Mn^{2+}-V_{Zn}^{-} charge transfer complexes in $Zn_{1-x}Mn_xTe$

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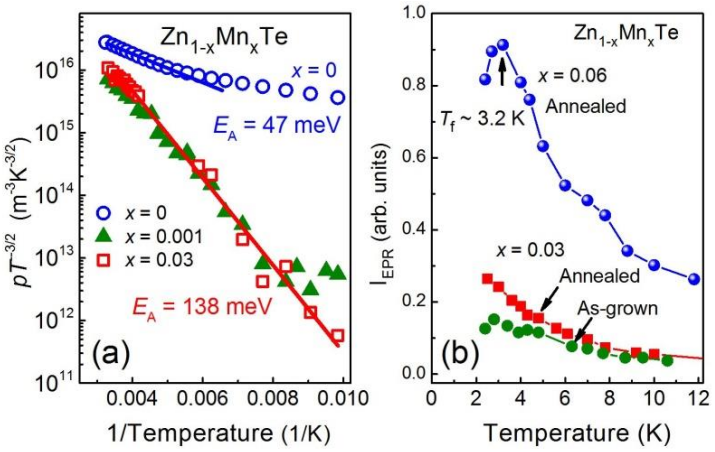
$Zn_{1-x}Mn_xTe$ dilute magnetic semiconductor (DMS) has recently attracted much attention due to the possibility of creation of the Mn-Mn ferromagnetic coupling [1] and fabrication of highly spin polarized red-green light emitting devices [2]. It is commonly believed that in $II_{1-x}Mn_xVI$ DMSs Mn^{2+} ions are electrically neutral. Recently, we have reported that in $Zn_{1-x}Mn_xTe$ doped with phosphorus (P) the Mn^{2+} ions strongly couple with P-acceptors giving rise to the compensation of the P-acceptors and the creation of Mn^{3+} ions [3].

In this communication, we report the results of the Hall effect, photoluminescence (PL), magneto-PL and electron paramagnetic resonance measurements performed on the undoped ZnTe and $Zn_{1-x}Mn_xTe$ crystals, which show a strong interaction between Mn^{2+} ions and singly negatively charged zinc vacancy defects V_{Zn}^{-} resulting in the formation of the Mn^{2+}-V_{Zn}^{-} charge transfer complexes. The Mn^{2+}-V_{Zn}^{-} coupling causes the transformation of the 0.047 eV $V_{Zn}^{-/0}$ shallow acceptor level, present in ZnTe, into a 0.138 eV $V_{Zn}^{--/-}$ deep acceptor level [see Fig. (a)]. This points to the compensation of the $V_{Zn}^{-/0}$ shallow acceptor level by Mn^{2+} ions. We have suggested a charge transfer mechanism which transforms the Mn^{2+}-V_{Zn}^{-} complexes into Mn^{3+}-V_{Zn}^{--} ones,



$$Mn^{2+}(3d^5,4s^2) + V_{Zn}^{-} \rightarrow Mn^{2+}(3d^5,4s^1) + V_{Zn}^{--} \rightarrow Mn^{3+}(3d^4,4s^2) + V_{Zn}^{--}.$$

The PL spectra measured under the 2.21 eV excitation for $Zn_{0.96}Mn_{0.04}Te$ sample exhibit two PL bands locating at 1.96 eV and 1.44 eV, which are attributed to the intrashell transitions of Mn^{2+} and Mn^{3+} ions, respectively.

The coexistence of the mixed valence Mn^{2+} and Mn^{3+} states leads to local ferromagnetic (FM) double exchange interaction between Mn^{2+} and Mn^{3+} ions by the Zener double exchange mechanism. The competition between the Mn^{2+}-Mn^{3+} FM double exchange interaction and the intrinsic Mn^{2+}-Mn^{2+} antiferromagnetic superexchange coupling gives rise to the paramagnetic–spin glass phase transition at T_f = 3.2 K in $Zn_{0.94}Mn_{0.06}Te$ sample [see Fig. (b)].

We have observed that the compensation of the acceptor impurities or cation vacancy defects by Mn^{2+} ions is the inherent property not only for $II_{1-x}Mn_xVI$ DMSs but also for $III_{1-x}Mn_xV$ alloys. This finding calls for a new strategy for the efficient *p*-type doping of the Mn-based DMSs.

[1] Le Van Khoi, A. Avdonin, and A. Mycielski, *Phys. Rev. B* **107**, 085206 (2023).
[2] Le Van Khoi and R. R. Gałązka, *Appl. Phys. Lett.* **98**, 112103 (2011).
[3] Le Van Khoi, W. Dobrowolski, T. Kazimierczuk, A. Rodek, P. Kossacki, R.R. Galazka, and W. Zawadzki, *Phys. Rev. B* **101**, 054440 (2020).