Photoinduced Paramagnetism of Group III Impurities in $A_{IV}B_{VI}$ Narrow-Gap Semiconductors.

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Abstract. At low temperatures some ionic, covalent and mixed bonding compounds, as well as semiconducting heterostructures and quantum wells exhibit persistent photoconductivity. This term is used to describe the striking observation that the conductivity of these compounds and/or structures is greatly enhanced by visible or infrared illumination and that the low resistance state is maintained for a long time after switching off the illumination. To describe this effect in variously doped ionic-covalent semiconductors the models of repulsive barrier for both electron emission and capture were introduced based primarily on the assumption of dopant's displacement in the host's crystal lattice. Here we report on the magnetic counterpart of this phenomenon, which however does not exactly meet the expectations based on transport measurements. It was found that the magnetic response of $A_{IV}B_{VI}$ narrow-gap semiconductors doped with C_{III} impurities possesses features of both relaxation phenomena and light-induced phase transition. Exposure of PbTe:Ga, PbTe:In and $Pb_{0.75}Sn_{0.25}$Te:In single crystals to white-light illumination at low temperatures resulted initially in an increase of the diamagnetic response and then in the appearance of a sharp paramagnetic peak at heating.

The objects of the present study belong to the unique family of $A_{IV}B_{VI}$ semiconductors constituted by nine binary compounds (Ge, Sn, Pb) - (S, Se, Te) and their solid solutions. All lead chalcogenides as well as high-temperature phases of germanium telluride and tin telluride possess the rocksalt structure [1]. On lowering the temperature GeTe at 670 K and SnTe at $T \leq 100$ K transform into the rhombohedral phase through the softening of transverse optical mode in [111] direction, while lead telluride remains a virtual ferroelectric with anomalously high dielectric constants [2]. While doped with C_{III} elements the inherently unstable $A_{IV}B_{VI}$ semiconductors show persistent photoconductivity, which is most pronounced if the impurity levels fall into the forbidden gap [3, 4]. In contemporary understanding [5], C_{III} impurities in $A_{IV}B_{VI}$ matrix dissociate, $2C_{III}^{0} = C_{III}^{-} + C_{III}^{+}$, into negatively charged C_{III}^{-} and positively charged C_{III}^{+} centers, creating therefore deep and shallow levels in the energy spectrum of the semiconductor. The transitions between these levels lead to the appearance of a resonant peak at the edge of fundamental adsorption in the $A_{IV}B_{VI}$:C_{III} spectra of photoconductivity. However, the microscopic picture for

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this deep-shallow transformation is far from being clear. Both C_{III}^- and C_{III}^+ being in singlet states are diamagnetic, but the intermediate metastable C_{III}^0 state may carry a magnetic moment. To get additional insight into the processes of photoexcitation of C_{III} dopants in $A_{IV}B_{VI}$ semiconductors the magnetic properties of PbTe:Ga, PbTe:In and $Pb_{0.75}Sn_{0.25}Te$:In single crystals were studied under various regimes of white-light illumination along with the measurements of transport properties.

The resistivity of the bulk samples ($1 \times 1 \times 5$ mm^3) was measured with the help of the four-probe technique in a brass chamber equipped with a miniature incandescence lamp. Its radiation parameters were chosen to fit the resonant peak of photoconductivity in PbTe:Ga. At cooling in darkness the resistivity of $Pb_{0.75}Sn_{0.25}Te$:0.5at.%In and PbTe:0.3at.%Ga show the semiconducting behaviour as expected for the activation of electrons from deep levels into the conduction band. Illumination within a few seconds (~ 20 mW/cm^2) at low temperatures resulted in a decrease of resistivity by a few orders of magnitude persisting for many hours. At heating, as shown in Fig. 1, the resistivity of the samples increased reaching maximums at T ~ 20 K in $Pb_{0.75}Sn_{0.25}Te$:0.5at.%In and at T ~ 70 K in PbTe:0.3at.%Ga. The heating of the samples under permanent illumination (~ 2 mW/cm^2) resulted in a decrease of the resistivity peaks, but their positions remain practically unchanged. The effect of persistent photoconductivity was less pronounced in PbTe:1at.%In, since the In level in PbTe falls into the conduction band.

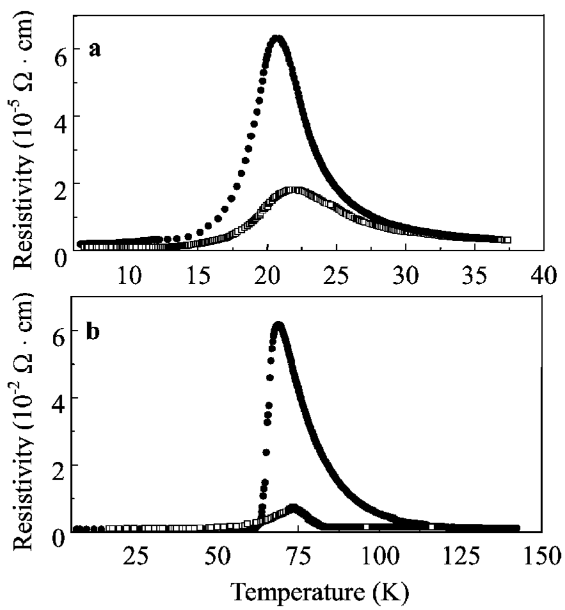

FIGURE 1. Temperature dependencies of resistivity at heating after brief illumination at low temperature (solid circles) and under permanent illumination (open circles). **a**, $Pb_{0.75}Sn_{0.25}Te$:0.5at.%In; **b**, PbTe:0.3at.%Ga.

The influence of illumination on the magnetic properties of $A_{IV}B_{VI}$:C_{III} compounds was studied mostly by a Faraday balance technique. The construction of this apparatus did not allow for the complete screening of the sample from the daylight. Additional illumination of the sample was provided by the incandescense lamp through the channel of measuring device. The sample mounted on Kevlar thread was cooled down to liquid helium temperature in the absence of a magnetic field and then it was briefly illuminated (~ 20 mW/cm^2). After that the source of additional illumination was switched off and measurements were performed at heating with the rate of about 1K/min at H = 4.28 kOe. Surprisingly, the results of magnetic measurements did not meet the expectations proceeding from the transport measurements.

The temperature dependencies of magnetic susceptibility of PbTe:1at.%In, $Pb_{0.75}Sn_{0.25}Te$:0.5at.%In and $Pb_{0.75}Sn_{0.25}Te$:2at.%In are shown in Fig. 2. At low temperatures the illumination of samples resulted in an increase of diamagnetic response compared with the reference data of undoped sample of PbTe (see the inset in Fig. 2**a**). At heating an additional diamagnetism was lifted off and at approximately 50 K strong paramagnetic peak with sharp high temperature edge appeared. As can be seen from the comparison of curves for $Pb_{0.75}Sn_{0.25}Te$:0.5at.%In and $Pb_{0.75}Sn_{0.25}Te$:2at.%In (Fig. 2**b**), an increase of impurity content resulted in an increase of both paramagnetic background and paramagnetic peak.

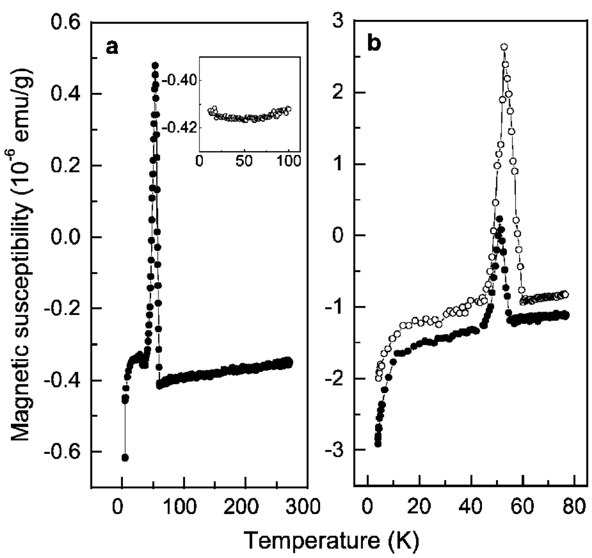

FIGURE 2. Temperature dependencies of magnetic susceptibility at heating after brief illumination at low temperature. **a**, PbTe:1at.%In; **b**, $Pb_{0.75}Sn_{0.25}Te$:0.5at.%In (solid circles) and $Pb_{0.75}Sn_{0.25}Te$:2at.%In (open circles). The inset to panel **a** shows the temperature dependence of the magnetic susceptibility of the undoped sample of PbTe.

The magnetic properties of PbTe:0.3at.%Ga were studied by both Faraday balance and SQUID magnetometer techniques. In Faraday balance measurements this sample shows mainly the same behaviour as other $A_{IV}B_{VI}:C_{III}$ compounds. The SQUID measurements revealed another unexpected feature of paramagnetic singularity. In this case no illumination of the sample by incandescence lamp was employed, but prior to measurements the sample was exposed to daylight at room temperature and then was cooled to liquid helium temperature. Once again the behaviour similar to that described above was present, however at subsequent cooling in dark chamber of SQUID magnetometer the paramagnetic peak was not observed at all and the diamagnetic downturn at low temperatures was substituted by a paramagnetic upturn. The increase of the exposure to white-light illumination at room temperature resulted finally in the appearance of both diamagnetic downturn and paramagnetic peak, as shown in Fig. 3. In general, the magnetic response of a PbTe:0.3at.%Ga single crystal resembles the behaviour of a spin glass system, showing a paramagnetic peak in the zero field cooled regime and a smooth paramagnetic upturn in the field cooled regime. At any temperature the magnetic response of the sample consisted of field dependent paramagnetic and field independent diamagnetic parts, but the pronounced hysteresis of the magnetization could be observed (Fig. 4) only below the paramagnetic peak temperature.

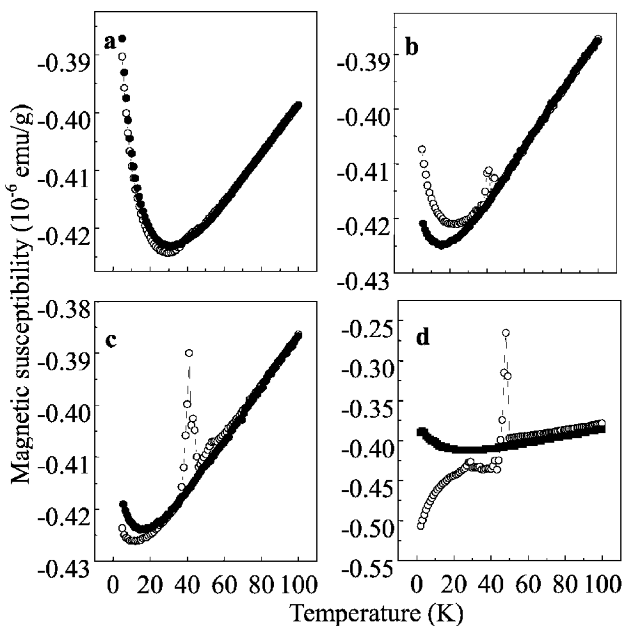

FIGURE 3. Temperature dependencies of magnetic susceptibility of PbTe:0.3at.%Ga both at heating (open circles) and cooling (solid circles) measured in the dark chamber of SQUID magnetometer after different exposures to white-light illumination (t_{exp}) at room temperature. **a**, $t_{exp} = 5 \times 10^2$ sec; **b**, $t_{exp} = 5 \times 10^3$ sec; **c**, $t_{exp} = 1.5 \times 10^4$ sec; **d**, $t_{exp} \geq 10^5$ sec.

In our opinion, the difference in critical temperatures for singularities in transport and magnetic properties reflects a previously hidden aspect of the interaction of light with $A_{IV}B_{VI}$:C_{III} compounds. At cooling in darkness the electrons leaving the conduction band occupy dopant centers, C_{III}^- being a substitute for metal in octahedral surrounding of chalcogene ions and C_{III}^+ being shifted probably in the [111] direction. Illumination of the sample resulted in the recharging of C_{III}^- and C_{III}^+ centers leading to a metastable situation where the charges of some impurities do not correspond to their local surroundings. Different light-induced displacements of dopants could result in the formation of an energy level either in the conduction band or in the gap. In the former case it would result in persistent photoconductivity, in the latter case it would lead to variations in magnetic properties. The recharging of C_{III}^- and C_{III}^+ centers always requires redistribution of two electrons, otherwise the illumination of sample at low temperatures would be accompanied by a paramagnetic upturn and not by a diamagnetic downturn. The electrons at shallow impurity levels in the gap presumably possess higher radii of localization, providing therefore the increase of diamagnetic response at low temperatures. At heating, the probability of overcoming the potential barrier separating stable and metastable states of impurities increases. The relaxation of elastic stresses at any center overcoming the potential barrier is followed at the paramagnetic peak temperature by an avalanche-like process of recharging due to the proximity of the system to a phase transition. This simulation of a phase transition is accompanied by a sharp increase of paramagnetic susceptibility in

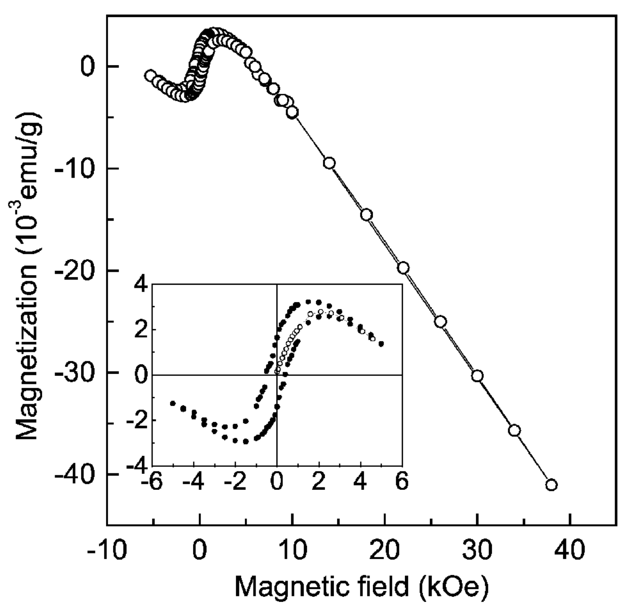

FIGURE 4. Field dependence of PbTe:0.3at.%Ga magnetization at T = 5K. The inset shows the hysteresis in low magnetic field.

the same way as it occurs at phase transitions in $A_{IV}B_{VI}$ semiconductors [6]. A remarkable feature of the obtained results is the spin glass behaviour of a system, nominally not containing any magnetic ingredients. It means that in some crystal environments atoms of non-transition metals may carry a magnetic moment as was predicted in [7, 8] and, moreover, may even interact, a small number of electrons being present in the conduction band [9].

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