Probing Hole-Induced Ferromagnetic Exchange in Magnetic Semiconductors by Inelastic Neutron Scattering

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The effect of hole doping on the exchange coupling of the nearest neighbor (NN) Mn pairs in $Zn_{1-x}Mn_xTe$ is probed by inelastic neutron scattering. The difference in the NN exchange energy ΔJ_1 in the presence and in the absence of the holes is determined. The obtained value of ΔJ_1 is in good agreement with the predictions of the Zener/RKKY model, even on the insulator side of the metal-insulator transition.

Recent comprehensive research on the nature of carrier-controlled ferromagnetism in III-V and II-VI Mn-based diluted magnetic semiconductors (DMS) has clearly shown that these systems combine intricate properties of charge-transfer insulators and strongly correlated disordered metals with the physics of impurity and band states in heavily doped semiconductors [1]. Because of this complexity, there are diverging opinions about the dominant microscopic mechanisms accounting for the ferromagnetism in these materials. For instance, according to *ab initio* computations, the holes associated with the presence of Mn in III-V compounds reside in the Mn *d* band, which implies that the relevant spin-spin coupling mechanism is double exchange [2]. Other workers, guided by photoemission results [3], assume that the Mn *d* band is deep in the valence band. This means that the holes which mediate the ferromagnetic coupling originate from effective mass acceptors produced by Mn in III-V compounds and by extrinsic dopants, such as N, in II-VI DMS. However, even if this is the case, a number of possible scenarios can *a priori* be envisaged. In particular, if the holes stay localized by the parent acceptors, the ferromagnetic transition can be viewed as the percolation threshold of bound magnetic polarons [4]. Alternatively, the hole-mediated ferromagnetic coupling can be assigned to virtual transitions of the holes from the acceptor levels to the valence band [5]. If, however, the relevant hole states are extended or their localization length is much greater than an average distance between the acceptors, exchange interactions will be effectively mediated by the itinerant carriers, so that the Zener or Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanisms will operate [6–8]. In this situation, attempts to simulate the properties of these systems numerically have been undertaken [9], although it is still a formidable task to take into account the effects of both disorder and carrier-

carrier correlation near the Mott-Anderson transition even in nonmagnetic semiconductors [10].

On the experimental side, there is no evidence so far for the *d*-band transport and for the associated colossal magnetoresistance in III-V and II-VI ferromagnetic semiconductors. This seems to suggest that the double exchange is not the dominant spin-spin coupling mechanism in these systems. On the other hand, in both III-V [11] and II-VI [12] Mn-based DMSs, the ferromagnetism occurs on both sides of the metal-insulator transition (MIT) which, similarly to other extrinsic semiconductors, is of the Anderson-Mott type and occurs when the hole concentration is varied. Interestingly, the corresponding Curie temperatures show no critical behavior across the localization boundary [11,12]. It is, therefore, hard to tell based on macroscopic magnetization measurements whether the holes bound by individual acceptors or, alternatively, the holes residing in weakly localized or extended states mediate ferromagnetism in these compounds. In order to address this question experimentally, we have examined the magnitude of the exchange energy between the nearest neighbor (NN) Mn pairs by inelastic neutron scattering in $Zn_{1-x}Mn_xTe$. By comparing results for undoped and doped crystals, we determine rather directly the contribution to the exchange brought about by the presence of the holes. According to our electrical measurements, the sample studied remains on the insulator side of the metal-to-insulator transition. Nevertheless, the hole-induced contribution to the pair energy is by a factor of 4 smaller than that calculated under the assumption that the holes reside on individual acceptors. By contrast, if the hole states are assumed to be metallic-like at length scales of the NN distance, the calculated value is smaller than the experimental one by a factor of 1.5, a discrepancy well within the combined uncertainties in input parameters to theory and to experiment.

Furthermore, no visible broadening of the scattering line is observed in the presence of doping, again indicating that the hole states exhibit no substantial fluctuations expected for the strongly localized regime. We conclude that the ferromagnetic exchange is mediated by itinerant holes, even on the insulator side of the MIT.

Because of the small magnetic cross section, inelastic scattering measurements cannot be completed on films grown by molecular beam epitaxy commonly employed in order to overcome the thermal equilibrium solubility limits of relevant dopants in DMS [11,12]. However, it has been shown previously by some of us that large single crystals of $Zn_{1-x}Mn_xTe$:P can be prepared [13], in which Mn and hole concentrations are sufficiently high to observe ferromagnetic ordering. Our $Zn_{1-x}Mn_xTe$ crystals are grown by the high pressure Bridgman method from $(ZnTe)_{1-x}(MnTe)_x$ solution in an evacuated (10^{-6} Torr) quartz ampoule, with phosphorus corresponding to the doping level of 5×10^{19} cm^{-3} added in the form of Zn_3P_2. The crystals obtained in this way are 10–20 mm in diameter and about 60 mm long. The x-ray energy dispersive fluorescence analysis demonstrates a uniform distribution of Mn along the central part of the ingots. X-ray diffraction studies do not reveal any second phase inclusions and show that the lattice constant increases linearly with the Mn content in accord with Vegard's law.

According to Hall effect measurements carried out at room temperature, the hole concentration in the as-grown material is about 1.3×10^{19} cm^{-3} in the case of ZnTe, but decreases strongly with the Mn content, dropping down to 2×10^{16} cm^{-3} for $Zn_{0.95}Mn_{0.05}Te$. This suggests that the incorporation of Mn results in the creation of rather efficient compensating centers. A microscopic mechanism accounting for this effect is unknown at present but since the tetrahedral radius of Mn^{2+} (1.33 Å) is larger than the tetrahedral radius of Zn^{2+} (1.225 Å) [14], interstitial Mn atoms acting as donors might be involved. It has been found, however, that appropriate heat treatment can significantly increase the hole concentration. In particular, annealing of $Zn_{0.95}Mn_{0.05}Te$ under nitrogen pressure of 4 MPa at 800 °C for a week has resulted in a hole concentration as large as 5×10^{18} cm^{-3}. Nevertheless, according to low temperature resistance measurements such samples remain on the insulating side of the MIT, an observation that is consistent with previous data for $Zn_{1-x}Mn_xTe$:N [12] and with the small value of the acceptor Bohr radius in ZnTe, $a_B = 13$ Å [12]. On the other hand, according to previous SQUID measurements, the annealed samples exhibit the presence of ferromagnetic correlation, which leads to the Curie-Weiss ferromagnetic temperature of about 2 K [13].

Our inelastic neutron measurements of Mn pair spectra were carried out on a Fermi chopper time-of-flight spectrometer [15] at the Center for Neutron Research at NIST. The incident neutron energy was 3.55 meV. Two single crystal specimens were used: a 3 cm³ doped

$Zn_{0.95}Mn_{0.05}Te$:P and a 6 cm³ undoped $Zn_{0.98}Mn_{0.02}Te$ as a reference sample. Inelastic scattering spectra were measured at 10 and 40 K. The doped sample was investigated twice: in the as-grown, high resistivity state and after being annealed, as described above.

For a random distribution of Mn ions over the fcc cation sublattice at $x = 0.05$, 54% of ions are singlets, 24% are members of NN pairs studied here, 11% belong to triads, and the remainder to larger clusters [16]. The net value of the Mn-Mn exchange constant J_i for an ith neighbor shell is determined by two contributing effects—a hole-induced ferromagnetic interaction J_i^h and an intrinsic component J_i^{int}. The latter is known to arise from a strong but short-range antiferromagnetic superexchange [17], which is essentially insensitive to the presence of carriers. Thus, the difference in the value of J_1 obtained from measurements with and without holes yields the magnitude of the carrier-induced component J_1^h that can be compared with the predictions of theoretical models [4,6–8].

An antiferromagnetically coupled ($J < 0$) isolated pair of Mn^{2+} spins ($S_i = S_j = \frac{5}{2}$) with an interaction Hamiltonian $\mathcal{H} = -2J\mathbf{S}_i \cdot \mathbf{S}_j$ has eigenstates with total spin $S_T = |\mathbf{S}_i + \mathbf{S}_j| = 0, 1, \ldots 2S$ and energy eigenvalues $E(S_T) = |J|S_T(S_T + 1) = 0, 2|J|, 6|J|, \ldots, 30|J|$, as shown in the inset in Fig. 1. It is known [18] that inelastic neutron scattering processes are associated with transitions between adjacent eigenstates (the selection rules permit $\Delta S_T = \pm 1$). The neutron energy gain or loss may thus take values $\Delta E = \pm 2|J|, \pm 4|J|, \ldots, \pm 10|J|$. The accuracy of J determination depends only
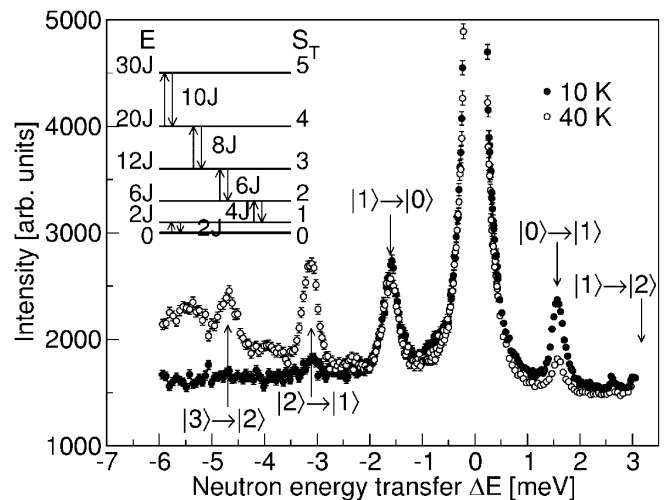

FIG. 1.   Neutron inelastic spectra measured on the annealed p-type $Zn_{0.95}Mn_{0.05}Te$ sample at 10 and 40 K. At low temperature (dark data points) only transitions between the ground state and the first excited level are seen. At 40 K additional peaks corresponding to the $|2\rangle \rightarrow |1\rangle$ and $|3\rangle \rightarrow |2\rangle$ transitions show up due to increased population of the excited states. At the same time, the decreased ground state population leads to the lower $|0\rangle \rightarrow |1\rangle$ line intensity.

on the precision of neutron energy transfer measurements and does not rely on the randomness of magnetic ion distribution over the cation lattice. In fact, the inelastic neutron scattering method is the most direct way of determining the exchange coupling constants in diluted systems [17].

A general view of inelastic neutron scattering spectra obtained for our samples is displayed in Fig. 1. The peak on the right side of the strong elastic line (neutron energy loss scattering process) corresponds to the $|0\rangle \rightarrow |1\rangle$ transition from the ground state to the first excited level. The peak intensity visibly decreases when temperature rises from 10 to 40 K due to the diminished ground state population. Owing to the low incident energy, only one inelastic line occurs in the energy loss side of the spectrum. On the energy gain (negative ΔE) side, there is a strong $|1\rangle \rightarrow |0\rangle$ transition line and a very weak $|2\rangle \rightarrow |1\rangle$ line at 10 K. The intensity of the latter increases strongly at 40 K, and a third line corresponding to $|3\rangle \rightarrow |2\rangle$ emerges. The broad feature underneath is most likely caused by phonon scattering. These peaks are shown in an expanded scale in Fig. 2, to make the differences between the results for particular samples visible. We note that all the inelastic peak positions measured on the as-grown (prior to annealing) sample agree within experimental error with those observed on the reference sample. In contrast, the presence of the holes leads to a small but clearly detectable shift of the transition energies to lower values, without affecting the line shape or scattering intensity. The decrease in the magnitude of the exchange constant for the sample with the higher hole concentration demonstrates the ferromagnetic character of the hole-induced contribution J_1^h.

The $|0\rangle \rightarrow |1\rangle$ transition peaks obtained for the as-grown and annealed $Zn_{0.95}Mn_{0.05}Te:P$ sample are shown in Fig. 2(a). The peak positions obtained by fitting Gaussian line shapes and a sloped background are 1.609 ± 0.005 meV and 1.577 ± 0.005 meV, respectively. This corresponds to the $J_1^h = 0.016 \pm 0.004$ meV. Shown in Figs. 2(b) and 2(c) are peaks corresponding to transitions $|2\rangle \rightarrow |1\rangle$ and $|3\rangle \rightarrow |2\rangle$, respectively. Here the data

for the annealed sample is compared with the respective data for the undoped reference sample. For the above two transitions the shift in the peak positions due to the hole-induced ferromagnetic interaction is now expected to increase by a factor of 2 and 3, respectively. The observed shift values are 0.052 ± 0.004 and 0.096 ± 0.016 meV, respectively, so that the average value of J_1^h obtained from the full set of the peaks is 0.015 ± 0.003 meV.

Since transport measurements [12,13] show that the p-type sample in question remains on the insulator side of the MIT, we begin the interpretation of our findings by evaluating the expected magnitude of the hole-induced energy shift if the holes were strongly localized at individual acceptor sites. From earlier studies of bound magnetic polarons in p-type DMSs [19], we know that the Mn spins residing at the distance r from the acceptor experience a molecular field,

$$H^*(r) = r_{so}\beta \exp(-2r/a_B)/(2\pi a_B^3 g \mu_B), \quad (1)$$

where $r_{so} = 0.8$ is the reduction factor due to spin-orbit interaction; $\beta = 0.062$ eV nm^3 is the p-d exchange integral describing the kinetic exchange interaction between the hole and Mn spins in $Zn_{1-x}Mn_xTe$ [20]; a_B is the acceptor Bohr radius; and $g = 2.0$ is the Mn Landé factor. Because of the exponential decay of the interaction strength, each Mn ion remains under the influence of a single hole, only so that the expected mean shift of the maximum of the $|0\rangle \rightarrow |1\rangle$ line reads

$$\delta E = \int d\mathbf{r}\, p g \mu_B H^*(r) = r_{so}\beta p/2 = 0.12 \text{ meV}, \quad (2)$$

for the hole concentration $p = 5 \times 10^{18}$ cm^{-3}. This value is greater by a factor of 4 than the experimental shift, $\delta E = 2J_1^h = 0.030 \pm 0.006$ meV. Furthermore, for the Bohr radius [12] $a_B = 1.3$ nm, large fluctuations in the value of δE are to be expected, from zero up to 2.4 meV for a Mn pair located nearby an acceptor. No evidence for such a doping-induced line broadening is seen in our results summarized in Fig. 2.
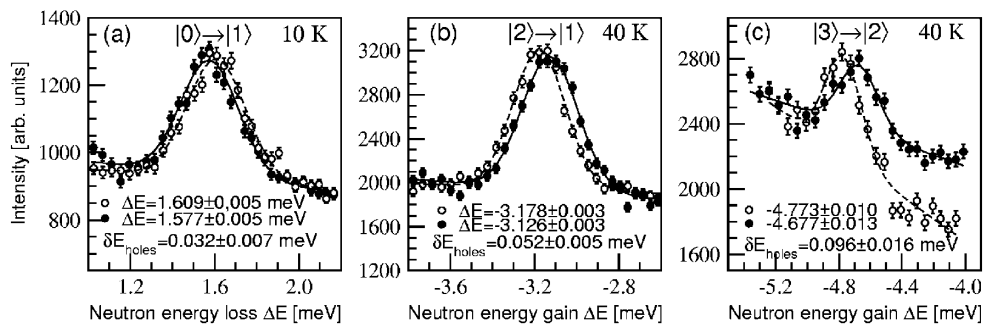

FIG. 2.   Inelastic neutron scattering maxima: (a) transition $|0\rangle \rightarrow |1\rangle$ at 10 K for annealed (solid circles) and nonannealed (open circles) $Zn_{0.95}Mn_{0.05}Te:P$ samples; (b),(c) transitions $|2\rangle \rightarrow |1\rangle$ and $|3\rangle \rightarrow |2\rangle$, respectively, at 40 K for annealed (solid circles) $Zn_{0.95}Mn_{0.05}Te:P$ and undoped reference (open circles) $Zn_{0.98}Mn_{0.02}Te$ samples.

We turn, therefore, to those models which assume that—owing to the proximity of the metal-insulator transitions—the holes are weakly localized. According to the scaling theory of the Anderson-Mott MIT [10], at distances smaller than the localization radius (which diverges right at the MIT), the states retain a metallic character. Therefore, in order to evaluate the effect of the holes on the NN Mn pairs, we refer to the RKKY theory, which, neglecting crystal anisotropy, gives the carrier-induced exchange energy between Mn spins located at the distance r in the well known form [6,12]

$$J_1^h(r) = \frac{A_F r_{so}' k_F^4 m^* \beta^2}{4\pi^3 \hbar^2} \left[\frac{\sin(2k_F r) - 2k_F r \cos(2k_F r)}{(2k_F r)^4} \right]. \tag{3}$$

Here $A_F = 1.2$ is the Fermi liquid parameter describing the enhancement of the interaction by the hole-hole exchange [8]; $r_{so}' = 0.48$ is the reduction coefficient due to the spin-orbit interaction [12]; m^* is the effective mass; and k_F is the Fermi wave vector. Since for the NN pair $r_{NN} k_F \ll 1$, we obtain

$$J_1^h(r_{NN}) = A_F r_{so}' \beta^2 m_t^* p / (8\pi\hbar^2 r_{NN}), \tag{4}$$

where $m_t^* = 0.77 m_o$ is the sum of the heavy and light hole masses in ZnTe. For these parameters, we arrive at $J_1^h(r_{NN}) = 0.010$ meV, which is seen to be somewhat smaller than the experimental value 0.015 ± 0.003 meV. We should note at this point that the magnitude of A_F may be enhanced on the insulator side of the MIT. Furthermore, the crystal anisotropy makes the NN RKKY interaction enlarged [21]. Moreover, three effects conspire in causing the underestimation of the hole concentration by the Hall resistance measurements: the anomalous Hall effect, the Hall scattering factor, and the presence of two-carrier transport (heavy and light holes). In light of these arguments, we regard the agreement between the experimental and theoretical values of the hole-induced exchange energy as satisfactory.

In conclusion, our inelastic neutron scattering data have provided direct experimental information on the character of electronic states mediating ferromagnetic coupling in a p-type II-VI ferromagnetic semiconductor. The data demonstrate that the correct description of the results is possible in terms of the Zener/RKKY theory, even for the hole concentration as low as 5×10^{18} cm^{-3}, which corresponds to the insulator side of the MIT.

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