K at $H = 0$. The magnetic field was then applied. The $n(T)$ and p(T) functions were measured in the process of warning up the specimen to ~ 100 K and subsequent cooling to 4.2 K in a fixed magnetic field. The average rate of change of temperature was $|\partial T/\partial t| = 3$ K min^{-1} at $T \sim 100$ K and ≈ 0.5 K min^{-1} at $T \sim 4.2$ K.

The results obtained for alloys with $x \approx 0.20$ and 0.30 are shown in Fig. 1. The plots taken on heating are shown by arrows ←, on cooling by arrows →. The application of a magnetic field $H > H_{uql}$ at $T = 4.2$ K leads to a reduction in n and p. We notice immediately that the Hall factor $A = n\text{-}ecR$ in $Pb_{1-x}Sn_xTe$ alloys on passing from the classical high field regime to fields $H > H_{uql}$ differs from unity by not more than $\sim 5\%$. The results obtained for undoped alloys is evidence of this. Over the narrow temperature range from ~ 12.5 to ~ 18 K, the electron concentration on warming increases sharply, reaching a maximum value at the point $T = T_c \approx 19$ K. The same qualitative relationships in the $p(T)$ behavior are followed for an alloy with $x \approx 0.30$. However, the form of the $p(T)$ curves depends to a large extent on the rate of heating the specimen, and a continuous increase

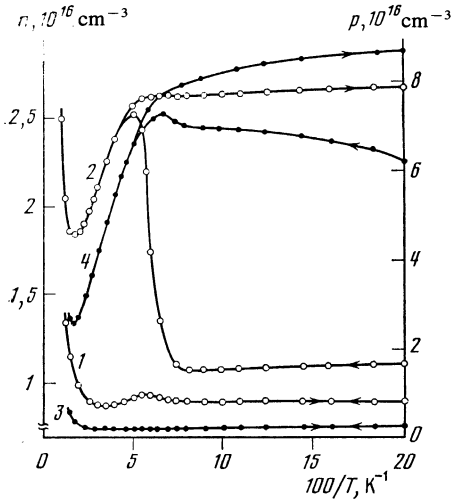

FIG. 1. Temperature dependences of the equilibrium (→) and nonequilibrium (←) current carrier concentration in the $Pb_{1-x}Sn_xTe$(In) alloys studied at $P = 1$ bar: 1) $x \approx 0.20$, $H = 1$ kOe; 2) $x \approx 0.20$, $H = 58$ kOe (n type); 3) $x \approx 0.30$, $H = 1$ kOe; 4) $x \approx 0.30$, $H = 58$ kOe (p type)

in the hole concentration is observed on lowering the temperature below $T \sim T_c$. The value of T_c for an alloy with $x \approx 0.30$ is ~ 14 K.

To determine the nature of the current carrier flow processes indicated above on applying a magnetic field $H > H_{uql}$, the kinetic dependences of the relative change in concentration $n_{uql} - n = \Delta n(t)$ and $p_{uql} - p = \Delta p(t)$ were studied. The equilibrium values of the concentrations n_{uql} and p_{ugl} are determined by Eq. (1) at $\varepsilon_F(H) = \varepsilon_F^0$ and could be obtained experimentally by measuring the Hall coefficient on transient heating of the specimen to a temperature $T > T_c$, followed by cooling to 4.2 K in a fixed field $H > H_{uql}$. Experimental curves of $\Delta n(t)$ for the alloy with $x \approx 0.20$ at

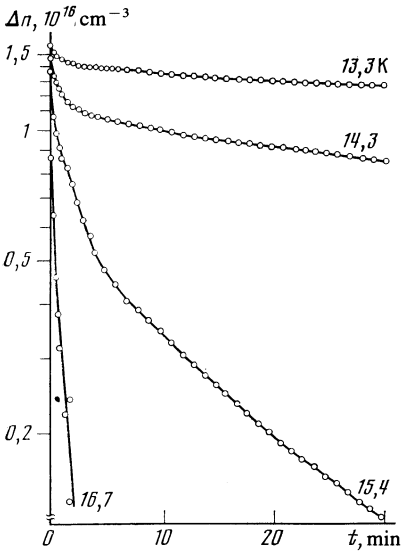

FIG. 2. The form of the kinetic dependences of the relative change in the nonequilibrium electron concentration $\Delta n = [n_{uql}(H) - n]$ for the alloy $Pb_{0.80}Sn_{0.20}Te$(In), $H = 58$ kOe. The numbers against the curves are the specimen temperature

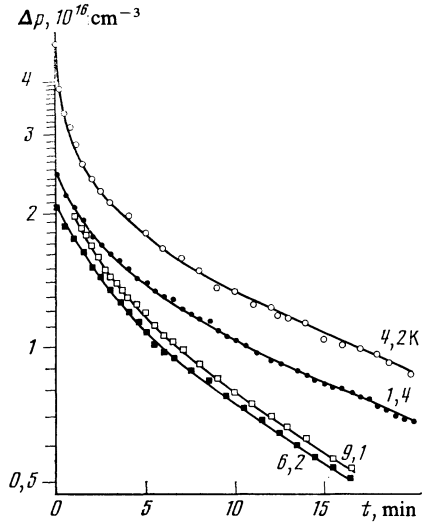

FIG. 3. The form of the kinetic dependences of the relative change in the nonequilibrium hole concentration $\Delta p = [p_{uql}(H) - p]$ for the alloy $Pb_{0.70}Sn_{0.30}Te(In)$, $H = 40$ kOe. The numbers against the curves are the specimen temperature

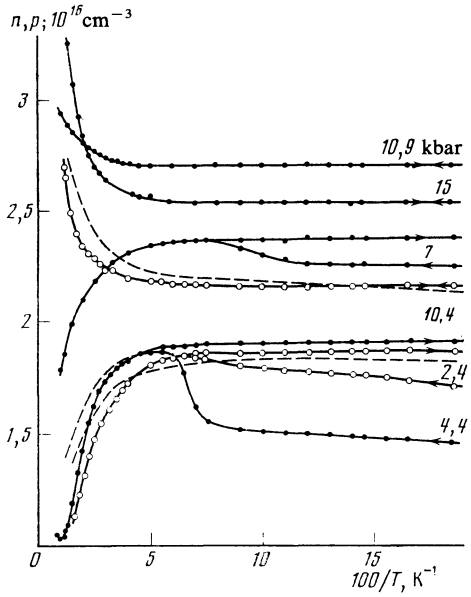

FIG. 4. Temperature dependences of the equilibrium (→) and nonequilibrium (←) electron concentrations in the alloys $Pb_{0.80}Sn_{0.20}Te(In)$ (dark circles) and $Pb_{0.70}Sn_{0.30}Te(In)$ (light circles; $H = 58$ kOe $> H_{uql}$. Numbers against the curves are the pressure in kbar, the dashed curves are calculated

$H = 58$ kOe and of $\Delta p(t)$ for the alloy with $x \approx 0.30$ at $H = 40$ kOe are shown in Figs. 2 and 3 respectively. The parameter of the curves is the specimen temperature. As can be seen from Fig. 2, the $\Delta n(t)$ relation is, on the whole, nonexponential To describe the electron flow process, the instantaneous relaxation time τ_{inst} was therefore calculated for each experimental point of the curves. Analysis of the results shows that, starting from some instant, the relaxation time in the final state of the LR processes

$$\tau_{inst}(t) = \frac{n_{uql} - n}{\partial (n_{uql} - n)/\partial t}$$

becomes constant for a fixed T. The value of τ_{inst} depends strongly on temperature in the region 13 K $\lesssim T \lesssim$ 17 K and is ~ 300, ~ 90, ~ 19 and ~ 3.6 min respectively at temperatures $T \approx 13.3$, 14.3, 15.4 and 16.7 K. The values of τ_{inst} exceed 10^5 s at 4.2 K $\lesssim T \lesssim$ 10 K and are ~ 1 s in the region $T \sim T_c$. The last estimate is made on the basis of analyzing hysteresis phenomena on increasing the measured signal strongly. The $\Delta n(t)$ curves were also measured in magnetic fields of 20 and 40 kOe. It was found that variation of H does not lead to an appreciable change in the form of the $\Delta n(t)$ dependence.

A characteristic feature of the relaxation kinetics for the alloy with $x \approx 0.30$ is the absence of a noticeable change in the form of the $\Delta p(t)$ curves in the temperature range 1.4–9.1 K (see Fig. 4). The instantaneous relaxation time increases nonlinearly with time, reaching ~ 25 min. However, more than 60% of the holes flow with times $\tau_{inst} < 1$ min. Increasing the temperature to $T \gtrsim 10$ K leads to a rapid acceleration of the flow process. In this case, the equilibrium state is realized in a time $t \lesssim 1$ min. And finally at $T \sim T_c$, the time resolution of the measuring method used ($\tau_{inst} \sim 1$ s) is reached.

When the magnetic field is removed, when the state with an increased current carrier concentration has been previously frozen, the nonequilibrium value of the Fermi energy exceeds the level $\varepsilon_F^{(0)}$ and the return flow of electrons or holes from the forbidden band to th level ε_t starts. Comparison of the results for forward and reverse relaxations shows that the reverse flow of current carriers, in both an alloy with electron and also with hole type of conduction, takes place an order of magnitude faster than the forward, for all values of H over the whole temperature range. It should be remarked here that if the direct flow process can only be produced with the help of a quantizing magnetic field, the reverse process is analogous with LR processes on switching off IR radiation. The process of current-carrier capture by impurity centers can be studied with high accuracy in the dielectric phase of $Pb_{1-x}Sn_xTe(In)$ alloys using IR techniques.[8]

4. THE INFLUENCE OF PRESSURE ON THE PARAMETERS OF RELAXATION PROCESSES AND ON THE GALVANOMAGNETIC CHARACTERISTICS

The equilibrium $n_0(T)$ dependences were measured for the alloy with $x \approx 0.20$ in a weak magnetic field $H = 1$ kOe at different pressures. In accordance with the transformation diagram of the energy spectrum of the alloy $Pb_{0.80}Sn_{0.20}Te(In)$, under the action of pressure[10] in the region of the direct spectrum ($\varepsilon_g > 0$, $P < P_i$ is the pressure at which a gapless state is realized) an increase in pressure P and an increase in overlap of the level ε_t with the conduction band at first leads to an increase in electron concentration. A maximum value is reached at $P = P_i \approx 10.5$ kbar and in the region of the inverse spectrum ($\varepsilon_g < 0$, $P > P_i$), n_0 decreases monotonically. Application of pressure leads to an appreciable change in the form of the temperature dependences $n_0(T)$. In the region of the direct spectrum an increase in P leads to a

more significant minimum in electron concentration in the temperature region $T \gtrsim 20$ K, and as P increases the minimum in $n_0(T)$ shifts to higher temperatures and for $P \gtrsim 7$ kbar is already unobservable in the temperature interval investigated, 4.2 K $\lesssim T \lesssim$ 100 K. At the point $P = 10.9$ kbar, close to P_i, some increase in electron concentration with increasing temperature precedes the section corresponding to a reduction in n_0 with increasing T. In the region of the inverse spectrum, the section of $n_0(T)$ increasing becomes the main part and the point of the maximum in the $n_0(T)$ dependence shifts to higher temperatures.

The $n(T)$ dependences for the alloy with $x \approx 0.20$ and p(T) for the alloy with $x \approx 0.30$ in a strong magnetic field $H = 58$ kOe $> H_{uql}$, measured on heating ($\leftarrow$) and cooling ($\rightarrow$), are shown in Fig. 4. As can be seen, when the pressure is increased the difference between the equilibrium and nonequilibrium electron concentrations at $T < T_c$ decreases, and at $P > 10$ kbar the form of the $n(T)$ curves stops depending on the measuring process. At the temperature T_c the characteristic flow times and the fraction of slow transitions decrease, while the interval for the sharp change in τ_{inst} broadens slightly with temperature. The change in the form of the equilibrium $n(T)$ dependences for $H > H_{uql}$ under the action of pressure is qualitatively similar to that which was observed in a weak field: in the region of the direct spectrum, $n(T)$ decreases at $T \gtrsim 20$ K, and in the region of the inverse it increases. An increase in pressure, both for the alloy with $x \approx 0.30$ and for the alloy with $x \approx 0.20$, leads to two effects: an increase in the rate of flow of nonequilibrium holes, accompanied by a shift in T_c to lower temperatures, and a qualitatively different form of $p(T)$ dependences for $P \lesssim 8$ kbar and for $P > 8$ kbar at temperatures $T > 15$ K (for the alloy $Pb_{0.70}Sn_{0.30}Te$(In), $P_i = 4.3$ kbar and the maximum of $p(P)$ at $T = 4.2$ K is $P_m \approx 8$ kbar[10]). A section of decreasing hole concentration with decreasing temperature is observed in the $p(T)$ curves at $P \lesssim 8$ kbar, at $P = 8.1$ kbar p is practically independent of T up to ~ 100 K and at $P > 8.1$ kbar p starts to increase with increasing temperature.

5. DISCUSSION OF THE RESULTS

5.1. Transformation of the energy spectrum with change in temperature

One of the causes of the $n_0(T)$ and $p_0(T)$ variations can be a shift in the stabilized Fermi level relative to the L-band edge (ε_c, ε_v) in $Pb_{1-x}Sn_xTe$(In) alloys with a change in temperature. A calculation of the energy diagrams, reflecting this shift for the alloys with $x \approx 0.20$ and 0.30, was carried out within the framework of the two band approximation used earlier to construct the transformation diagram for the spectrum of these alloys in the composition-pressure space parameters.[5,10] In this approximation, with degenerate charge carrier statistics, the electron concentration is given by the expression

$$n_0 = \frac{32\pi}{3(2\pi\hbar)^3\alpha^2 v^3}\left[(\varepsilon_F^0)^2 - \frac{1}{4}\varepsilon_g^2\right]^{3/2}. \quad (2)$$

The $\varepsilon_F^{(0)}(T)$ dependence can be calculated according to Eq. (2), using experimental values of $n_0(T)$ at fixed pressure. In the calculation, the anisotropy coefficient of the Fermi surface α^2 was taken as equal to 10.5, the analog of the Kane matrix element $v = 0.22 \times 10^8$ cm s^{-1}, the pressure coefficient $\partial\varepsilon_g/\partial P \approx 7.4$ meV kbar^{-1} (Refs. 5, 10). The width of the forbidden band ε_g was determined by using the relation[12]

$$\varepsilon_g(x, T) = 171{,}5 - 535x + [(12{,}8)^2 + 0{,}19(T+20)^2]^{1/2}, \quad (3)$$

where ε_g is in meV and T in K. A typical form of the diagram obtained is shown in Fig. 5 for the alloy with $x \approx 0.20$ for pressures of 1 bar and 15 kbar. It was established that the shift in Fermi level takes place linearly with temperature in the region $\varepsilon_F > \varepsilon_c$.

The coefficients $\partial\varepsilon_F/\partial T$ decrease monotonically in absolute value with increasing pressure from ~ 0.12 meV K^{-1} at $P = 1$ bar to ~ 0.04 meV K^{-1} at $P = 15$ kbar in the alloy with $x \approx 0.20$ and from about -0.13 meV K^{-1} ($P = 1$ bar) to zero ($P \gtrsim 10$ kbar) in the alloy with $x \approx 0.30$.

As follows from the diagrams obtained, an approach of ε_F and ε_c occurs in the region of the direct spectrum ($P < P_i$) in the alloy with $x \approx 0.20$ or of ε_F and ε_v in the alloy with $x \approx 0.30$. The Fermi level intersects the allowed band edge at some temperature $T = T_I$ and with further increase in T falls in the forbidden band. The degeneracy of the electron gas is then lifted. In the region of intermediate and nondegenerate statistics, the position of ε_F was evaluated by standard formulae within the framework of a two band model of the spectrum. Since, over the whole temperature range, the concentration of electrons n or holes p is much greater than the intrinsic concentration, the generation of charge carriers across the forbidden band need not be taken into account. An example of the calculation of the position of ε_F by using the experimental $n_0(T)$ dependence is shown in Fig. 5, a (dashed line) for the alloy with $x \approx 0.20$ at $P = 1$ bar. The calculation carried out shows that the nonmonotonic dependence of $n_0(T)$ and $p_0(T)$ over the whole range of temperatures and pressures, in particular near $T = T_I$, is explained naturally by the smooth (practically linear) shift in the stabilized Fermi level relative to the edge of the allowed band on change of temperature.

The nonmonotonic character of the stationary $n_{uql}(T)$ and $p_{uql}(T)$ relations in a high magnetic field $H > H_{uql}$ is more strongly marked than for the same $n_0(T)$ and $p_0(T)$ dependences for $H = 0$ (see Fig. 1). The $n_{uql}(H)$ and $p_{uql}(H)$ dependences can also be calculated from the diagram of the shift in band edge and ε_F with increase in temperature, obtained above for degenerate statistics for the current carriers, by using Eq. (1). An example of such a calculation is shown in Fig. 4 by dashed lines. Qualitative and satisfactory quantitative agreement is observed between the results obtained by calculation and experimentally. The approach used by Takaoka *et al.*[13] can be used for a more exact description of the $n_{uql}(T)$ and $p_{uql}(T)$ dependences, taking account in its application to $Pb_{1-x}Sn_xTe$(In) alloys of the broadening of the Landau Γ levels. The approximation[13] is meaningful under the condition that $\hbar\omega c \gg \Gamma = \hbar e/\mu m(\varepsilon_F)$, where $m(\varepsilon_F)$ is the transport mass at the Fermi level. For sufficiently large energies $(\varepsilon_F - \varepsilon_c) \gg \Gamma$, the correction associated with the broadening of the Landau levels can be ignored, since the

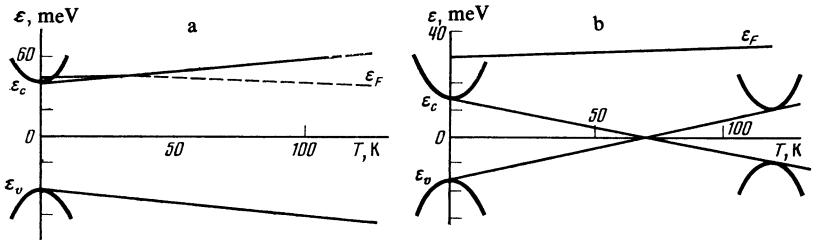

FIG. 5. Diagrams illustrating the transformation of the energy spectrum of the alloy $Pb_{0.80}Sn_{0.20}Te(In)$ with change in temperature: a) $P = 1$ bar, b) $P = 15$ kbar

total number of states below the Fermi level remains constant. In the alloys studied, the current carrier mobility μ changes from $\sim 10^5$ cm^2 V$^{-1}\cdot$ s^{-1} at $T = 4.2$ K to $\sim 10^4$ cm^2 V$^{-1}\cdot$ s^{-1} at $T \sim 100$ K. The calculated value of Γ then increases from ~ 1 to ~ 10 meV. It can be shown that the electron concentration n_{uql} for $(\varepsilon_F - \varepsilon_c) \sim \Gamma$, calculated from the equations given,[13] is about 1.5–2 times less than is calculated by Eq. (1). It is easy to see that this case is realized for the alloys studied in the temperature region $T \sim T_n$ where the $n_{uql}(T)$ and $p_{uql}(T)$ relations (Fig. 4) have a local minimum and a divergence of just such an order exists between the experimental and calculated (dashed) values of the concentration. Since the level broadening is in general a function of magnetic field and energy, in view of the approximate nature of the equations,[13] it can be considered that the stationary dependences $n_{uql}(T)$ and $p_{uql}(T)$ obtained experimentally are described satisfactorily by the two-band model of the spectrum, taking account of the shift of the Fermi level with increasing T and the broadening of the Landau levels.

We may point out that the transition from a falling $n_{uql}(T)$ [$p_{uql}(T)$] relation to a rising one at temperatures $T < T_I$ on going from the direct ($P < P_i$) to the inverse ($P > P_i$) spectrum, is sharply revealed in $Pb_{1-x}Sn_xTe(In)$ alloys thanks to the effect of stabilization of the position of ε_F and the increase in the density of states in a quantizing magnetic field. This transition is determined uniquely by the change in sign of the temperature coefficient $\partial\varepsilon_F/\partial T$ at the point $P = P_i$ and can serve as the criterion for the inversion of L bands.

Stabilization (pinning) of the chemical potential at finite temperatures in $Pb_{1-x}Sn_xTe(In)$ alloys has been considered theoretically[14,15] within the framework of different assumptions about the nature of the impurity states. It can be shown, by following the phenomenological model of Kagan and Kikoin,[3] that for the most probable[16] case of capture of two electrons in localized states, the temperature dependence of ε_F is determined by the expression

$$\varepsilon_F = \frac{1}{2}\varepsilon^{**} - \frac{1}{2}kT\ln\frac{1+r}{1-r}, \quad r = \frac{n+p_{v_0}}{N_D}, \tag{4}$$

where ε^{**} is the minimum of the adiabatic potentials for the free and bound states of two electron ($\varepsilon_t = \varepsilon^{**}2$ in that case), N_D is the concentration of compensated holes. In the temperature range studied we have $n \ll p_{v_0}$ and it follows from Eq. (4) that the $\varepsilon_F(T)$ relation is linear. In the case of a two-electron center the sign of $\partial(\varepsilon_F - \varepsilon^{**}/2)/\partial T$ is uniquely determined; it is negative for any value of r. The experimental results show that the difference $\varepsilon_F - \varepsilon_c$ falls with increasing T according to a law close to linear. If it is considered that the $\varepsilon_g(T)$ relation is mainly determined by the $\varepsilon_v(T)$ function, while $\varepsilon_c(T) = \text{const}$,[17] then the $\varepsilon_F(T)$ relation is directly determined from the diagram obtained (Fig. 5). It is not difficult to verify that $\partial\varepsilon_F/\partial T < 0$ in agreement with theoretical calculations. The same calculations are also appropriate for the alloy with $x \approx 0.30$.

5.2. Long-term relaxation processes

Several models have recently been proposed to interpret the long-term electron relaxation phenomena in $Pb_{1-x}Sn_xTe(In)$. The hypothesis of variable In valency[15] has been supplemented by the suggestion of ordering in the impurity charge distribution (empty In^{+3} and full In^{+1} states) and the formation of a gap in the spectrum of impurity two electron states. The phenomenological model[3] connects the phenomenon of electron localization on a substitutional donor impurity with the formation of a barrier W between band and impurity states, not only with a lattice of high dielectric susceptibility ($\varkappa_0 \sim 10^3$), but also with a soft phonon spectrum brought about by the existence of a displacement type of phase transition for large x. This theory also allows, in principle, localization at impurity centers of not only one but also of two electrons. Two-electron models explain the absence of the usual Langevin paramagnetism and of epr signals in $Pb_{1-x}Sn_xTe(In)$ and remove a number of other contradictions inherent in one-electron models.

A microscopic approach to the problem has been developed.[2,16] In the most recent work, attention is paid to the fact that the role of In in $Pb_{1-x}Sn_xTe(In)$ can amount to the development (catalysis) of a spectrum of intrinsic lattice defects, for example Te vacancies. The formation of a barrier W in configurational space between localized and band states is, in the Volkov and Pankratov model,[2] connected with Jahn-Teller splitting (JT) of the doublet defect level on capture of an electron at it. The authors later[16] showed that up to three pairs of electrons can be captured at a JT center. It is highly significant that the readjusted level is positioned on the background of the allowed spectrum, which also determines the existence of metastable electron states in the system. The energy levels of the In atoms themselves were not calculated in these models.[2,16] The models mentioned thus remain closed internally. It can, at the same time, be expected that the theories [2,16] take on a more general character and the transformed level can be associated with an In atom or with an In + lattice point defect complex. With the introduction of the possibility of capture of a pair of electrons at a JT center, the difference between the theoretical concepts discussed will only show up in the details.

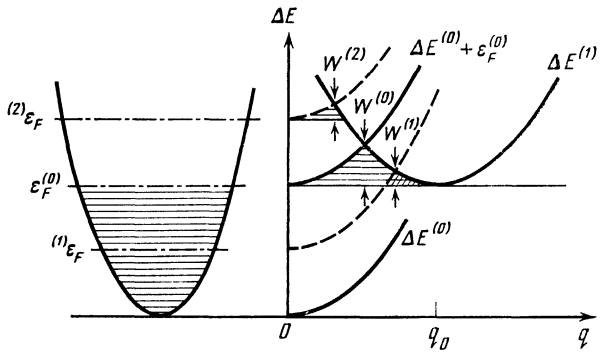

FIG. 6. Energy spectrum of a semiconductor (conduction band) and the configurational diagram showing the adiabatic change in the total energy of the crystal on deformation of the lattice around an impurity center.

We shall show below that if the comments made are taken into account, the observed electron distribution relaxation process is described successfully in the most general features by the theories of metastable electron states[2,16] (see also Ref. 3). For this pupose we consider the energy diagram shown in Fig. 6. On the left is shown the conduction band (spectrum in the direction k_z, $\mathbf{H}\|z$). In the equilibrium state the band is filled with electrons to the level $\varepsilon_F(0)$. The configurational diagram reflecting a change ΔE in the total energy of the crystal (electron + lattice) is shown on the right as a function of the generalized coordinate q, which describes the deformation of the lattice around the impurity center. Having in mind the extraction of the most characteristic relationships, we shall consider one-electron quasilocalized states (QLS). Assuming a linear shift of the electron level of the split doublet on deformation of the lattice, the change in total energy ΔE can be written in the form:[2]

$$\Delta E^{(l)}=q^2/2q_0+(E_0-q)l, \tag{5}$$

where the first term represents the elastic self energy of the lattice, the second the electron energy, E_0 the energy splitting of the doublet level and l is the number of electrons captured. The energy is reckoned from the bottom of the conduction band. The wings $\Delta E^{(1)}$ and $\Delta E^{(0)}$ are shown in Fig. 6. The minimum in the energy $\Delta E^{(1)}$, reached at $q=q_0$, determines the position of $\varepsilon_F^{(0)}$.

The capture of an electron from the Fermi level in a QLS can be represented in the following way. As q increases, the elastic energy $\Delta E^{(0)}$ grows, while the electron level E_0-q is lowered. In some configuration this level reaches the Fermi level and an electron transition to a QLS becomes possible. In the model considered, the barrier W between band states and a QLS is thus formed by the $\Delta E^{(1)}$ and $\Delta E^{(0)}+\varepsilon_F$ parabolas. It is easy to calculate that in equilibrium, $\varepsilon_F=\varepsilon_F{}^{(0)}$, the value of $W^0=q_0/8$. We shall carry out some numerical estimates. We will assume that at $T\sim 20$ K, transitions across the barrier are thermally activated.[2] In this case the relaxation time of the system is determined by the expression

$$\tau=\tau_0\exp(W/kT). \tag{6}$$

Using the values of $\tau(T)$ obtained in Sec. 1, we obtain $W^{(0)}\sim 25$ meV. In a field $H>H_{\text{uql}}$, applied at $T=4.2$ K, the quasi-equilibrium Fermi level ${}^{(1)}\varepsilon_F$ is at first lowered and in the process of relaxation rises again to the initial value $\varepsilon_F{}^{(0)}$. The maximum difference $|{}^{(1)}\varepsilon_F-\varepsilon_F{}^{(0)}|_{\max}$ can be calculated by Eq. (1), assuming that in the limiting case ($\tau\to\infty$), $n_{\text{uql}}(H)=n_0$. On the return flow of electrons from the allowed band into the QLS, $|{}^{(2)}\varepsilon_F-\varepsilon_F{}^{(0)}|_{\max}$ is already determined by Eq. (2), where the equilibrium value of $n_{\text{uql}}(H)$ in the field used $H>H_{\text{uql}}$ has to be substituted for n_0 to calculated ${}^{(2)}\varepsilon_F$. The corresponding calculations carried out for the alloys with $x\approx 0.20$ and ≈ 0.30 over the whole pressure range, show that the value of $|{}^{(1,2)}\varepsilon_F-\varepsilon_F{}^{(0)}|$ reaches 10–20 meV, i.e. is comparable with W.

The $\Delta E^{(0)}+\varepsilon_F$ parabolas are shown in Fig. 6 both for the case ${}^{(2)}\varepsilon_F>\varepsilon_F{}^{(0)}$ and for the case ${}^{(1)}\varepsilon_F<\varepsilon_F{}^{(0)}$ (dashed curve). It can be seen that as the degree of nonequilibrium of the system $|{}^{(1,2)}\varepsilon_F-\varepsilon_F{}^{(0)}|$ increases, both the heights of the barriers $W^{(1)}$ and $W^{(2)}$ and the areas under the barriers (the shaded sections in Fig. 6) decrease appreciably, both for the direct and reverse transitions. If account is taken that in the theory[2] the probability of decay of a QLS is determined by both the height and width of the barrier, then a sharp reduction in relaxation time can be expected with an increase in the modulus of the difference $|{}^{(1,2)}\varepsilon_F-\varepsilon_F{}^{(0)}|$. But just such a picture is observed in the experiment (see Sec. 3 and Figs. 2 and 3): the instantaneous relaxation time increases with the passage of time by several orders of magnitude in separate cases. Account must be also be taken of the fact that thermally activated transitions can predominate over tunneling for broad barriers. This case is evidently realized for the alloy with $x\approx 0.20$ at $P<2$ kbar. At the same time the zero-point oscillation level $\hbar\omega_0/2\sim 1$–3 meV must be borne in mind for small W, washing out the activated barrier. Closeness to this level can determine the rapid sections of relaxation observed in the initial stages of the LR process.

The kinetic equation for the capture of two electrons in a QLS—the most probable case[16]—describing the change in electron concentration with time, is determined by the probability $\omega_{\pm}(\varepsilon,\varepsilon')$ of capture (+) and emission (−) of a pair of electrons from the QLS with energies ε and ε' in the conduction band. Since the calculation of $w(\varepsilon,\varepsilon')$ was not carried out, we only show that the kinetics of the LR process is also determined to a certain extent by the energy spectrum of electrons in the conduction band. In particular, an appreciable reduction in the density of states at the Fermi level takes place in a field $H>H_{\text{uql}}$ at sufficiently high values of ε and complete spin polarization of the charge-carrier gas. For this reason the rate of flow of electrons from the conduction band to a QLS for $H=0$ exceeds the rate of decay of a QLS in a field $H>H_{\text{uql}}$, which corresponds to the experimental results.

The temperature dependence of the probability of the formation or decay of a QLS on considering the electron-vibrational levels of a system has been analyzed by Volkov and Pankratov[2] (see also Ref. 3). The calculations carried out show that at $T\lesssim 4$–6 K, the transition probability is independent of temperature. This does occur in the experimentally determined relaxation times (see Fig. 3). A rapid growth in the optimum percolation level takes place at $T>6$ K and

there is a rapid fall in the relaxation time. An increase in T from 10 to 20 K changes τ by 5–7 orders of magnitude,[2] and LR processes disappear. Just such a picture is observed in all the experiments.

A reduction in the temperature T_c and in the relaxation time take place under the action of pressure. The pressure coefficient $\partial T_c/\partial P$ is ~ 1 K · kbar^{-1} in the alloy with $x \approx 0.20$ and ~ 0.2 K · kbar^{-1} in the alloy with $x \approx 0.30$. Since both the height and width of the barrier (Fig. 6) decrease with an increase in "stiffness" of the lattice and since there is reason[19] to consider that the "stiffness" increases with an increase in pressure, the tendencies for the relaxation times to change with an increase in P become understandable. It should be noted here that it is the local compressibility of the lattice around a dislocation or impurity atom, rather than a nonumiform change in elastic constants of the lattice itself under the action of pressure, that influences the value of the pressure dependence of W and the area under the barrier.

All the existing experimental results can thus be described qualitatively within the framework of existing theoretical ideas. For a stricter consideration of the kinetics of relaxations of the electron distributions, two important considerations must also be taken into account. As follows from the experimental results of studying LR processes in $Pb_{1-x}Sn_xTe$(In), impurity centers in these compounds in the nonequilibrium state induced by IR radiation[8] are nonequivalent in their parameters. This fact shows up in the work of Pankratov and Foĭgel',[20] where a scatter in the values of E_0 and q_0 around mean values was introduced to describe LR processes. In addition, correlation in the rearrangement of impurity centers is possible in the system, interacting among themselves through the deformation fields[21] or Coulomb fields.[18] It has been assumed[18] that empty and filled impurity centers can form different correlated configurations which have an appreciable influence on relaxation processes.

The analysis carried out shows that in the example of $Pb_{1-x}Sn_xTe$(In) we have a system consisting of a subsystem of band electrons with a practically unperturbed spectrum and a disordered subsystem of impurity centers at which localized or quasilocalized states can arise, separated from the bands by a barrier W in configurational space. The kinetics of charge-carrier exchange between these subsystems for a stabilized Fermi level is determined by: the strong departure $|^{(1,2)}\varepsilon_F - \varepsilon_F{}^{(0)}|$ of the subsystem of band electrons from the equilibrium state, comparable in magnitude with the barrier W, the scatter of the impurity center parameters due to their surroundings being nonequivalent, and a possible correlation between these centers.

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