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Magnetization steps in iron-based diluted magnetic semiconductors

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The high-field magnetization of diluted magnetic semiconductors (DMS) has been calculated for magnetic ions with spin and orbital momenta. In particular, it is shown that, in addition to the spin-only case (Mn^{2+}), also for Fe-based DMS characteristic steps in the low-temperature magnetization should be detectable. The position of the first step in the magnetization, being almost insensitive for crystal-field parameters and sample orientation, can be used to establish the nearest-neighbor interaction (J_{NN}), provided that $|J_{\text{NN}}|$ exceeds a critical value.

I. INTRODUCTION

Diluted magnetic semiconductors (DMS) generally consist of a nonmagnetic semiconducting host in which a controlled fraction of cations is replaced by isovalent magnetic ions. Until recently the investigations were almost exclusively restricted to DMS containing Mn^{2+} as the magnetic ion.¹ An increasing number of papers at the moment, however, deal with DMS containing other transition elements, such as Co^{2+} or Fe^{2+} . Magnetically the latter ions represent a more general, though more complex, case since, in addition to the spin, orbital momenta are also involved.²

Notwithstanding the increasing number of investigations devoted to these compounds, the experimental status is still somewhat poor. In contrast to Mn DMS, for instance, no experimental data have been reported yet which enable one to determine the nearest-neighbor (NN) interaction strength J_{NN} in a straightforward way. The strength and sign of J_{NN} are of great fundamental interest and are intimately related to the band structure and the location of the electronic levels within the *s* and *p* bands of the anions.³ In Fe DMS, to which we will restrict ourselves in this paper, the antiferromagnetic *d-d* interactions have only been estimated experimentally from the high-temperature susceptibility, which includes model-dependent parameters.⁴

For Mn DMS the location of steps in the magnetization, among others, has been used as a direct probe of the determination of J_{NN} .⁵ In this Rapid Communication we will show that, despite the complexity of the Fe^{2+} energy-level scheme, in this case magnetization steps should also be detectable and could be used to determine J_{NN} , provided that $|J_{\text{NN}}|$ exceeds a certain critical interaction. Moreover, we will show that the position of the first magnetization step is almost independent of sample orientation and crystal-field parameters. These results therefore offer experimentalists the opportunity to establish the Fe^{2+} - Fe^{2+} exchange interaction from the high-field magnetization.

II. THE Fe-Fe PAIR

The quantum-mechanical treatment of the isolated Fe^{2+} ion, substituted in a semiconducting host, has been

elaborately evaluated by Slack, Roberts, and Vallin and others.⁶ In addition to their treatment for Fe-doped crystals, a Heisenberg-type Fe^{2+} - Fe^{2+} interaction has been included for DMS (see our previous paper⁷):

$$\mathcal{H} = \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{EXCH}} + \mathcal{H}_B, \quad (1)$$

$$\mathcal{H}_{i,\text{EXCH}} + \mathcal{H}_{i,B} = -2J\mathbf{S}_i \cdot \mathbf{S}_j + \mu_B \mathbf{B} \cdot (\mathbf{L}_i + g\mathbf{S}_i). \quad (2)$$

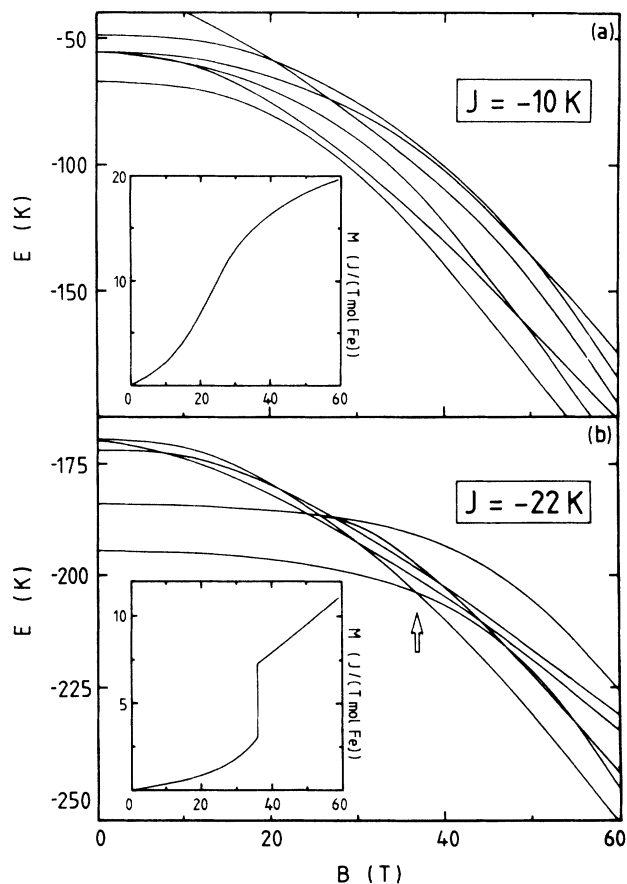


FIG. 1. Low-lying energy levels and magnetization, at $T=0$ (see insets), of the Fe^{2+} pair for \mathbf{B} along the crystallographic [111] axis; (a) $J = -10$ K, (b) $J = -22$ K, the arrow indicates the position of the magnetization step.

The basis for (2) is formed by a ${}^5E \times {}^5E$ subspace, where 5E represents the ten low-lying eigenfunctions of the cubic crystal-field Hamiltonian including spin-orbit interaction ($\mathcal{H}_{CF} + \mathcal{H}_{SO}$).^{6,7} From the field dependence of the eigenvalues the magnetization for one-mole Fe^{2+} ions can be calculated by

$$\mathbf{M} = -R/2 \sum_i \left(\frac{\partial E_i}{\partial \mathbf{B}} \right) \frac{e^{-E_i/k_B T}}{\sum_j e^{-E_j/k_B T}} \mathbf{B} / |\mathbf{B}|, \quad (3)$$

with i and j running from 1 to 100.

For uncoupled pairs ($J=0$) the situation is relatively simple. For $B=0$ we recall that the low-lying A_1 , T_1 , E , T_2 , and A_2 are separated roughly by $6\lambda^2/\Delta$, where λ represents the spin-orbit parameter and Δ (or $10 Dq$) the crystal-field splitting. For the calculations we used the parameters for $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$: $\lambda = -95 \text{ cm}^{-1}$, $\Delta = 2940 \text{ cm}^{-1}$; see Sec. III. In the presence of the external field, mixing with higher states repulses the magnetically inactive ground state, thereby inducing a net magnetic moment. For small fields the ground state varies with $-B^2$, yielding at low temperatures the so-called Van Vleck-type of paramagnetism.

For antiferromagnetically coupled pairs ($J < 0$) the energy schemes become very complicated and it follows, somewhat remarkably, that a critical interaction strength $|J_{\text{crit}}|$ ($J_{\text{crit}} \approx -13/-17 \text{ K}$ depending on the field direction) is present, above which the steps in the magnetiza-

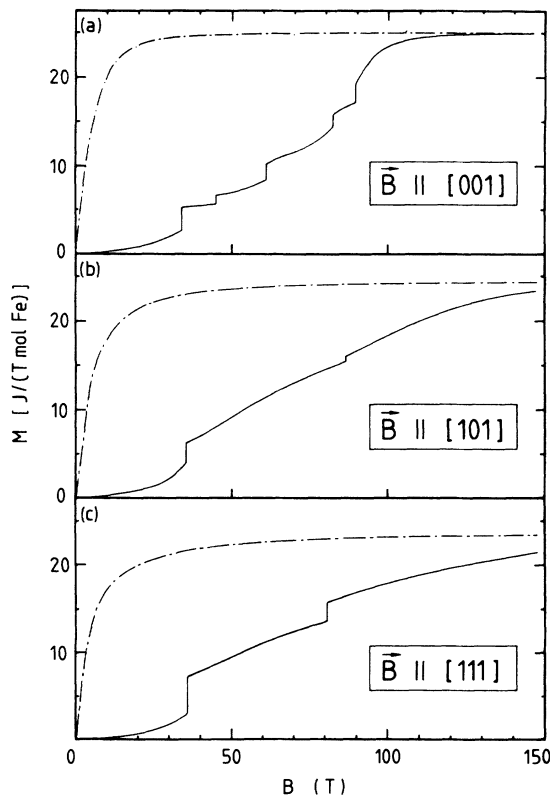


FIG. 2. Magnetization, at $T=0$, of an Fe^{2+} single ion ($J=0$, ---) and an Fe^{2+} pair ($J=-22 \text{ K}$, —), for \mathbf{B} along three crystallographic axes: (a) [001], (b) [101], (c) [111].

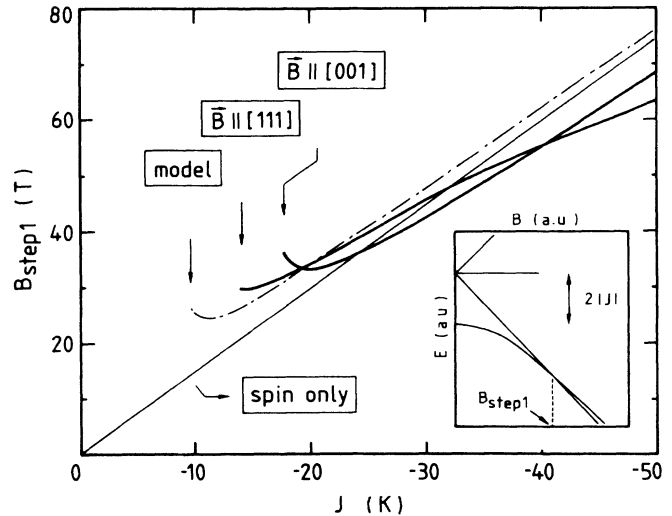


FIG. 3. Position of the first magnetization step as a function of interaction strength, for \mathbf{B} along the crystallographic [001] and [111] axis; the spin-only case ($g\mu_B B_{\text{step1}} = 2k_B |J|$) and the results within the introduced model (see the inset) are also shown.

tion are visible. The occurrence of such a critical interaction results from the interplay of the terms in the full Hamiltonian (1): crystal field including spin-orbit coupling, exchange, and magnetic field. For $|J| < |J_{\text{crit}}|$ the relatively large degree of mixing repulses the ground state in the amount that excited states cannot intersect. The downward bending of the ground state is quantified by the zero-temperature susceptibility χ which depends on the crystal-field parameters λ^2/Δ and the interaction J . For increasing J the susceptibility of the pair decreases and in the limit of large J (with an antiferromagnetic ground state) χ becomes zero. This reduction of χ with increasing J creates the crossing phenomenon. As an illustration, energy levels and magnetization for $J = -10$ and -22 K are plotted in Fig. 1. We will return to this subject in the discussion.

In general, the position of the steps depend strongly on the field direction as illustrated in Fig. 2 for \mathbf{B} along the [001], [101], and [111] axes. We want to emphasize that, as far as the first step is concerned (see Figs. 2 and 3) the field direction does not influence its position significantly (always within 10%), but only the size of the step. Quite surprisingly, it also appears that, despite the complex energy scheme of the Fe^{2+} pair, a close resemblance with the spin only situation ($g\mu_B B_{\text{step1}} = 2k_B |J|$) is obtained, even for J closely approaching J_{crit} . Furthermore, we checked the sensitivity of the first-step position on the crystal-field parameter λ . An increase from -95 to -105 cm^{-1} , which actually increases the single-ion splitting by 22%, induces a step shift of roughly 5%.

III. THE ACTUAL CRYSTAL

Using the results of Sec. II one is now able to describe the magnetization of an actual DMS crystal. In this communication we will confine ourselves to $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$,

which, from the magnetic point of view, is representative for several Fe-containing DMS originating from the II-VI group [e.g., $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ (Ref. 8)]. Moreover, the crystal-field parameters are quite well established^{6,7,9} and in addition, from the high- T susceptibility J_{NN} [-22 K (Ref. 4)] has been estimated.

To calculate the magnetization of such a random array of Fe ions, one usually⁵ decomposes the array in singles (no nearest neighbors), nearest-neighbor pairs, triples, and higher-order arrays as determined by statistics (cluster approximation). This approach, however, is valid in case the exchange interaction is restricted to nearest neighbors only. In principle the long-range character of J should be taken into account, which couples every spin with others. In such a case the system can be described within the so-called extended nearest-neighbor approximation (ENNPA).¹⁰ For ZnFeSe it has been suggested that $J \sim R^{-6.8}$.⁷ The evidence, however, is rather weak and a sharper decrease with distance, which reduces J to J_{NN} only, cannot be excluded.

In Fig. 4 the results for both cases, i.e., ENNPA and cluster approximation (restricted to singles and pairs), are drawn for $x=0.05$, showing the characteristic step in the [111] magnetization. Only minor differences between the two approximations can be distinguished due to the energetically close resemblance between isolated and weakly coupled ions. Since in fact these differences are restricted to small fields, where $g\mu_B B \approx k_B |J|$ for J beyond the NN, we may conclude that the steps are insensitive to the tail of J . Neglect of internal fields so far, however, can possibly affect the position of the steps seriously.¹¹ The influence of a nonzero temperature is also depicted in Fig. 4. It is clear that due to thermal population of excited states, which is relatively important at fields in the vicinity of B_{step} , a broadening of the steps will be induced.

The actual change in the magnetization at B_{step} , brought about by the nearest-neighbor pairs, is indepen-

dent of any approximation. In contrast to the Mn case the step size is not completely determined by statistics only, but also depends on parameters such as J , λ^2/Δ , and field orientation. As an illustration, for $J_{\text{NN}} = -22$ K and $\mathbf{B} \parallel [111]$ it follows that $\delta M \approx 30 \times P_{\text{pair}}(x)$ emu/g, $P_{\text{pair}}(x)$ based on randomly distributed Fe ions [$=12x(1-x)$]¹⁸. For $x=0.05$ this results in a step size of ≈ 0.35 emu/g. As a consequence, δM can serve as a probe for the randomness of the magnetic system, which, by this means, has been verified for Mn containing DMS.⁵

To our knowledge no experimental data exist on the magnetization in the regime where, on the basis of the present calculations, steps should occur. For $B < 15$ T, data are reported for $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ (Ref. 8) and $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$,⁷ and a reasonable description within the pair approximation can be obtained; see the supplementary data in Fig. 4. However, since these data do not extend to the magnetization step, which is the subject of this communication, we will not attempt any further interpretation.

IV. DISCUSSION

The calculations revealed the existence of a critical value $|J_{\text{crit}}|$ below which no steps in the magnetization can be observed. In addition to the comments made before, we will introduce a simple model which explains the observed phenomena in a more transparent way. The part of the complicated energy scheme of the Fe pair, which intuitively is responsible for the occurrence of magnetization steps, can be approximated by the following assumptions: (i) the singlet ground state varies quadratically with field: $E_0 = -\chi_{\text{pair}}(T=0)B^2$, obeying the Van Vleck type of paramagnetism; (ii) the first intersection with E_0 will be brought about by states closely following the spin-only eigenfunctions of a pair: $E_1 = m_{s,\text{pair}}g\mu_B B$, $m_{s,\text{pair}} = -1$; and (iii) for $B=0$, E_0 and E_1 are separated by $2|J|$, which is in principle only valid for spin-only eigenfunctions of a pair ($J \gg \lambda^2/\Delta$). The difference between the ground and the first excited state can be written as

$$E_0 - E_1 = -\chi_{\text{pair}}(T=0)B^2 + g\mu_B B - 2k_B |J|, \quad (4)$$

where the pair susceptibility can be obtained by treating \mathcal{H} for vanishing small fields. Figure 3 is supplemented with the first positive root of Eq. (3); the second root is unphysically large. The existence of a critical interaction strength ($J_{\text{crit}} = -10$ K), though somewhat smaller in magnitude than observed in the exact treatment ($J_{\text{crit}} = -13/-17$ K), is indeed predicted. It is clear from Fig. 3 that this simple model apparently contains the essential elements from both the crystal-field part and the spin-only part of \mathcal{H} , thereby inducing the phenomena observed by treatment of the full Hamiltonian.

Experimentally, the existence of the step magnetization in Fe-based DMS is not as evident as suggested by the present calculations since obviously, if $|J_{\text{NN}}| < |J_{\text{crit}}|$, which is not excluded,¹² no characteristic steps will be observed. For $|J_{\text{NN}}| > |J_{\text{crit}}|$, we already discussed the close relation between randomness and the height of the magnetization step. Apart from that we should also consider the width of the step as a limiting factor. The

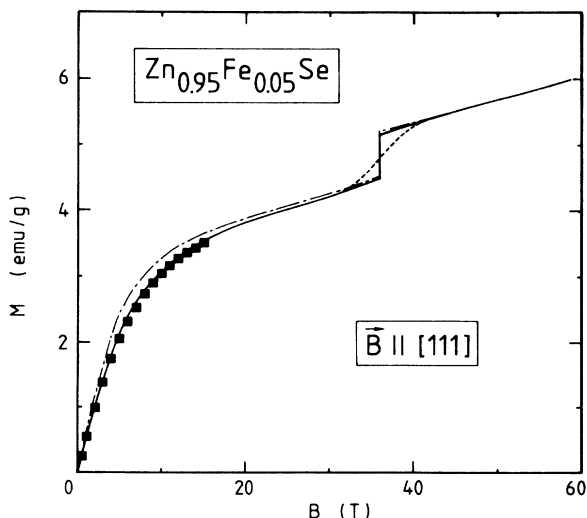


FIG. 4. Magnetization of $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{Se}$ for \mathbf{B} along the crystallographic [111] axis, using ENNPA with $J = -22R^{-6.8}$ K ($T=0$, —; $T=1.5$ K, ---) and the cluster approximation with $J = -22$ K ($T=0$, - - -), the squares represent data from Ref. 7.

influence of the temperature can be reduced by performing the experiments well below 4.2 K. Additional broadening of the step could be induced by any extra matrix element in the Hamiltonian. As an example, it has been shown very recently for Mn,¹³ that a DM anisotropy, though very small, would lift the degeneracy of the ground state at B_{step} , thereby widening the step. Further, internal fields¹¹ and even the experimental conditions (static versus pulsed field)¹³ are also believed to affect the structure of the magnetization step.

Despite the complicating factors listed above, we feel encouraged by our present numerical treatment of the Fe^{2+} - Fe^{2+} pair that steps in the magnetization of Fe-containing DMS should be detectable, thereby offering the unique possibility to establish the exchange interaction between adjacent Fe^{2+} ions in a rather straightforward way. The experimental conditions that the high-field magnetization should be subject to can be summarized as

follows: (a) temperature should be kept well below 4.2 K for an optimal population of the ground state; (b) observation of at least the first magnetization step would require fields of the order of 50 T; (c) the use of oriented single crystals is preferable, though not essential, for the position of the first step; fields parallel to the [111] axis should produce maximal step sizes; and (d) an Fe concentration $x \approx 0.052$ should be chosen to maximize the NN pairs.

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¹²We already argued that the expression which determines J_{NN} from the high-temperature expansion of χ includes numerical model-dependent expressions which could obscure this approximation; further, in compounds other than ZnFeSe, having slightly different crystal-field parameters, the value of J_{crit} itself will be somewhat different apart from the fact that J_{NN} is also *a priori* different from that in ZnFeSe Ref. 4.

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