Room-temperature ferromagnetism in diluted magnetic semiconductor Pb$_{1-x}$Cr$_x$Te

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Abstract. The temperature and magnetic field dependencies of magnetization ($T=5$-340 K, $B \leq 0.5$ T) as well as electron paramagnetic resonance (EPR) ($T=80$-400 K) in Pb$_{1-x}$Cr$_x$Te ($x \leq 0.045$) have been studied. It was shown that all samples are ferromagnetic with a clear hysteresis loop up to the room temperature and magnetic saturation moment rises with increasing of the chromium content. Using temperature dependencies of magnetization $M(T)$ ferromagnetic Curie temperatures up to 330 K were revealed. EPR spectra in the paramagnetic phase were satisfactorily approximated by a single Dysonian line. Temperature dependence of magnetic susceptibility was estimated and paramagnetic Curie temperature was determined. In ferromagnetic phase pronounced distortion and splitting of the EPR spectra on two Dysonian lines were revealed. Using approximation by the Lorenz-type curves with Dysonian terms, temperature dependencies of the main parameters for each absorption line were obtained.

1. Introduction
Doping of PbTe with chromium induces an appearence of deep impurity level, situated approximately 100 meV higher the bottom of conduction band [1, 2]. Typically an increase of the chromium concentration in the p-type Pb$_{1-x}$Cr$_x$Te alloys leads to the p-n conversion ($x \geq 0.001$), increase of the free electron concentration and stabilization of Fermi level by the resonant chromium level ($x \geq 0.002$). It was shown that lightly doped Pb$_{1-x}$Cr$_x$Te ($x \leq 0.01$) alloys are diluted magnetic semiconductors (DMS), which reveal a Brillouin type paramagnetism due to the presence of the magnetically active Cr$^{3+}$ ions, substituting lead atoms in the host crystal lattice [2, 3]. It was also found that ferromagnetic precipitations of unknown nature in most of investigated samples are available, but the authors did not analyze the ferromagnetic share, subtracting it from the magnetization data [3]. Recently the high-temperature ferromagnetism was revealed in Pb$_{1-x-y}$Ge$_y$Cr$_x$Te ($y=0.01$-0.08) alloys [4]. Thus, one can suppose that in the heavily doped Pb$_{1-x}$Cr$_x$Te alloys the high-temperature ferromagnetic ordering may take place also.

To investigate the magnetic properties of the heavily doped with chromium lead telluride and to reveal the new room-temperature ferromagnetic DMS temperature and magnetic field dependencies of magnetization as well as electron paramagnetic resonance in Pb$_{1-x}$Cr$_x$Te ($x \leq 0.045$) have been studied.

2. Experimental details
Single crystal Pb$_{1-x}$Cr$_x$Te ingot has been grown by the Bridgman method. The ingot was cut into slices
approximately 1.5 mm thick perpendicular to the growth direction. The chemical composition was determined using the X-ray fluorescent analysis. It was found that in accordance with the typical for group IV-VI solid solutions exponential distribution of substitution components the chromium concentration monotonously grows from the origin to the end of ingot (x=0.004–0.044). The crystal structure of the samples was controlled by powder high-resolution X-ray diffraction, carried out at room temperature with CuKα radiation source on Rigaku X-ray diffractometer with monochromator. It was shown that there are no secondary magnetic phases in the samples.

Magnetic measurements were performed on the samples of the weight 0.05-0.1 g glued onto a plastic holder. The temperature and magnetic field dependencies of the magnetization were measured in the magnetic field up to B=0.5 T using vibrating sample magnetometer EG & G PARC M155 detecting the magnetic moments down to 5×10⁻⁵ emu. For the temperature variation (5≤T≤340 K) the liquid helium gas-flow cryostat equipped with a heater was used.

Electron paramagnetic resonance was measured using X-band EPR spectrometer CMS 8400 (ADANI) (f=9.1-9.6 GHz, B≤0.7 T) equipped by a low temperature mount with the temperature controller tSTAT335, operating in the range T=80-470 K. The crystal samples for EPR experiments were crushed into powder to decrease the skin effect and to avoid broadening out of the resonance signal caused by the influence of the surface strains.

3. Magnetic properties
In the whole temperature range investigated clear hysteresis loops on the magnetic field dependencies of magnetization were revealed (figure 1). One can see the noticeable linear contribution on magnetization curves indicating the coexistence of the ferromagnetism and paramagnetism in the samples under study as shown in figure 1. One can suppose that the existence of additional paramagnetic share is caused by the presence of isolated chromium ions, which may serve as a source of paramagnetic and paramagnetic contributions to the main ferromagnetic response. The magnitudes of ferromagnetic and paramagnetic contributions monotonously rise with the increase of chromium content in the alloys. In the samples with maximal chromium content magnetization attains approximately 0.3 emu/g. The residual magnetization Mr almost linearly grows up to the 0.15 emu/g with increasing of chromium concentration, while coercivity passes through the maximum, achieving 0.13 T at T=78 K.

Assuming that the magnetic moment arises from the Cr impurity atoms and using values of magnetic saturation moment the effective magnetic moment per chromium atom has been estimated. It was found that it is 0.1–0.3 μB, slightly increasing with the chromium content. This value is significantly lower than the moment per Cr atom in the known ferromagnetic chromium compounds: 2.0–3.8 μB for CrTe, Cr1.5Te4, Cr1.7Te8 and even in the recently investigated Pb1-x-yGexCryTe alloys [4]. However, the chromium concentration in our samples is relatively low by compare with Cr concentration range studied in [4]. We suppose that essential paramagnetic march observed indicates that the part of chromium introduced does not participate in the short magnetic order coupling those results in lowering of effective magnetic moment.

The temperature dependencies of the magnetization M(T) (figure 2) is rather concave type with a broaden maximum at temperatures 130-150 K for all samples under study (figure 2). The amplitude of this maximum decreases with decreasing the magnetic field. On the temperature dependencies of residual magnetization M(T) this maximum disappears and we observed monotonous increase of magnetization with the decrease of temperature. In order to obtain the ferromagnetic Curie temperature the M² versus temperature dependencies were plotted and linear extrapolation of these dependencies to its temperature intercept were performed. It was shown that the ferromagnetic ordering temperature rises with increasing chromium content in the alloys, achieving maximal value TC≈330 K (see inset in figure 2).

4. Electron paramagnetic resonance
EPR study has been performed for Pb1-xCrxTe (x=0.026, 0.044) alloys in the temperature range 270–400 K, at lower temperatures EPR signal disappeared probably due to the high electron conductivity in
Figure 1. Hysteresis loops at T=78 K for the Pb$_{1-x}$Cr$_x$Te alloys.

Figure 2. Temperature dependencies of magnetization at B=0.4 T for Pb$_{1-x}$Cr$_x$Te. On inset - Curie temperature T$_C$ versus Cr content.

the samples under study. In the paramagnetic phase at temperatures T>330 K the EPR spectra show a broad asymmetrical line of Dysonian shape (figure 3a) and satisfactorily ascribed by the single Lorenz-type curve with Dysonian term. Effective g-factor, deduced from this approximation, tends to the saturation value $g=2.06\pm0.01$, while the linewidth $\Delta H=0.1$ T at the highest temperatures. Under the decrease of temperature and approaching the ferromagnetic Curie temperature g-factor slowly increases, while the linewidth falls approximately two times. Obtained experimental results significantly deviate from the previously reported data for the lightly doped Pb$_{1-x}$Cr$_x$Te ($x\leq0.01$): $g=1.93-1.99$ and $\Delta H=0.005$ T at helium temperatures [5]. One can suppose that this discrepancy may originate by strong dependencies of these parameters on the temperature and Cr content in the alloys.

The temperature dependence of magnetic susceptibility $\chi$ in the paramagnetic phase was estimated by double integration of the first-derivative absorption line. It was shown that value of $\chi$ varies with temperature in accordance with the Curie-Weiss law. Estimations of the paramagnetic Curie temperature $\Theta$, deduced from $1/\chi(T)$ dependence, give us value $\Theta=330$ K for $x=0.026$, which is close to the ferromagnetic Curie temperature T$_C$, obtained from the magnetic measurements.

At the temperature T=325 K, which coincides with the Curie temperature T$_C$, the pronounced distortion of the EPR spectrum appears (see figure 3b). In ferromagnetic phase further decrease of temperature leads to the significant splitting of the spectrum into the two distinct absorption lines, one of which remains virtually unchanged while another strongly shifts to lower fields. In order to obtain parameters of each line resolved an approximation of experimental EPR spectra by the Lorenz-type curves with additional Dysonian terms were performed (see examples plotted by dotted lines for T=315 K, 325 K in figure 3b). So, temperature dependencies of g-factors were obtained and revealed a sharp anomaly in the vicinity of the ferromagnetic ordering temperature T$_C$ (see inset in figure 3a).

The magnitude of linewidths $\Delta H$ for each line passes through a minimum (approximately 0.04 T and 0.05 T) at 340 K as the temperature decreases and then increases up to approximately 0.085 T and 0.12 T at T=275 K accordingly.
Figure 3. Evolution of the first-derivative absorption EPR spectra in Pb$_{1-x}$Cr$_x$Te (x=0.026) with temperature (lines – approximation according to the Dyson’s theory). On inset – temperature dependencies of g-factor (closed circles – normal term, open circles – anomalous term).

5. Conclusion
The room-temperature ferromagnetism in the Pb$_{1-x}$Cr$_x$Te alloys was revealed. It was shown, that ferromagnetic Curie temperature, obtained by extrapolating of the linear part of $M^2$ versus temperature dependencies to its temperature intercept, grows with the increase of chromium content and achieves $T_C \approx 330$ K at $x \approx 0.045$.

In paramagnetic phase effective g-factor deduced from the EPR spectra slowly decreases with increasing temperature and tends to the saturation value $g = 2.06 \pm 0.01$. It was shown that temperature dependence of magnetic susceptibility obeys Curie-Weiss law and paramagnetic Curie temperature $\Theta$, which is close to $T_C$, was determined. Near the ferromagnetic ordering temperature distortion of the EPR spectra and its following splitting on two Dysoni an lines were found. Parameters of resolved lines were determined and pronounced anomalies in the temperature dependencies of g-factor and linewidths were revealed.

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