

Mn³⁺ in the Zn_{1-x}Mn_xTe Crystals Heavily Doped with Phosphorus

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Dilute magnetic semiconductors (DMS) exhibiting colossal magnetoresistance (CMR) are of a great interest for the spintronic device applications. Production of DMS with CMR requires the search for a dopant capable to change the charge state of magnetic ions. In this communication we report that doping Zn_{1-x}Mn_xTe with phosphorus (P) results in the formation of Mn³⁺ ions. The charge state of Mn ions was directly studied by monitoring the variation of intensity I_{Mn} of the Mn²⁺ photoluminescence (PL) with P doping level and magnetic field. Photoluminescence results indicate the presence of excitation energy bypass channel for the Mn²⁺ ions. This channel is suggested to form by Mn³⁺ cations resulting from the charge transfer process: $Mn^{2+} + P^{2-} \leftrightarrow Mn^{3+} + P^{3-}$.

The Zn_{1-x}Mn_xTe crystals doped with different P densities in the range of 10^{24} m^{-3} were grown by the high pressure Bridgman technique at 1400^o C. The PL measurements were performed on three Zn_{1-x}Mn_xTe samples with very similar Mn content $x \approx 0.03$, but with different P densities: undoped (labelled S1), $1 \times 10^{24} \text{ atoms/m}^3$ (S2), and $5 \times 10^{24} \text{ atoms/m}^3$ (S3).

Figure 1(a) shows the PL spectra for S1. The 0 T spectrum displays a strong Mn²⁺ emission band located at 1.956 eV which is due to the internal Mn²⁺ transitions: ${}^4T_1 \rightarrow {}^6A_1$. It is observed that the I_{Mn} is reduced by a factor of about 10 in S2 (Fig. 1(b)), and is completely quenched in S3 (Fig. 1(c)). In an external magnetic field of 4 T, I_{Mn} of S1 increases by a factor of 2.4 (1(a), red line), whereas I_{Mn} of S2 does not change. No Mn emission from S3 is observed in magnetic field up to 6 T. However, it was found that, in increasing excitation power (10 times), the Mn²⁺ emission reappears in S3 (Fig. 1(d)).

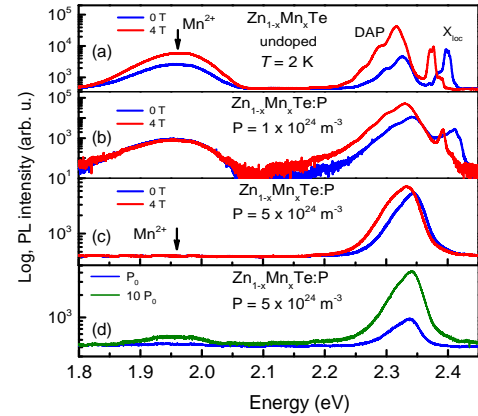


Figure 1

The variation of I_{Mn} with P densities and magnetic field in S2 and S3, and the recurrence of the Mn²⁺ emission in S3 clearly indicates that in the presence of P acceptors the Mn cations exist in mixed valence states. The first is the divalent Mn²⁺ ions corresponding the Mn²⁺ emission, the second causes the deactivation of the Mn²⁺ ions. It is known that in S2 and S3 the trivalent P³⁻ dopants substituting for the divalent Te²⁻ anions not only strongly alter the crystal field around Mn sites but can give rise to the charge transfer between the Mn²⁺ cations and P²⁻ anions. At low temperature when free holes are recaptured to the P³⁻ acceptors the P²⁻ anions occur. Since the electronegativity of P atoms (2.19) is greater than that of Mn atoms (1.55), it can cause the charge transfer from the Mn²⁺ cations to P²⁻ anions: $Mn^{2+} + P^{2-} \leftrightarrow Mn^{3+} + P^{3-}$. The Mn³⁺ ions with non zero orbital angular momentum inducing a strong Mn spin-lattice relaxation form an excitation energy bypass channel which gives rise to the suppression of the Mn²⁺ PL emission in S2 and S3.

The coexistence of the Mn²⁺ and Mn³⁺ ions in Zn_{1-x}Mn_xTe doped with P may induce the ferromagnetic double exchange interaction, spin glass phase, small polaron conduction, and colossal magnetoresistance.