Journal of the Physical Society of Japan
Vol. 70, No. 8, August, 2001, pp. 2242–2244

Magnetic Counterpart of Persistent Photoconductivity in Narrow-Gap Semiconductors

Alexander N. Vasil'ev*, Tatyana N. Voloshok, Jolanta K. Warchulska[1] and Hiroshi Kageyama[2]

Low Temperature Physics Department, Moscow State University, Moscow 119899, Russia
[1]*International Laboratory of High Magnetic Fields and Low Temperature, Wroclaw 53-421, Poland*
[2]*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581*

(Received April 19, 2001)

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 phenomenon in which the conductivity of these compounds and/or structures is observed to be greatly enhanced by visible or infrared illumination and 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, models of repulsive barriers for both electron emission and capture were introduced based primarily on the assumption of dopants 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 upon heating.

KEYWORDS: narrow-gap semiconductors, persistent photoconductivity, magnetic susceptibility

The materials in the present study belong to the unique family of $A_{IV}B_{VI}$ semiconductors consisting of nine binary compounds (Ge,Sn,Pb)–(S,Se,Te) and their solid solutions. The appearance of a narrow gap in their energy spectrum stems genetically from the Peierls splitting of quasi-one-dimensional zones formed by p-orbitals of metals and chalcogenes.[1)] All lead chalcogenides as well as high-temperature phases of germanium telluride and tin telluride possess a rocksalt structure.[2)] On lowering the temperature, GeTe at 670 K and SnTe at $T \leq 100$ K transform into the rhombohedral phase through the softening of the transverse optical mode in the [111] direction, while lead telluride remains a virtual ferroelectric with anomalously high dielectric constants.[3)] When 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.[4,5)] In the contemporary understanding,[6)] C_{III} impurities in the $A_{IV}B_{VI}$ matrix dissociate, $2{C_{III}}^0 = {C_{III}}^- + {C_{III}}^+$, into negatively charged ${C_{III}}^-$ and positively charged ${C_{III}}^+$ centers, creating 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 this deep-shallow transformation is far from 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 gain 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 using 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.[7)] On cooling in darkness, the resistivity of $Pb_{0.75}Sn_{0.25}$Te:0.5 at.%In and PbTe:0.3 at.%Ga show semiconducting behaviour as expected for the activation of electrons from deep levels into the conduction band. Illumination within a few seconds ($\sim$20 mW/cm^2) at low temperatures resulted in a decrease of resistivity by a few orders of magnitude persisting for many hours. Upon heating, as shown in Fig. 1, the resistivity of the samples increased, reaching maximums at $T \sim 20$ K in $Pb_{0.75}Sn_{0.25}$Te:0.5 at.%In and at $T \sim 70$ K in PbTe:0.3 at.%Ga. The heating of the samples under permanent illumination ($\sim$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:1 at.%In, since the In level in PbTe falls into the conduction band.[8)]

The influence of illumination on the magnetic properties of $A_{IV}B_{VI}$:C_{III} compounds was mainly studied by a Faraday balance technique. The construction of this apparatus did not allow for the complete screening of the sample from daylight. Additional illumination of the sample was provided by the incandescense lamp through the channel of the measuring device. The sample, mounted on Kevlar thread, was cooled to liquid helium

*Correspondence and requests for materials should be addressed to A.N.V. E-mail: vasil@lt.phys.msu.su

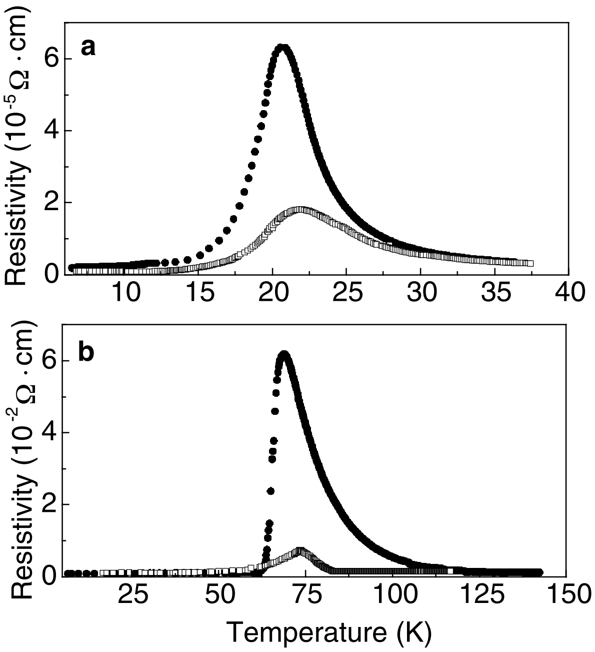

Fig. 1. Temperature dependencies of resistivity upon heating after brief illumination at low temperature (solid circles •) and under permanent illumination (open squares □). (a) $Pb_{0.75}Sn_{0.25}Te$:0.5 at.%In; (b) PbTe:0.3 at.%Ga.

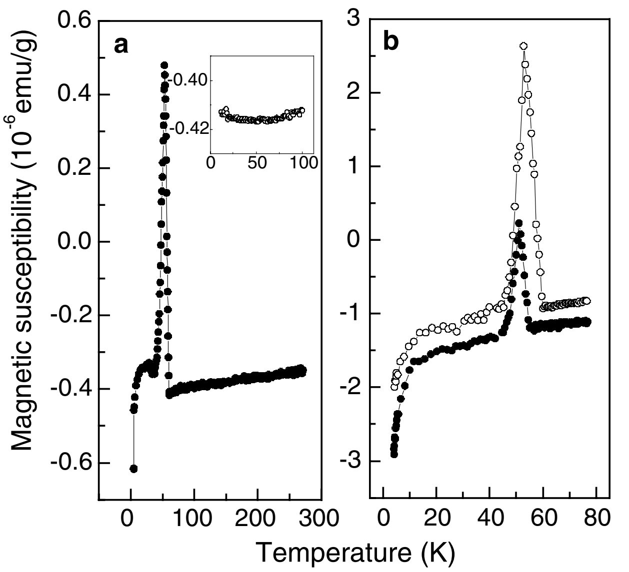

Fig. 2. Temperature dependencies of magnetic susceptibility upon heating after brief illumination at low temperature. (a) PbTe:1 at.%In; (b) $Pb_{0.75}Sn_{0.25}Te$:0.5 at.%In (solid circles •) and $Pb_{0.75}Sn_{0.25}Te$:2 at.%In (open circles ∘). The inset in panel (a) shows the temperature dependence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

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 upon heating at the rate of about 1 K/min at $H = 4.28$ kOe. Surprisingly, the results of magnetic measurements did not meet the expectations suggested from the transport measurements.

The temperature dependencies of magnetic susceptibility of PbTe:1 at.%In, $Pb_{0.75}Sn_{0.25}Te$:0.5 at.%In and $Pb_{0.75}Sn_{0.25}Te$:2 at.%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 an undoped sample of PbTe [see the inset in Fig. 2(a)]. Upon heating an additional diamagnetism was removed and at approximately 50 K, a strong paramagnetic peak with a sharp high temperature edge appeared. As can be seen from the comparison of curves for $Pb_{0.75}Sn_{0.25}Te$:0.5 at.%In and $Pb_{0.75}Sn_{0.25}$-Te:2 at.%In Fig. 2(b), an increase in the impurity content resulted in an increase in both paramagnetic background and paramagnetic peak.

The magnetic properties of PbTe:0.3 at.%Ga were studied by both Faraday balance and SQUID magnetometer techniques. In Faraday balance measurements, this sample shows mainly the same behavior 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 an incandescence lamp was employed, but prior to the measurements the sample was exposed to daylight at room temperature and then was cooled to liquid helium temperature. Once again the behavior similar to that described above was present, however upon subsequent cooling in a dark chamber of the SQUID magnetometer, the paramagnetic peak was not observed at all and the diamagnetic downturn at low temperatures was replaced 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 a paramagnetic peak, as shown in Fig. 3. In general, the magnetic response of a PbTe:0.3 at.%Ga single

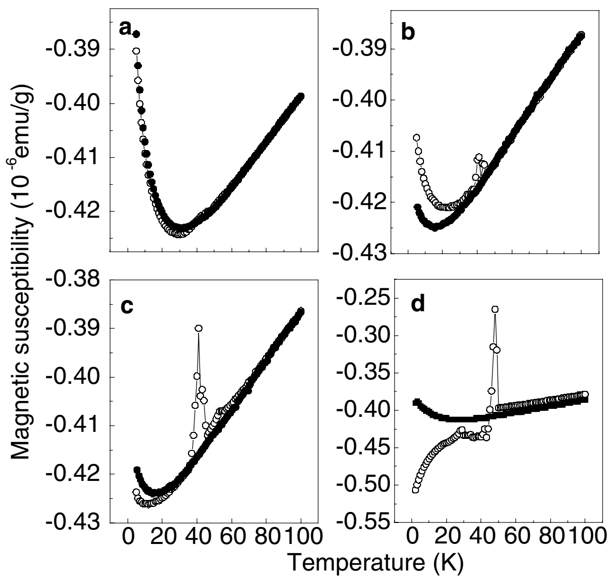

Fig. 3. Temperature dependencies of magnetic susceptibility of PbTe:0.3 at.%Ga both upon heating (open circles ∘) and cooling (solid circles •) measured in the dark chamber of SQUID magnetometer after different exposures to white-light illumination (t_{exp}) at room temperature. (a) $t_{exp} = 5 \times 10^2$ 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.

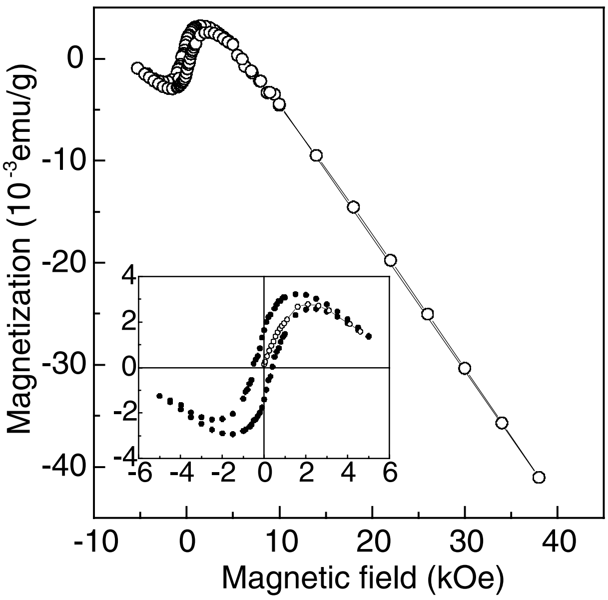

Fig. 4. Field dependence of PbTe:0.3 at.%Ga magnetization at $T = 5$ K. The inset shows the hysteresis in a low magnetic field.

crystal resembles the behavior 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.

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. Upon cooling in darkness, the electrons leaving the conduction band occupy dopant centers, $C_{III}{}^{-}$ being a substitute for metal in the 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, and 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 a 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. Upon 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 in paramagnetic susceptibility in the same way as one occurs during phase transitions in $A_{IV}B_{VI}$ semiconductors.[9–11] A remarkable feature of the obtained results is the spin glass behaviour of a system nominally not containing any magnetic ingredients. This means that in some crystal environments, atoms of nontransition metals may carry a magnetic moment as was predicted in refs. 12 and 13 and, moreover, may even interact with each other, a small number of electrons being present in the conduction band.[14]

We thank B. A. Volkov and D. I. Khomskii for discussions on theoretical aspects of the observed phenomena.

1) J. Dimmok: *The Physics of Semimetals and Narrow Gap Semiconductors*, ed. D. L. Carter and R. T. Bate (Pergamon Press, New York, 1971) p. 319.
2) P. B. Littlewood: J. Phys. C **13** (1980) 4855.
3) H. Kawamura: The Lecture Notes on Physics **133** (1980) 470.
4) B. A. Akimov, V. A. Bogoyavlenskiy and S. P. Zimin: Semicond. Sci. Technol. **14** (1999) 679.
5) A. Martinez, R. J. Abbundi, B. Houston, J. L. Davis and R. S. Allgaier: J. Appl. Phys. **57** (1985) 1165.
6) I. A. Drabkin and B. Ya. Moizhes: Sov. Phys. Semicond. **15** (1981) 625.
7) S. P. Grishechkina, A. A. Zhuravlev, K. P. Mollmann and K. H. Herrmann: Sov. Phys. Semicond. **25** (1991) 409.
8) S. A. Nemov, V. I. Proshin and T. G. Abaidulina: Sov. Phys. Semicond. **30** (1996) 676.
9) B. M. Baginskii, R. O. Kikodze and G. V. Lashkarev: Sov. Phys. Solid State **19** (1977) 588.
10) V. I. Litvinov and V. K. Dugaev: Sov. Phys. JETP **77** (1979) 335.
11) G. V. Lashkarev, A. V. Brodovoi and S. D. Letyuchenko: Sov. Phys. Semicond. **21** (1987) 1921.
12) P. W. Anderson: Phys. Rev. **124** (1961) 41.
13) J. Kondo: *Solid State Physics* (Academic Press, New York, 1969) Vol. 23, p. 184.
14) G. Bastard and C. Lewiner: Phys. Rev. B **20** (1979) 4256.