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THE d-d EXCHANGE INTERACTION IN THE DILUTED MAGNETIC SEMICONDUCTOR $\text{Cd}_{1-x}\text{Fe}_x\text{S}$

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We have measured the magnetic susceptibility of $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ ($x < 0.09$) and found a typical Curie-Weiss behaviour above 100K. Basing on the high temperature expansion series developed for Fe-based diluted magnetic semiconductors, we estimate the nearest neighbour exchange coupling constant $J_{NN} = -20\text{K}$.

Diluted magnetic semiconductors (DMS) are materials based on classical semiconductors, such as CdTe, ZnS or InAs, for which a controlled fraction of nonmagnetic cations is substituted by magnetic ions such as Mn, Co or Fe [1]. From magnetic point of view DMS are systems of localized magnetic moments (associated with d-electrons of magnetic ions), randomly distributed over a nonmagnetic host lattice and coupled by the d-d exchange interaction. The situation for Mn- and Co-DMS is relatively simple, since for both Mn^{2+} and Co^{2+} ions, the ion ground state is an orbital singlet, which results in a spin-only magnetic moment. The case of Fe-DMS is different. The cubic crystal field splits the ^5D ground term into an orbital doublet ^5E and an orbital triplet $^5\text{T}_2$ (located about 4000K above ^5E) [2,3]. Spin-orbit interaction yields further splittings, in particular the ^5E state is split into a singlet A_1 , a triplet T_2 , a doublet E , a triplet T_2 and a singlet A_2 [2,3]. The separation between these five states is roughly 15-20K. As a consequence of a singlet ground state A_1 , the Fe^{2+} ion reveals typical Van Vleck-type paramagnetic behaviour [4].

For all Mn-, Co- and Fe-DMS antiferromagnetic coupling between magnetic ions was observed [5,6]. In the case of Mn-DMS it was rather well established, both by experimental and theoretical study, that this interaction is dominated by superexchange [7,8]. Although no theoretical model was developed for the exchange interaction between Fe ions, it is expected that also in this case superexchange is the driving

force behind the interaction. In view of that the study of chemical trends of exchange for Fe-DMS may be very helpful in formulating a proper model for d-d exchange in these materials. We therefore thought it worthwhile to complete the available data by studying exchange interaction in $\text{Cd}_{1-x}\text{Fe}_x\text{S}$. In the present work we estimated the nearest neighbour coupling constant from magnetic susceptibility data, using the high temperature expansion series developed for Fe-DMS. It was shown that susceptibility for high temperatures can be expanded as a Curie-Weiss law [9]:

$$\chi = \frac{C(x)}{T - \theta(x)}$$

where the Curie constant

$$C(x) = \frac{\mu_B^2 N \langle M_z^2 \rangle}{k_B} x = C_0 x$$

and a Curie-Weiss temperature

$$\theta(x) = \left(\frac{\langle M_z^2 \rangle \langle E \rangle - \langle M_z^2 E \rangle}{\langle M_z^2 \rangle k_B} \right) + \left(\frac{2 \langle M_z S_z \rangle^2}{\langle M_z^2 \rangle} \sum z_p \frac{J_p}{k_B} \right) x$$

$$= A + \theta_0 x,$$

where x is the concentration of Fe ions, $\langle \dots \rangle$ denotes the average value of energy (E), magnetic moment (M) and spin (S) operators calculated for isolated (noninteracting) Fe ion eigenfunctions at infinite temperature. J_p is the exchange integral for the p -th coordination sphere, z_p is the coordination number, N is the number of Fe ions in 1g of CdFeS, μ_B is the Bohr magneton and k_B is Boltzmann's constant. The above equations were used to estimate the nearest neighbour (NN) interaction for several Fe-DMS [9,4,10,11].

We studied hexagonal, single phase $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ crystals with $x < 0.1$. The Fe concentration in our crystals was determined by atomic absorption on selected pieces, giving values of 0.0081, 0.0159 and 0.087. In the case of the first two crystals the exact value of x was important for the determination of parameters. Therefore we compared low temperature (4.2K) magnetization of the pieces checked by atomic absorption and those, for which susceptibility was measured. In this way the actual concentration was obtained from the atomic absorption value scaled by the ratio of the magnetization measured at the same magnetic field and temperature. The resulting concentrations were about 10% lower: $x=0.0071$ and 0.014.

We measured magnetization (using a SQUID magnetometer) at 2T and 5T in the temperature range 70-350K. Since in our temperature and field range magnetization is isotropic, the samples were not oriented in respect to the magnetic field. The susceptibility χ was obtained as $\chi=M/B$. The data were corrected for the diamagnetic susceptibility of the CdS lattice ($\chi_d = -3.7 \cdot 10^{-7}$ emu/g [13]). At the lowest temperatures ($T < 100\text{K}$) we found that susceptibility determined in 5T is slightly (about 1%) smaller than that at 2T. This indicates that at 5T and below 100K, we are beyond the linear response limit. For $T > 100\text{K}$ the difference between 2T and 5T was below experimental accuracy. Nevertheless we based our analysis on susceptibility obtained at 2T.

In Fig.1 we display inverse susceptibility as a function

Fig.1 Inverse magnetic susceptibility of $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ as a function of temperature. Straight lines show Curie-Weiss law with parameters given in Tab.1.

Table I

Relevant parameters for $\text{Cd}_{1-x}\text{Fe}_x\text{S}$

x	C ($\cdot 10^{-4}$ emu $\cdot$ K/g)	Θ (K)
0.0071	1.66 ± 0.01	-8 ± 1
0.014	3.47 ± 0.02	-14 ± 1
0.087	27.4 ± 1	-75 ± 8

of temperature. A typical Curie-Weiss behaviour is observed above 100K. Negative Curie-Weiss temperatures indicate antiferromagnetic interaction between Fe ions, similarly as for the other Fe-DMS. Extrapolation of χ^{-1} versus T , in the temperature range 150-350K, gives Curie-Weiss constants and temperatures, which are tabulated in Tab.1. For the $\text{Cd}_{0.9929}\text{Fe}_{0.0071}\text{S}$ and $\text{Cd}_{0.986}\text{Fe}_{0.014}\text{S}$ samples the Curie-Weiss temperatures are a few times smaller than the temperature range used for the extrapolation of Θ , which justifies our high temperature regime. This is however not the case for $\text{Cd}_{0.913}\text{Fe}_{0.087}\text{S}$, for which Θ is only 2-4 times smaller than the experimental temperature range. Therefore this crystal was excluded from the analysis which follows.

The exchange parameter ($\sum_p J_p$) can now be determined from the equations given above. We first notice that both $\Theta(x)$ and $C(x)$ extrapolate to zero as $x \rightarrow 0$ (Fig.2). A detailed fit yields $\Theta_0 = -(857 \pm 100)\text{K}$, $A = -(1.9 \pm 4)\text{K}$ and $C_0 = (2.4 \pm 0.2) \cdot 10^{-2}$ emuK/g. The obtained value of C_0 corresponds to $\langle M_z^2 \rangle = 9.28$.

Fig.2 Concentration dependence of the Curie constant $C(x)$ and the Curie-Weiss temperature $\Theta(x)$ of $\text{Cd}_{1-x}\text{Fe}_x\text{S}$. Solid lines represent $C_0 = 0.0240$ emu $\cdot$ K/g and $\Theta(x) = (-1.9-857x)\text{K}$.

In order to derive the value of $\Sigma_p J_p$ we calculated quantum averages $\langle \dots \rangle$ using Fe^{2+} single ion eigenfunctions, as proposed by Slack et al. [3]. For details of calculations we refer to [14]. The eigenstates are parametrized by the crystal field parameter Dq , parameters describing hexagonality v , v' and a spin-orbit parameter λ . Following Ref. 14 we chose: $Dq=274.8 \text{ cm}^{-1}$, $v=0$, $v'=35.2 \text{ cm}^{-1}$ and $\lambda=-88.5 \text{ cm}^{-1}$. The summation in the averages $\langle \dots \rangle$ is performed over ten states of 5E term, since the experimental temperature range is an order of magnitude smaller than the 5E - 5T_2 splitting. Therefore our temperature range can be considered to be a high temperature regime in respect to the split the 5E term, and, at the same time, a low temperature regime relative to the 5E - 5T_2 splitting. Detailed calculations of χ (resulting from the strict diagonalization of an isolated Fe ion and a Fe-Fe pair - so called Extended Nearest Neighbour Approximation [4,15]) shows however that this simplification (i.e. truncation of eigenfunctions basis) yields an overestimation of $\langle M_z^2 \rangle$, as well as the parameter $\Sigma_p J_p$ of the order of 10%. This effect is not larger than the experimental inaccuracy of Θ_0 and was therefore neglected.

We obtained $\langle M_z^2 \rangle = 10.93$ (to be compared to 9.28, the value resulting from the experimental C_0 value), $\langle M_z^2 S_z \rangle = 4.24$, $\langle M_z^2 E \rangle = -131.9 \lambda^2 / 10Dq$ and $\langle E \rangle = -11.82 \lambda^2 / 10Dq$. We first observe that the resulting $A = +1.00 \text{ K}$ is within the limits of the experimental value of this parameter. Next we find $\Sigma_p J_p = -(261 \pm 30) \text{ K}$, which gives the upper estimate for the NN interaction: $|J_{NN}| < 22 \text{ K}$. The actual NN value is lower due to the next neighbours' contribution in the sum $\Sigma_p J_p$. A precise determination of this contribution would require information about the interaction range in CdFeS, which is however not available [4,5,6]. Assuming the same $J(R)$ dependence for Fe-DMS as was found for Mn-DMS ($J(R) = J_0 R^{-n}$, $n=6.8$ [16,5]), we get $\Sigma_p J_p = J_{NN} J_{NN}^* 1.09$, and finally $J_{NN} = -(20 \pm 2) \text{ K}$.

The obtained J_{NN} is very close to the value for ZnFeSe (Tab.2). We notice that the ZnSe and CdS host lattices have a very similar NN distance (Tab.2).

As we mentioned above no theory of d-d exchange for Fe-DMS has been developed so far, but in principle the same mechanisms which give rise to superexchange for Mn-DMS (i.e. jumping of the valence band electrons to the empty d-orbitals and back) should also be present in Fe-DMS. Moreover, from this point of view, the electronic configurations of the d-level of Mn^{2+} and Fe^{2+} are very similar: $\text{Mn}: d^5 = e_{+2}^1 t_{-1}^1 e_{+1}^1 t_{-1}^1 e_{-1}^1$, $\text{Fe}: d^6 = e_{+2}^1 t_{-1}^1 e_{+1}^1 t_{-1}^1 e_{-1}^1 t_{-1}^1$, where t and e denote one-electron orbitals of t and e symmetry, subscripts $+$ and $-$ correspond to spin up and down, respectively, and superscripts indicate the occupation of the orbitals. In particular both ions have the same number of empty t_{-1} -orbitals. We recall that t -orbitals hybridize strongly with the valence band and then provide a very effective superexchange channel [18]. If we assume superexchange as the dominant exchange mechanism, then we should expect an

Table II

Nearest neighbour coupling constants and nearest neighbour distances for Fe-DMS

material	J_{NN} (K)	NN distance (Å)
ZnFeS	-37 [11]	3.83
ZnFeSe	-22 [9]	4.01
CdFeS	-20 this paper	4.12
CdFeSe	-19 [9,17]	4.28
HgCdFeSe	-18 [17]	
HgFeSe	-18 [17]	4.30
CdFeTe	-11 [10]	4.58

increasing strength of the exchange with an increase of hybridization, or more precisely, an increase of the matrix element corresponding to the electron transfer between d-level and the valence band, and a decrease of the energy gap between the d-level and the top of the valence band [7,18]. On the other hand the matrix element results from the overlap of the wavefunctions and therefore strongly decreases with increasing anion - (magnetic) cation distance. Inspection of Tab.2 shows that such a trend is indeed observed: $|J_{NN}|$ decreases with increasing NN distance, being the largest for ZnS and the smallest for CdTe. Although a more precise analysis requires information about the location of the d-level relative to the top of the valence band (which is not currently available for Fe-DMS), we notice that the NN distance (and then the matrix element value) seems to be the most important for Fe-DMS. This is particularly well noticeable for the materials with the same anion, where the energy gap between the d-level and the valence band should be roughly cation independent (since the valence band is mostly built of p-type orbitals of the anion). In that sense one could expect that within the group of sulphates (or selenides, tellurides) exchange should vary according to the NN distance, which seems to be the case (cf. Tab.2). However, more pertinent conclusions can only be derived if the superexchange theory for Fe-DMS is elaborated.

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