Nature and charge states of a Ga impurity in PbTe

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(Submitted 24 March 1995)
Pis'ma Zh. Éksp. Teor. Fiz. **61**, No. 9, 768–773 (10 May 1995)

The temperature dependence of the resistivity ρ and the magnetic susceptibility χ has been measured during low-intensity illumination of a compensated PbTe(0.3 at. % Ga) single crystal, which exhibits a persistent photoconductivity. The $\rho(T)$ dependence is exponential at $T\geqslant 72$ K, deviating toward smaller values at low temperatures. The magnetic susceptibility obeys a Curie–Weiss law over the temperature interval $4.2\leqslant T\leqslant 45$ K with a cutoff temperature $\Theta=-5.8$ K. There is a sharp increase in the paramagnetic component of χ in the temperature interval $45\leqslant T\leqslant 72$ K, in the diamagnetic region. At higher temperatures, the diamagnetic susceptibility falls off monotonically. The temperature dependence $\chi(T)$ is interpreted in terms of a mixed valence of Ga in PbTe and the existence of an s^1p^2 paramagnetic state of this impurity. © *1995 American Institute of Physics.*

A persistent photoconductivity is observed in gallium-doped lead telluride at low temperatures.[1] When a compensated PbTe(Ga) sample is illuminated by visible or IR light, the conductivity increases by several orders of magnitude and then remains high for a long time after the illumination is turned off. This persistent photoconductivity is observed only below a certain critical temperature $T_c\sim 80$ K. The nature of the observed effect is governed by particular features of the shaping of the lead telluride energy spectrum and by the unusual nature of the doping of this semiconductor with gallium. The valence and conduction bands in PbTe are constructed from atomic p-orbitals formed by two p-electrons of Pb and four p-electrons of Te. The s-electrons of the outer shells of these atoms do not participate in the formation of covalent bonds.[2] If the Ga would replace Pb in its s^2p^1 ground electronic configuration, it would behave as a singly charged acceptor. Instead, it acts as a singly charged donor up to a Ga concentration $\sim 10^{19}$ cm^{-3}, while it behaves as a neutral impurity in the concentration range (1–3) $\times 10^{19}$ cm^{-3}, as was shown in Ref. 3. These charge states of Ga are possible if a Ga level in the PbTe lattice falls in the band gap.[4] The Ga initially replaces Pb in an s^0p^3 donor configuration. When the valence band becomes completely filled, it replaces the lead in an s^1p^2 configuration, which is neutral with respect to the lattice.[5]

Magnetic measurements may shed some light on the nature and charge states of a Ga impurity in PbTe. In the s^2p^1 and s^0p^3 configurations, the Ga is diamagnetic material,

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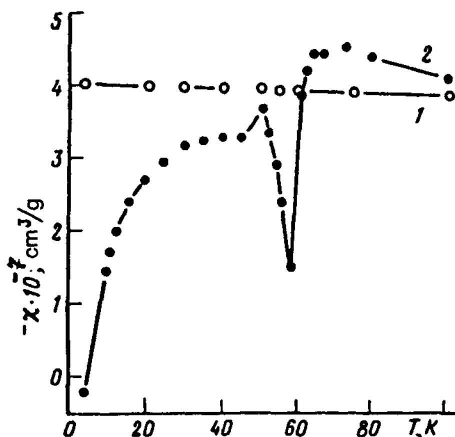

FIG. 1. Temperature dependence of the magnetic susceptibility χ of (*1*) PbTe and (2) PbTe(0.3 at. % Ga) during low-intensity illumination from the cap of the cryostat.

while in the s^1p^2 configuration it has an unfilled inner shell, i.e., a net magnetic moment. As the temperature is varied, or as the sample is illuminated at a low temperature, the number of paramagnetic centers may change substantially, and there is the possibility in principle of the onset of an impurity–impurity interaction between these centers.[6,7]

The temperature dependence of the magnetic susceptibility χ of single crystals of PbTe and PbTe(0.3 at. % Ga) was measured by the Faraday method in magnetic fields up to 10 kOe over the temperature range 4–100 K. The results are shown in Fig. 1. These measurements were taken during illumination from the cap of the cryostat; the temperature was scanned at a rate on the order of 1 K/min. The temperature dependence and magnitude of the diamagnetic susceptibility of PbTe (curve *1* in Fig. 1) correspond to data in the literature.[8] The temperature dependence of the magnetic susceptibility of PbTe(Ga) is extremely unusual (curve *2* in Fig. 1). At liquid-helium temperature, this sample is paramagnetic. As the temperature is raised, it goes into a diamagnetic state. In the temperature interval $T^*=45$ K $\leqslant T \leqslant 72$ K$=T^{**}$ we observe a very nonmonotonic behavior of χ. At $T>T^{**}$, the diamagnetic susceptibility falls off smoothly. If we extrapolate the diamagnetic susceptibility of PbTe(Ga) out of the high-temperature region and subtract it from curve *2*, we find that the difference (Fig. 2) can be described by a Curie–Weiss law at $T \leqslant T^*$ with a cutoff temperature $\Theta = -5.8$ K. The negative value of Θ corresponds to an antiferromagnetic type of impurity–impurity exchange interaction.

Using a doped sample with a resistivity $\rho_0 \sim 10^{-1}$ $\Omega\cdot$cm at room temperature, we also measured the temperature dependence of the resistivity ρ during illumination at various levels. We determined the electron concentration in the conduction band: $\sim 10^{16}$ cm^{-3} at $T=100$ K. As the sample was cooled in a shielded chamber, we observed an exponential rise of the resistivity over the entire temperature range (curve *1* in Fig. 3). The characteristic energy $\epsilon_a = 66$ meV corresponds to an activation of carriers from impurity centers into the conduction band.[1] The width of the PbTe band gap is considerably greater: $\epsilon_g = 190$ meV at $T=4.2$ K and $\epsilon_g = 220$ meV at $T=77$ K. Illumination of

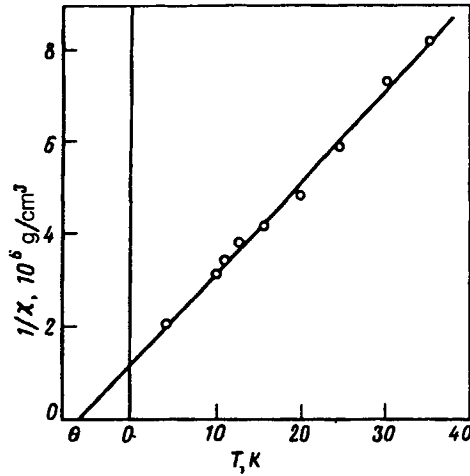

FIG. 2. Curie–Weiss behavior of the magnetic susceptibility of PbTe(0.3 at. % Ga) at low temperatures.

the sample with an incandescent pea lamp at liquid-helium temperature puts the sample in a highly conducting metastable state, which persists even after the illumination is turned off. The temperature dependence of ρ changes substantially (curve *3* in Fig. 3). As the temperature is raised, the resistivity of the sample initially changes only very slightly. At $T \sim T^*$, ρ begins to rise rapidly, and at $T \sim T^{**}$ the rise gives way to an exponential decay. When the sample is cooled in an unshielded chamber, and the conditions correspond approximately to the conditions under which χ was measured, illumination from

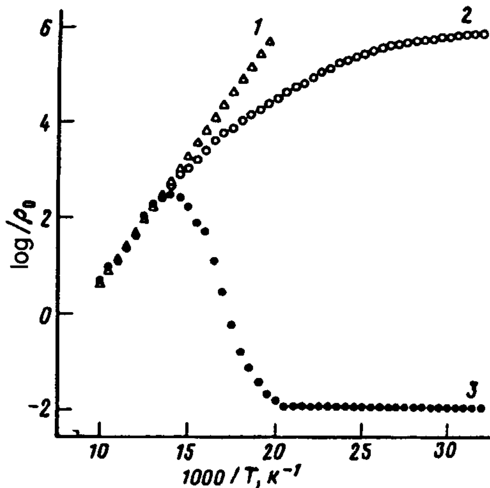

FIG. 3. Temperature dependence of the resistivity ρ of PbTe(0.3 at. % Ga) in a shielded chamber (curve *1*), during low-intensity illumination from the cap of the cryostat (2), and after illumination by an incandescent pea lamp at $T = 4.2$ K (*3*).

the cap of the cryostat leads to a substantial deviation of $\rho(T)$ from an exponential law at $T<T^{**}$ (curve *2* in Fig. 3). The results of the low-temperature measurements depend on the rate of operation, since the sample has an integrating effect with respect to visible and thermal radiation.

We can thus distinguish several special points on the temperature dependence of χ and ρ. At $T\sim T^*$, there is sharp change in the slope of the $\rho(T)$ curve found after illumination at low temperatures. The $\chi(T)$ curve deviates from the Curie–Weiss law which holds at low temperatures. At $T\sim T^{**}$, the resistivity becomes independent of the illumination, while the susceptibility begins a monotonic diamagnetic decay.

The temperature dependence of the PbTe(Ga) susceptibility can be explained on the basis that the impurity is present in different electronic states, one of which is paramagnetic. In this case the susceptibility of the crystal can be written

$$\chi=\chi_d+\chi_p, \tag{1}$$

where χ_d is the diamagnetic susceptibility of the ideal crystal, and χ_p is the paramagnetic susceptibility of the impurities.

The impurity component of the susceptibility can be described by a Curie–Weiss law only in the region in which the concentration of paramagnetic centers, n_p, is independent of the illumination and the temperature:

$$\chi_p=\frac{n_p\beta^2}{3k(T+\Theta)}. \tag{2}$$

Here $\beta=\mu_B g[s(s+1)]^{1/2}$; μ_B is the Bohr magneton, g is the Landé factor; $s=1/2$ is the spin of an electron; k is the Boltzmann constant; and Θ is a temperature characterizing the impurity–impurity interaction.

According to Ref. 9, we can write the diamagnetic susceptibility of a narrow-gap semiconductor as

$$\chi_d\approx-\frac{e^2v}{3\pi^2\hbar c^2}\ln\frac{\epsilon^*}{\epsilon_g+\mu}, \tag{3}$$

where e is the charge of an electron, v is the rate of interband transitions, c is the velocity of light, ϵ^* is an energy on the order of magnitude of the distance to the remote bands, ϵ_g is the width of the band gap, and μ is the chemical potential.

The level of the chemical potential at thermodynamic equilibrium can be found from the equation of electrical neutrality

$$\int d\epsilon N_c(\epsilon)f(\epsilon-\mu)-\int d\epsilon N_v(\epsilon)[1-f(\epsilon-\mu)]=N-(1-n)N_{\mathrm{Ga}}. \tag{4}$$

Here N_c and N_v are the densities of states in the conduction and valence bands, $f(\epsilon-\mu)$ is a Fermi distribution, N is the carrier concentration set up by impurities or defects, N_{Ga} is the Ga concentration, and $(1-n)$ is the number of p-electrons furnished by Ga atoms to the PbTe p-bands. In the s^2p^1 configuration we have $n=2$; in the s^1p^2 configuration we have $n=1$; and in the s^0p^3 configuration we have $n=0$. The degree of ionization of the s-shell can be described by introducing an effective Hamiltonian

$$H=(\epsilon_s-\mu)(n_\uparrow+n_\downarrow)+Un_\uparrow n_\downarrow, \tag{5}$$

where $n_\uparrow$ and $n_\downarrow=0,1$ are the numbers of electrons with spins up and spins down in the Ga s-shell; ϵ_s is the activation energy of an impurity center required for a valence change $s^2p^1 \leftrightarrow s^1p^2$, s^0p^3; and U is the potential at the interaction of s-electrons with oppositely directed spins. The partition function of such a system is given by

$$Z=\mathrm{Tr}\{\exp(-H/kT)\}, \tag{6}$$

and the number of electrons at a center is given by

$$n=kT(\partial \ln Z/\partial\mu)=\frac{2\exp[(\mu-\epsilon_s/kT]}{1+2\exp[(\mu-\epsilon_s)/kT]+\exp[(2\mu-2\epsilon_s-U)/kT]}$$
$$+\frac{2\exp[(2\mu-2\epsilon_s-U)/kT]}{1+2\exp[(\mu-\epsilon_s)/kT]+\exp[(2\mu-2\epsilon_s-U)/kT]}. \tag{7}$$

The first term here gives us the number of s^1p^2 paramagnetic centers, while the second gives us the number of s^2p^1 diamagnetic centers. We see from (7) that we should distinguish between the cases of an effective repulsion of s-electrons ($U>0$) and an attraction ($U<0$).

In the case $U>0$, the Ga s-shell is filled in the following manner. At $\mu>\epsilon_s+U$, the s^2p^1 diamagnetic states are predominant. At $\epsilon_s+U>\mu>\epsilon_s$, the s^1p^2 paramagnetic states are predominant. Finally, at $\mu<\epsilon_s$, the diamagnetic s^0p^3 states are predominant. At $U>0$, there can be two regions of a pinning of the chemical potential: at $\mu=\epsilon_s+U$ (the $s^2p^1\leftrightarrow s^1p^2$ transition) and $\mu=\epsilon_s$ (the $s^1p^2\leftrightarrow s^0p^3$ transition). In the case $U<0$, the s^2p^1 states are predominant at $\mu>\epsilon_s+U$. The s^0p^3 states are predominant at $\mu<\epsilon_s+U$. A pinning of the chemical potential is possible only at $\mu=\epsilon_s+U$ (the $s^0p^3\leftrightarrow s^2p^1$ position). This assertion means that there are no paramagnetic centers at low temperatures in the case of an attraction of s-electrons, while such centers can arise only in a thermal-activation process at high temperatures.

The expressions derived here can be used to interpret measurements of the magnetic susceptibility only at thermodynamic equilibrium. For PbTe(Ga), this case corresponds to either measurements in a shielded chamber, over the entire temperature range, or measurements during illumination at high temperatures, at which long-term relaxation of nonequilibrium carriers can be ignored. At a qualitative level, however, these expressions make it possible to explain the temperature dependence of χ even in the case of low-intensity illumination. In this case the number of carriers activated into the conduction band is negligible in comparison with the concentration of impurity centers.

To explain the paramagnetic anomalies in PbTe(Ga) we should assume that the potential of the interaction between electrons in the s-shell corresponds to a repulsion, and the chemical potential lies in the interval $\epsilon_s<\mu<\epsilon_s+U$ at low temperatures. The number (n_p) of paramagnetic centers found from the Curie–Weiss law with a Landé factor $g=2$ turns out to be $n_p\approx 6.7\times 10^{19}$ cm^{-3}, or about 2/3 of the impurity concentration $N_{\mathrm{Ga}}\sim 9\times 10^{19}$ cm^{-3}. The paramagnetic peak in the interval $T^*<T<T^{**}$ cannot be described in terms of deep paramagnetic centers, since the size of this peak with $g=2$ would require a Ga concentration an order of magnitude higher. We are left with the

assumption that this peak is due to electrons with a Landé factor considerably greater than 2. Such a g-factor is characteristic of electrons in the PbTe conduction band,[10] but they make only a diamagnetic contribution to the susceptibility. A paramagnetic contribution can be made by localized states split off from the bottom of the conduction band. They have a large g-factor since they are genetically related to band electrons, and the diamagnetism is suppressed because of localization and the filling factor. Such states can exist because the screening of the nucleus of a Ga atom for band p-electrons is weakened in the s^1p^2 and s^0p^3 configurations, because of the incomplete filling of the s-shell. The effect is to give rise to an attractive potential for these electrons.[11]

Gallium atoms in PbTe thus form not only a deep impurity level with an activation energy $\epsilon_a = 66$ meV but also a shallow hydrogen-like level. As the temperature is lowered, intense transitions occur to the shallow level at $T \leq T^{**}$. These transitions are accompanied by a sharp increase in the paramagnetic component of χ. In this temperature region, however, we must also consider the long-term relaxation of nonequilibrium carriers induced by the external illumination. Comparison of curves *1* and *2* in Fig. 3 shows that the role of these processes increased rapidly with decreasing temperature. The emptying of the shallow level by the illumination is manifested by an equally sharp decrease in the paramagnetic component. In a narrow temperature interval near T^*, there is a change in the relation between the contributions of electrons in the shallow and deep levels. This change is manifested as a deviation from a monotonic behavior on the temperature dependence of the magnetic susceptibility in this region. As the temperature is lowered further, the Curie–Weiss law is described by the paramagnetism of electrons in the deep impurity level, as mentioned above.

In summary, the results obtained in this study are evidence in favor of a mixed valence of group-III elements in IV–VI semiconductors. These results support the hypothesis that these impurities may exist in a paramagnetic state because of an incomplete filling of the s-level.

One of us (B.A.V.) wishes to thank the Russian Fund for Fundamental Research for financial support (Project 93-02-14700) and the Ministry of Science (Project 1-013).

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Translated by D. Parsons