Transport peculiarities and phase transition in diluted magnetic semiconductors CdGeAs$_2$: Mn at high hydrostatic pressure

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Abstract. Pressure dependences of resistivity $\rho(P)$ and Hall coefficient $R_H$ have been measured for the novel high-temperature ferromagnetic semiconductor $p$-Cd$_{1-x}$Mn$_x$GeAs$_2$ ($x=0$-0.36) at the room temperature. Structural phase transitions with positions shifting towards low pressures, when percentage of manganese increases from 5.9 GPa for CdGeAs$_2$ to 4.8 GPa for $p$-Cd$_{0.64}$Mn$_{0.36}$GeAs$_2$, are found out. Some anomalies of dependence $R_H(P)$, which we attribute to magnetic properties and the presence of impurities, are found out for the crystals with the greater percentage of manganese ($x\geq0.18$).

1. Introduction

Today, the research of new functional magnetic materials for spintronics applications is included into a number of the major scientific fields worldwide[1]. It is possible to formulate some basic requests to which such materials should satisfy: they should be ferromagnetics with high enough Curie temperatures (well above the room range) and possess both magnetic and semiconducting properties. These requirements in the great extent are fulfilled for diamond-like semiconductors $\text{AIBV}_2\text{C}_2$ where high mobility of charge carriers, their small effective masses and the greater ratio of electron mobility to the hole one are inherent. Controlled bringing in of transition elements like Mn, Fe, Cr, etc. to anionic and cationic sublattices of these compounds may switch semiconducting material into the ferromagnetic state with a high Curie temperature.

Recently, Marenkin et al. [2] had synthesized bulk CdGeAs$_2$-based compounds, including their single crystalline forms, where the content of manganese has been changed from $x=0$ to $x=0.36$. According to X-ray analysis all synthesized samples were homogeneous chalcopyrites with Curie temperature $T_C$ reached to 355 K - a largest value for the $\text{AIBV}_2\text{C}_2$-$\text{Mn}$ family known up today. The present work is stimulated by our interest in high pressures research of CdGeAs$_2$:Mn compounds and their electrophysical properties in the vicinity of polymorphic transformation.
2. Experimental technique and crystals
Measurements were carried out for single crystalline and polycrystalline p-Cd$_{1-x}$Mn$_x$GeAs$_2$ samples at hydrostatic pressures up to 9GPa at the room temperature. The fluoroplastic 80 mm$^3$ capsule with 8 lead-in contacts was used as a sample containing cell. The cell was set in the solenoid with magnetic field intensity of $H\sim$5 kOe. Pressure was controlled with the manganin manometer, calibrated against to several reference points in the whole pressure range. Synthesis of samples has been carried out from high pure powders of monocrystals CdAs$_2$ and Ge. Samples had the form of a bar with dimension of 3x1x1 mm, and the uniformity of samples was checked through the resistivity and Hall coefficient measurements by means of the four-probe method. In more details, the experimental technique is described in [3, 4].

3. Results of measurements and discussions
Pressure dependences of resistivity $\rho$ and Hall coefficient $R_H$ for all investigated samples p-Cd$_{1-x}$Mn$_x$GeAs$_2$ are presented in figure 1 and figure 2. Structural phase transitions are found out for all samples around pressures $P=5.9; 5.7; 5.5; 5.4; 4.9; 4.8$ GPa, showing up on dependences of resistivity $\rho(P)$ (figure 1) and Hall coefficient $R_H(P)$ (figure 2) as abrupt declines. Also, the structural phase transitions are found out in the vicinity of pressures $P=2.9; 2.8; 2.7; 2.6; 2.5; 2.4; 2.3$ GPa when pressure falls. The position of phase transition shifts towards lower pressures with an increase in percentage of manganes. The similar picture is observed for position of phase transition at the falling pressure. The ratio of the conditional phase transition position at increasing pressure to the same value at falling pressure makes $P_{PT}=P_{PF}=2\div2.1$, i.e. the difference is within an experiment inaccuracy.

![Figure 1](image1.png)

**Figure 1.** Pressure dependences of resistivity of the investigated samples at rise of pressure.

![Figure 2](image2.png)

**Figure 2.** Pressure dependences of a Hall coefficient of the investigated samples at rise of pressure.

In figure 3, pressure dependences of resistivity and a Hall coefficient for the base sample CdGeAs$_2$ are presented. It is seen, that the resistivity slowly decreases while pressure increases up to point $P=5.3$ GPa and then sharply falls almost for three orders of magnitude at $P\geq5.3$ GPa, indicating the beginning of the phase transition, and after $P>6.5$ GPa tends to flat asymptotics (saturation region). The resistivity of saturation region, normalized to the atmospheric pressure value, makes $\rho/\rho_0=763$. In the region of saturation, conductivity is $\sigma=353$ $\Omega^{-1}$ sm$^{-1}$ that exceeds theoretically
calculated values of the minimal metallic conductivity which should be in our case \( \sigma = 200 \ \Omega^{-1} \text{sm}^{-1} \) [5]. This allows us to assume the metallic type of conductivity has taken a place. The hysteresis is well seen when pressure falls and the phase transition is observed around \( P=2.9 \) GPa. Values of resistivity at atmospheric pressure and at falling up to \( P=0 \) pressure are identical, i.e. \( \rho_0=\rho_0' \) (where \( \rho_0'=\rho (P\rightarrow 0) \) ), implying the reversibility of the transition.

Figure 3. Pressure dependence of resistivity (circles) and a Hall coefficient (squares) for the base sample \( p\text{-CdGeAs}_2 \). Full symbol – pressure rise (compression), open symbol – pressure fall (decompression)

Figure 4. Pressure dependence of resistivity (circles) and a Hall coefficient (squares) for the sample \( p\text{-Cd}_{0.94}\text{Mn}_{0.06}\text{GeAs}_2 \). Full symbol – pressure rise (compression), open symbol – pressure fall (decompression).

The Hall coefficient also slowly decreases until \( P<5.1 \) GPa, then after \( P=5.1 \) GPa falls abruptly almost for 5 orders of magnitude and tends to flat asymptotics when \( P>6.5 \) GPa. In the region of saturation, concentration of charge carriers is \( \approx 2.8 \times 10^{20} \text{sm}^{-3} \) that does not conflict with our assumption about metal type of conductivity in this region. At falling pressure, the wide hysteresis is observed and the phase transition occurs around \( P=2.9 \) GPa, so that \( R_{H0}=R_{H0'} \). From above mentioned, we suppose the reversible structural phase transition is observed for the base sample \( p\text{-CdGeAs}_2 \), accompanied with metal-insulator transition in the conductivity type. Considering pressure dependence of the resistivity for \( \text{Cd}_{0.94}\text{Mn}_{0.06}\text{GeAs}_2 \) (figure 4), note that resistivity varies very weakly until \( P<4.7 \) GPa, then sharply falls for 2 orders between \( P=4.7 \) GPa and \( P=6.1 \) GPa, leaving the transition region with values \( \rho_0/\rho_H=12, \sigma_H=12.3 \ \Omega^{-1} \text{sm}^{-1}, \rho_0=\rho_0' \). Phase transition is well pronounced in the \( \rho(P) \) curve at \( P_{PT}=2.7 \) GPa (falling pressure) as well. The dependence of the Hall coefficient on pressure is similar. Concentration of carriers in the saturation region is \( \approx 10^{18} \text{sm}^{-3} \), and \( R_{H0}=R_{H0'} \). Thus, relying on values of conductivity and Hall coefficient values prior to and after phase transition, we conclude that a reversible structural transition takes a place in the sample \( p\text{-Cd}_{0.94}\text{Mn}_{0.06}\text{GeAs}_2 \). For the sample \( p\text{-Cd}_{0.64}\text{Mn}_{0.36}\text{GeAs}_2 \) (figure 5) at high hydrostatic pressure, the resistivity increases weakly up to \( P=0.8 \) GPa, then falls and reaches a minimum at \( P=2 \) GPa, and then tends to flat asymptotics after \( P=3 \) GPa and falls again at \( P=4.1 \) GPa, indicating thereby the presence of phase transition. The resistivity also tends to the flat asymptotics, and in the saturation region of conductivity we have \( \sigma=17.8 \ \Omega^{-1} \text{sm}^{-1}, \rho_0=\rho_0' \). The dependence of Hall coefficient on pressure also has complex character. Hall coefficient does not vary almost up to \( P=0.8 \) GPa, then increases until \( P<1.6 \) GPa.
reaching a maximum, then falls at P≈2.3 GPa, then again grows and at P≈3 GPa reaches a maximum again and after P≈5.6 GPa tends to flat asymptotics. In the field of saturation concentration of charge carriers $\approx 8 \times 10^{19}$ cm$^{-3}$, and $\sigma$ reaches values typical for the metal conductivity. Thus, it is possible to assume, that in p-Cd$_{0.64}$Mn$_{0.36}$GeAs$_2$ the transition semiconductor-metal is observed. Found anomalies on curves $\rho(P)$ and $\rho_H(P)$ are most likely due to magnetic properties of samples or the presence of impurity (vacancy) sites.

4. The conclusion
Conditionally, all investigated samples fall into 3 groups: 1) the base sample CdGeAs$_2$ and weakly doped sample p-Cd$_{0.897}$Mn$_{0.003}$GeAs$_2$; 2) samples Cd$_{0.947}$Mn$_{0.053}$GeAs$_2$ and Cd$_{0.94}$Mn$_{0.06}$GeAs$_2$, for which anomalies of Hall coefficient pressure dependences are not observed, and 3) the group of samples, where anomalies of $R_H(P)$ dependence are observed - Cd$_{0.82}$Mn$_{0.18}$GeAs$_2$ and Cd$_{0.64}$Mn$_{0.36}$GeAs$_2$. Apart there is the sample Cd$_{0.7}$Mn$_{0.3}$GeAs$_2$: no anomalies for pressure dependence of a Hall coefficient have been observed despite the high enough doping level. The discussed features are intricate interplay between native acceptors in as-grown basic CdGeAs$_2$ sample [6] and Mn$^{2+}$ substitutions for Cd$^{2+}$ in Mn-doped samples [7]. We are planning to conduct an additional study to clarify the nature of these anomalies.

In summary, for all samples the structural reversible phase transitions, which position shifts towards low pressures with the increase in percentage of manganese, are observed. To what structural modification the chalcopyrite phase comes transformed as a result of a phase transition we cannot conclude without in situ X-ray diffraction analysis.

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