Two-electron capture and the parameters of the Jahn-Teller center in $Pb_{1-x}Sn_xTe$:In

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At low temperatures (< 30 K) the spectrum and kinetics of photoconductivity of n-$Pb_{1-x}Sn_xTe$:In show that two electrons are captured at the Jahn-Teller center. The parameters of the Jahn-Teller center are determined.

In $A^{IV}B^{VI}$ semiconductors a chalcogen vacancy forms in the conduction band a doublet level Γ_8^- which is subjected to a Jahn-Teller instability due to a change in the state of the defect.[1] The first direct proof that a Jahn-Teller center undergoes a structural change was obtained in experiments in which the photoconductivity of $Pb_{1-x}Sn_xTe$:In was optically suppressed. A suppression of this sort occurs when the energy of a photon is considerably higher than the width of the band gap.[2–4] A qualitative explanation of the measurement results was given in terms of a single-electron capture at the Jahn-Teller center, although theory[5] suggests that two or more electrons can be captured. In this letter we report an observation of a two-electron capture at the Jahn-Teller center and we present some numerical values of the parameters of the Jahn-Teller center.

We have studied the spectrum and the kinetics of photoconductivity of the epitaxial layers of n-$Pb_{1-x}Sn_xTe$:In/BaF_2 ($x \simeq 0.23$) with an indium concentration of 10^{19} cm^{-3} over a broad energy interval (0.03–2 eV) in the presence of a background radiation and without a background. Figure 1 is a trace of the photoconductivity signal at $T = 14$ K. Excitation was produced by modulating the globar light through a monochromator with a pulse intensity of $\sim 10^{14}$ photons/cm^2 in the presence of a background radiation at $T_b = 300$ K. The background intensity is $\sim 5 \times 10^{15}$ photons/cm^2·s over the spectral range 3–7 μm. At photon energies $h\nu \lesssim 240$ meV, there is only a positive photoconductivity signal with a relaxation time of ~ 1 ms and at $h\nu > 620$ meV, there is only a negative photoconductivity signal with a relaxation time of ~ 10 ms. In the energy interval $240 < h\nu < 620$ meV the positive photoconductivity signal is the same as the negative signal. The positive and negative signals were also detected when pumping was produced by a pulsed light from a YAG:Er laser with $h\nu = 422$ meV. At $T > 30$ K, we recorded only a positive photoconductivity signal at all photon energies.

Figure 2 shows the spectral dependence of the steady-state resistance of the sample, $R(h\nu)$, without a background at $T = 4.2$ K. Pumping was produced by cw-mode semiconductor lasers operating in the cw mode with different emission wavelengths and with an intensity $\sim 10^{17}$ photons/cm^2·s. At $h\nu < 54$ meV, the dark resistance of the sample, R_d, remains constant. The steady-state resistance $R(h\nu)$ is reached in a time ~ 1 min, which is determined by the pumping strength. When the pumping is

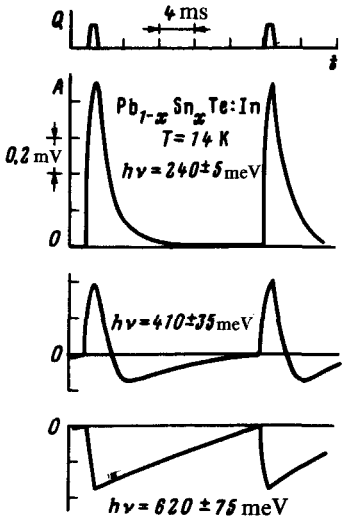

FIG. 1. The photoconductivity signal from the epitaxial layer of n-$Pb_{0.77}Sn_{0.23}Te$:In at $T = 14$ K produced by pumping the sample by a pulse-modulated light from a globar. $T_b = 300$ K.

turned off, the photoconductivity begins to relax in a nonexponential manner over a time greater than 10 h.

As the initial state of the sample we can also choose its low-resistance state with $R = R_{\min}$. This state can be obtained by initially exposing the sample to the light from a second laser with $h\nu_0 = 240$ meV. At $h\nu < 240$ meV, the sample then undergoes a gradual transition to a steady-state resistance $R(h\nu)$ in a manner similar to the relaxation in the absence of pumping. At $h\nu > 240$ meV, the steady-state resistance $R(h\nu)$ is reached rapidly—in a time of ~ 1 min, which is determined by the pumping intensity. A partial suppression occurs in this case before the photoconductivity is pumped.

The coexistence of positive and negative photoconductivity signals (Fig. 1) over a broad range of $h\nu$ energies is basically a new development which shows that the Jahn-Teller center has a many-electron structure. In the case of a single-electron capture, a

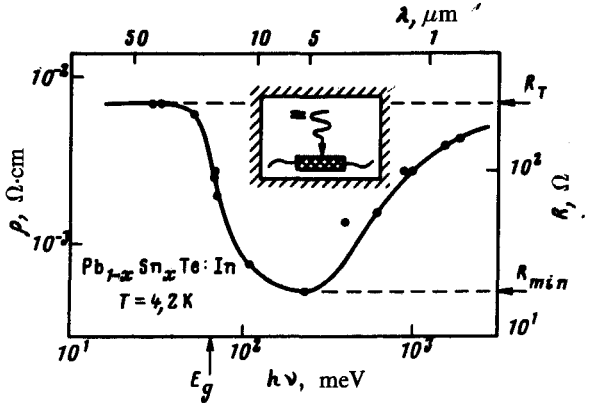

FIG. 2. Background-free spectral dependence of the steady-state resistance of the sample $R(h\nu)$ at $T = 4.2$ K.

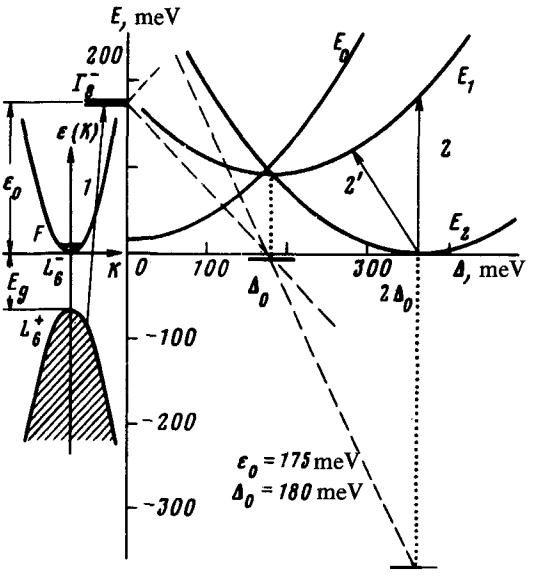

FIG. 3. Energy spectrum of the Jahn-Teller center. The band edges are shown on the left. The dashed lines represent a change in the electronic levels due to the capture of electrons by the Jahn-Teller center.

coexistence of this sort is impossible, since the transitions between the E_0 state (without an electron) and the E_1 state (with a single localized electron) give rise to either a positive or a negative photoconductivity signal. If, however, two electrons are localized in a Jahn-Teller center in the ground state (the E_2 state), the kinetics of relaxation of the photoconductivity could have the form shown in Fig. 1 because of the nonequilibrium filling of the E_1 excited state.

Figure 3 is an energy diagram of the Jahn-Teller center. The parameter Δ, which characterizes the splitting of the Γ_8^- doublet, serves as the configuration coordinate. The total energy of the system with $n = 0$, 1, 2 localized electrons and $(2 - n)$ free electrons is

$$E_n(\Delta) = \Delta^2/2\Delta_0 + n(\epsilon_0 - \Delta) + (2-n)F + U_n,$$

where $\Delta^2/2\Delta_0$ is the elastic energy, ϵ_0 is the energy of the Γ_8^- doublet, F is the Fermi level, $U_2 = e^2/\kappa r \sim 8$ meV is the Coulomb repulsion of two electrons which are localized at the Jahn-Teller center ($U_n = 0$ for $n = 0.1$), $r \sim 10$ Å is the radius of the bound state,[6] and $\kappa \sim 180$ is the dielectric constant with allowance for the spatial dispersion. The equilibrium state of the Jahn-Teller center with n electrons corresponds to the configuration coordinate $\Delta_n = n\Delta_0$.

At $T = 4.2$ K, all Jahn-Teller centers are in the E_2 state in the absence of a background. The measured residual electron density, $n \simeq 2 \times 10^{16}$ cm^{-3} ($F = 5$ meV), is a consequence of the fact that there are more electrons in the conduction band than there are free states in the Jahn-Teller center. The absence of a negative photoconductivity signal when there is no background illumination of the sample is further evidence that all Jahn-Teller centers are filled under these conditions. The activation energy $E_t \sim 3$ meV and the location of the minimum of the total energy $E_2 \sim 2E_t$ can

be determined from the temperature dependence (20–77 K) of the electron density.

Let us analyze the spectral functional dependence $R(h\nu)$ (Fig. 2). Light emitted at $h\nu < \epsilon_0 + E_g$ causes optical transitions 2 and 2′ which account for the E_1 excited state of the Jahn-Teller center. In this case, one electron moves into the conduction band (the positive photoconductivity signal). The E_1 state relaxes to the E_2 and E_0 states through small potential barriers w_{12} and w_{10} on the order of several meV. The quantities w_{12} and w_{10} depend on the characteristics of the Jahn-Teller center and the Fermi energy. At $\Delta_0 > \epsilon_0 - F$, the potential barrier is $w_{10} > 0$ and increases with increasing F, while the potential barrier w_{12} depends on $F - U$ and at typical values of the latter quantities lies within the limits $0 \leqslant w_{12} \leqslant w_{10}$, decreasing with increasing F. The relaxation of E_1 to the metastable E_0 state leads to an accumulation of electrons in the conduction band and determines the steady-state value of $R(h\nu)$. The value of $R_{\min}$ in Fig. 2 corresponds to the maximum filling of the E_0 state which is in a dynamic equilibrium with the E_1 and E_2 states. The probability of the transition 2′, which reaches a maximum at $\Delta = \text{const}$ (the transition 2), decreases with increasing energy of the photon, $h\nu$, and at $h\nu > \epsilon_0 + E_g$ transitions 1 corresponding to the capture of an electron by the Jahn-Teller center (the transition of the Jahn-Teller center from the E_0 to the E_1 state) arise. Since the valence-band hole produced in this case recombines[2,3] with the conduction-band electron in a time $< 10^{-7}$ s, the transition 1 is essentially an inverse transition with respect to the transitions 2′ and 2. Finally, the relationship between the potential barriers w_{10} and w_{12} indicated above accounts for the localization of the second electron. At $h\nu > 240$ meV, the two-electron capture dominates over the process 2′, which accounts for the increase in $R(h\nu)$ with the energy of the photon (Fig. 2). This process determines the negative photoconductivity signal (Fig. 1).

We will now explain how the positive and negative photoconductivity signals can coexist in a single relaxation process (Fig. 1). The background radiation ($h\nu \lesssim 0.2$ eV) is responsible for the transfer of electrons from the Jahn-Teller center to the conductivity band[2–4] and for the production of a certain number of free Jahn-Teller centers (the E_0 state) at a low temperature of the sample. Accordingly, in the presence of a background, a reasonably strong laser pulse with $h\nu \gtrsim \epsilon_0 + E_g$ causes the transitions 1, along with the transitions 2′. If the transitions 2′ are denoted by n_+ and the transitions 1 are denoted by n_-, we will have $(n_+ + n_-)$ Jahn-Teller centers in the E_1 state and $(n_+ - n_-)$ free electrons. For $n_+ > n_-$ this result corresponds to the initial spike in the photoconductivity signal. Since $w_{10} > w_{12}$, the relaxation of the nonequilibrium E_1 state involves primarily the capture of a free electron. After the transition of all $(n_+ + n_-)$ Jahn-Teller centers to the E_2 state, the number of free electrons decreases by $2n_-$, which corresponds to the transition from the positive to the negative photoconductivity signal. The next relaxation occurs because of the background illumination. Since the probability for the transitions 1 increases with increasing $h\nu$ because of the increase in the state density of the valence band, and since the probability for the transitions 2′ decreases because of the Franck-Condon principle, at the outset we have $n_- > n_+$, beginning with the energy $h\nu > 0.6$ eV, and we see only a negative photoconductivity signal. This effect is seen[3] right up to $h\nu \simeq 3.7$ eV.

In summary, a model for the capture of two electrons by a Jahn-Teller center accounts for the spectral dependence and the kinetics of the relaxation of the photo-

conductivity over a broad energy interval. The parameter values of the Jahn-Teller center are: $\epsilon_0 = 175$ meV and $\Delta_0 = 180$ meV. Using these parameters, we have calculated the potential barriers that divide the E_0, E_1, and E_2 states. The potential barrier which determines the thermal relaxation from the E_0 state to the E_2 state is greater than $\sim$40 meV, a value which was measured by us. This discrepancy can be eliminated by increasing the value of the parameter U_2. We believe, however, that this approach is not justifiable. A change in the charge state of a Jahn-Teller center is more likely accompanied by a change in the elastic constant Δ_0. Furthermore, the form of the energy diagram in Fig. 3 may be affected by the singlet state Γ_6 which, as the calculations of Ref. 6 have shown, is situated near the Γ_8^- state considered by us.

[1]B. A. Volkov and O. A. Pankratov, Dokl. Akad. Nauk SSSR **255**, 93 (1980) [Sov. Phys. Doklady **25**, 922 (1980)].
[2]I. I. Zasavitskiĭ, A. V. Matveenko, B. N. Matsonashvili, and V. T. Trofimov, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 456 (1983) [JETP Lett. **37**, 539 (1983)].
[3]I. I. Zasavitskiĭ, A. V. Matveenko, B. N. Matsonashvili, and V. T. Trofimov, Fiz. Tekh. Poluprovodn. **17**, 2184 (1983) [Sov. Phys. Semicond. **17**, 1396 (1983)].
[4]I. I. Zasavitskiĭ, K. Lishka, and H. Heinrich, Fiz. Tekh. Poluprovodn. **19**, 1110 (1985) [*sic.*].
[5]B. A. Volkov and O. A. Pankratov, Proceedings of the All-Union Conference on the Physics of Semiconductors, Baku, **2**, 119 (1982).
[6]B. A. Volov and O. A. Pankratov, Zh. Eksp. Teor. Fiz. **88**, 280 (1985) [Sov. Phys. JETP **61**, 164 (1985)].

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