

Magnetic properties of the diluted magnetic semiconductor $\text{Zn}_{1-x}\text{Fe}_x\text{S}$

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The specific heat and low-field susceptibility of the diluted magnetic semiconductor $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ ($x < 0.26$) have been measured for temperatures below 20 K and magnetic field up to 2.75 T. The specific-heat data for low Fe concentrations ($x < 0.03$) are well described in a simple crystal-field model taking into account isotropic Heisenberg-type antiferromagnetic interaction between Fe ions. Based on this model, the lower limit for nearest-neighbor (NN) antiferromagnetic exchange interaction is estimated as $|J_{\text{NN}}| > 22$ K.

I. INTRODUCTION

Diluted magnetic semiconductors (DMS's) or semi-magnetic semiconductors are materials based on II-VI, II-V, or IV-VI compounds in which controlled amounts of nonmagnetic cations have been replaced by magnetic ions of transition metals or rare-earth metals.¹ From a magnetic point of view, these materials represent systems of localized magnetic moments, randomly distributed in a nonmagnetic array and coupled by long-range interaction.

Most of the research performed on DMS's so far has been devoted to Mn-based DMS's (such as $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ or $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$). In these crystals substitutional Mn^{2+} has a d^5 electronic configuration, resulting in a degenerate 6A_1 spin-only ground state. Mn DMS's therefore represent a rather simple case of a system of permanent magnetic moments (so called Brillouin-type paramagnetism).¹

In contrast, substitutional Fe^{2+} (d^6) can serve as much more general case, since it possesses both spin ($S=2$) and orbital ($L=2$) momenta. This situation leads to an essentially different energy scheme of Fe^{2+} with respect to Mn. The free-Fe-ion ground term 5D is split by a tetrahedral crystal field into an orbital doublet 5E and an orbital triplet 5T_2 , separated by an energy gap of order of 4000 K. These terms are split furthermore by spin-orbit interaction. In particular, the 5E term, which determines the magnetic properties of the ion, is split into a singlet A_1 , a triplet T_1 , a doublet E , a triplet T_2 , and a singlet A_2 , all of them separated by energy gaps of the order of 20 K.^{2,3} Since the ground state of the Fe^{2+} ion is a singlet A_1 , there is no permanent magnetic moment associated with the Fe ion. Magnetic moments of Fe^{2+} ions can be only induced by an external magnetic field, leading to typical Van Vleck-type paramagnetism. Because of this interesting magnetic situation, Fe-based DMS's have been intensively investigated during recent years.^{4,5} Experimental data reported for Zn-Fe-Se,⁶⁻⁸ Cd-Fe-Se,⁹⁻¹¹ Cd-Fe-Te,¹² and Hg-Fe-Se (Refs. 9 and 10) seem to corro-

borate the simple model of Fe DMS's resulting from crystal-field and spin-orbit splittings, augmented by isotropic Heisenberg-type exchange interaction between Fe ions.¹³ In general, the magnetic properties of all the Fe DMS selenides studied so far show common behavior typical for the singlet ground state, irrespective of the very different band structure of the host crystals. Still, some controversy exists concerning the validity of the crystal-field model and its applicability for the actual crystals.¹⁰

The present paper deals with the magnetic properties of recently grown Zn-Fe-S. This material was chosen not only to complete the data for the Fe DMS family, but primarily because the heat capacity of Zn-S is the smallest of the whole II-VI group, which should provide the most accurate and reliable determination of the magnetic specific heat. Moreover, additional contributions like the Jahn-Teller effect should influence the 5E term only slightly for Zn-S. Both these facts should provide an optimum situation for checking our crystal-field model. Moreover, it was anticipated that the exchange coupling between the Fe ions would be stronger than for the other Fe DMS's.

II. EXPERIMENT

The Zn-Fe-S crystals were grown from powders of Zn-S and Fe (spec pure) by the modified Bridgman technique under the pressure of a neutral gas. The crystalline structure of the obtained crystals was cubic (zinc blende) in the whole range studied ($x=0.017, 0.024, 0.033, 0.084,$ and 0.26). The concentration and homogeneity of the crystals were checked by microprobe analysis. It was found that x can vary along the ingots up to 15% of its actual value.

A. Specific heat

The heat capacity (C_p) was measured by a standard heat-pulse method in the temperature range 1.44–20 K and magnetic field up to $B=2.75$ T.

The magnetic contribution (C_m) to the specific heat is usually obtained by subtraction of the heat capacity of the nonmagnetic lattice (C_{latt}) from the total heat capacity of the crystal (C_p):

$$C_m = C_p(\text{Zn}_{1-x}\text{Fe}_x\text{S}) - C_{\text{latt}}. \quad (1)$$

As we discussed recently,¹⁰ in the case of Zn-Fe-S, with the relatively small mass difference between Zn and Fe, the approximation of C_{latt} by the specific heat of pure Zn-S, $C_{\text{latt}} = C_p(\text{Zn-S})$, should be adequate.

In Fig. 1 we show the specific heat of $\text{Zn}_{0.983}\text{Fe}_{0.017}\text{S}$ and pure Zn-S and the resulting magnetic contribution C_m . We note that at low temperatures ($T < 10$ K) the specific heat is dominated by the magnetic contribution. The data for different Fe concentrations are presented in Fig. 2, where we plotted the magnetic specific heat per Fe ion (C_m/x). These data display the following general features, also observed in the other Fe-based DMS's,^{7,10,14}

(1) At low temperatures ($T < 5$ K), C_m increases exponentially with increasing temperature, which is typical for a Schottky-type anomaly (i.e., ground state separated from the excited states by an energy gap).

(2) C_m is practically magnetic field independent (Fig. 3), suggesting a singlet ground state of the Fe ions.

The observations are in agreement with the energy level scheme of the Fe ion discussed in the Introduction and could be expected for very diluted systems ($x < 0.01$) where the major contribution originates from isolated (noninteracting) Fe ions.

(3) Moreover, the magnetic specific heat per Fe ion

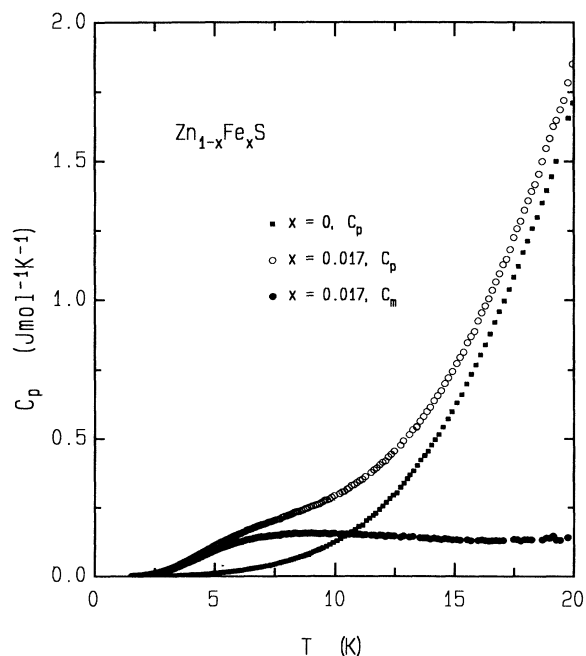


FIG. 1. Specific heat of $\text{Zn}_{0.983}\text{Fe}_{0.017}\text{S}$, pure Zn-S, and their difference, i.e., the magnetic contribution to the specific heat (C_m).

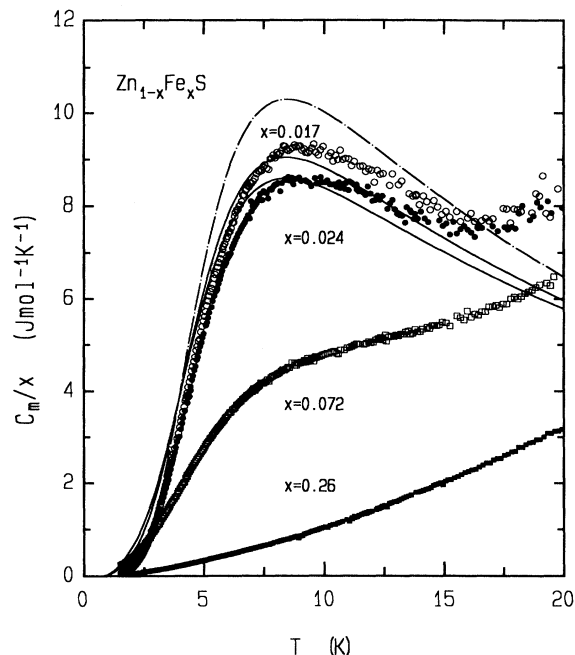


FIG. 2. Magnetic specific heat of $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ at $B = 0$. The lines represent calculations as described in the text for $x = 0.017$ and 0.024 ($Dq = 315.75 \text{ cm}^{-1}$, $\lambda = -94.75 \text{ cm}^{-1}$; solid lines: $J_{\text{NN}} = -25 \text{ K}$; dashed line: $J_{\text{NN}} = 0$).

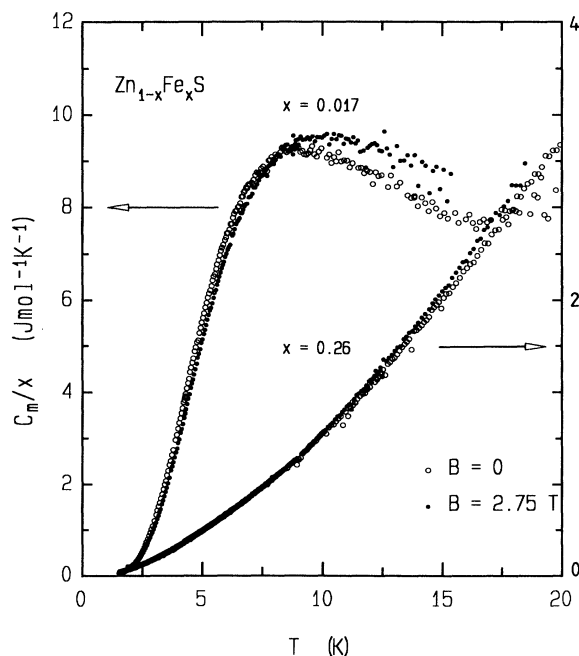


FIG. 3. Magnetic specific heat of $\text{Zn}_{0.983}\text{Fe}_{0.017}\text{S}$ and $\text{Zn}_{0.74}\text{Fe}_{0.26}\text{S}$ in the absence (open symbols) as well as in the presence of magnetic field (solid symbols, $B = 2.75 \text{ T}$).

(C_m/x) decreases with increasing Fe concentration x , which indicates an interaction between Fe ions (otherwise, C_m should scale with x).

B. Susceptibility

Low-field ($B=0.0001$ T) ac susceptibility was measured by a mutual inductance method. The results for several different concentrations are shown in Fig. 4. We note that the susceptibility per Fe ion decreases with increasing x , which indicates an *antiferromagnetic* interaction between the Fe ions. In distinction to the crystals doped with Fe,¹⁵ we observe no temperature-independent susceptibility at low temperatures ($T < 4-5$ K), which should be characteristic for Van Vleck-type paramagnetism and is predicted by the crystal-field model.¹³ Instead, for Fe concentrations $x < 0.1$, the susceptibility gradually increases with decreasing T . For high Fe concentration ($x > 0.15$), the susceptibility shows a non-monotonic behavior (Fig. 5). A similar behavior of the susceptibility was also found for all other Fe DMS's studied so far.^{7,9,16,17} The low-temperature increase of susceptibility was attributed to the presence of permanent magnetic moments (PMM's) in the considered crystals.^{17,16} There are several possibilities to create PMM's in our crystals (see Appendix), but whatever the source of the PMM, they should produce an excess susceptibility, which could be dominant at low temperatures and could completely mask the temperature-independent susceptibility of the regular Fe^{2+} ions.¹⁵

The nonmonotonic behavior of the susceptibility (i.e., the decrease below a certain temperature T_f (Fig. 5 and Refs. 9, 7, and 16) for the crystals with the highest con-

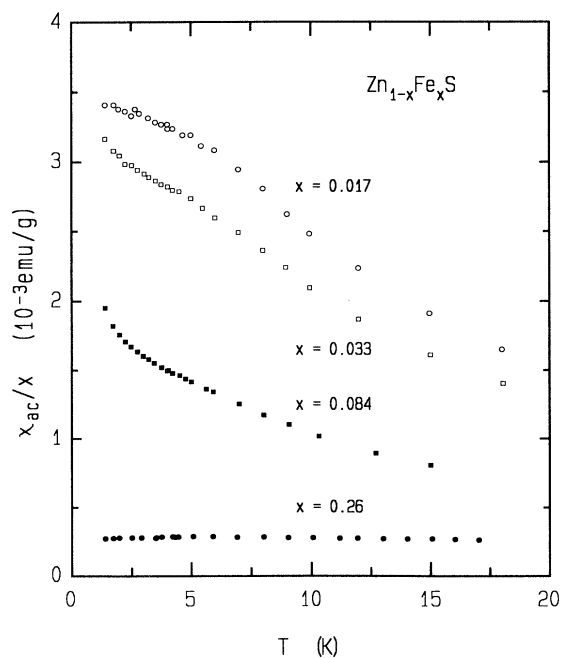


FIG. 4. Magnetic susceptibility per Fe ion of $\text{Zn}_{1-x}\text{Fe}_x\text{S}$.

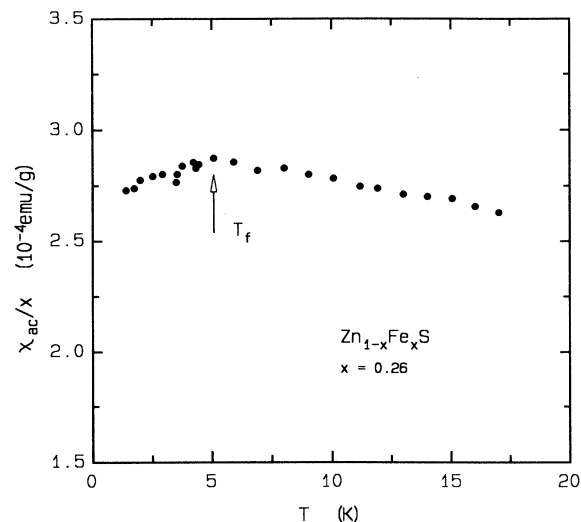


FIG. 5. Magnetic susceptibility per Fe ion of $\text{Zn}_{0.74}\text{Fe}_{0.26}\text{S}$. The arrow marks the freezing temperature T_f .

centration ($x > 0.15$) may be related to the formation of a spin-glass phase.^{9,7} The available data of T_f versus Fe concentration are collected in Fig. 6. In contrast to Mn DMS's,¹⁸ no universal behavior of T_f versus x seems to be observed. However, since there are only a limited number of data points, we think no pertinent conclusions can be drawn about a spin-glass transition at the present stage.

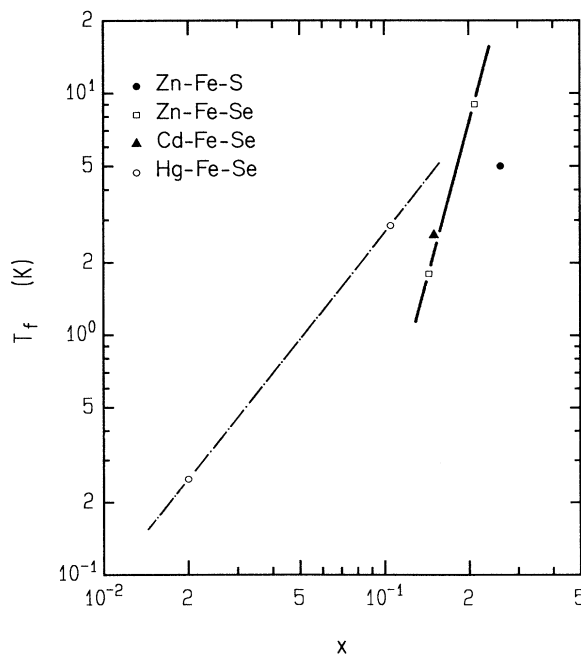


FIG. 6. Freezing temperature T_f (see text) vs Fe concentration x for Zn-Fe-S, Zn-Fe-Se (Ref. 7), Cd-Fe-Se (Ref. 9), and Hg-Fe-Se (Refs. 9 and 16). The lines are to guide the eye only.

There is no reason to assume that PMM's are not present at the crystals with $x > 0.15$, but apparently they do not manifest themselves in the susceptibility. Possibly, the PMM's are frozen or blocked because of the interaction with Fe ions. In that case this PMM freezing should occur simultaneously with the freezing of the Fe-ion system, i.e., at temperatures close to T_f .

III. DISCUSSION

The results for Zn-Fe-S presented above complete the data for the available Fe DMS's. Inspection of the data for Zn-S, Zn-Se, Cd-Se, and Hg-Se shows a similar magnetic behavior, dominated by the singlet ground state of Fe ions (isolated as well as coupled in the clusters). This observation is in agreement with the crystal-field model developed for the description of the magnetic properties of Fe DMS's.¹³

We briefly recall that in this model the system of Fe ions is factorized into isolated ions and nearest neighbor (NN) pairs of the ions coupled by exchange interaction.^{13,18,19} The key problem is therefore the Fe-Fe pair description. The most important terms in the Hamiltonian are the crystal field (cubic or hexagonal^{20,21}) spin-orbit interaction, magnetic field (Zeeman term), and isotropic Heisenberg-type coupling between ions. For details we refer to Refs. 13 and 21.

We should comment here on another term in the Hamiltonian which was often mentioned as potentially important, namely, the term describing the Jahn-Teller (JT) interaction with vibrational modes of the lattice.²² Recently the influence of this interaction was discussed for the energy spectrum of the 5E term.²³ It was found that, although the energy spectrum can be strongly modified by the JT effect (especially if there are low-energy lattice vibrational modes), magnetic properties such as the specific heat or magnetization are practically unchanged (at least for the phonon energies reported for II-VI compounds). In view of that, the exceptionally large values of the specific heat of Cd-Fe-Se (Ref. 10) are probably rather due to local phonons associated with the Fe ions in this material, rather than to the JT coupling.²³ On the other hand, Zn-S, with its rather high-energy phonons, should be very weakly affected by the JT coupling, and the effect on specific heat or magnetization is expected to be negligible.

One of the conclusions of the crystal-field model^{13,10} was that, although single-ion and Fe-Fe pair energy structures are relatively complicated, the specific heat (calculated on the basis of these energy structures) is dominated by the two different energy gaps of the isolated ions and pairs (whose contributions are weighted by the number of isolated ions and pairs). We recall that for a simple Schottky-type anomaly (i.e., singlet ground state separated by energy gap Δ from the excited multiplet, with g -folded degeneracy), at low temperatures, C_m can be written as

$$C_m(T) = xgN_A k_B (\Delta/k_B T)^2 \exp(-\Delta/k_B T). \quad (2)$$

Therefore, by plotting $\ln(C_m T^2/x)$ versus $1/T$, one should obtain a straight line with the slope $-\Delta/k_B$. A

similar linear behavior is found for C_m calculated on the base of the full (five-level) single-Fe-ion energy-level scheme (Fig. 12 in Ref. 10). The isolated ion energy gap ($A_1 - T_1$), inserted in the model, is recovered with accuracy better than 3%. Moreover, including pairs into calculations,¹³ one finds another linear part of the plot at very low temperatures,¹⁰ which corresponds to the pair energy gap. Since this gap is much smaller than the single-ion gap,¹³ it dominates the low-temperature specific heat.

In Fig. 7 the specific heat of $\text{Zn}_{0.983}\text{Fe}_{0.017}\text{S}$ is plotted as $\ln(C_m T^2/x)$ versus $1/T$. The contribution of isolated ions and pairs can be clearly distinguished by a change of slope. Similar plots for other Fe DMS's are collected in Fig. 8. The experimental data for various compounds indeed show a linear part at temperatures $T < 10$ K (Figs. 7 and 8), yielding the single-ion energy gaps which compare very well with the values obtained from FIR (far-infrared) spectroscopy (Table I).

The pair contribution is dominant for $T < 2.5$ K. Although the experimental temperature range is too limited to observe a distinct linear part of the plot, one can estimate upper limits for the pair energy gaps, which are also given in Table I. For comparison we also inserted the pair energy gap calculated using the exchange integral J_{NN} estimated from the high-temperature expansion (HTE) of the susceptibility (Table I).⁸ We note a strong reduction of the pair energy gap with respect to the isolated Fe ion, as expected, although the value obtained for Cd-Fe-Se from specific heat is somewhat smaller than the value resulting from HTE. Data for lower temperature ($T < 1.5$ K) are necessary to draw pertinent conclusions.

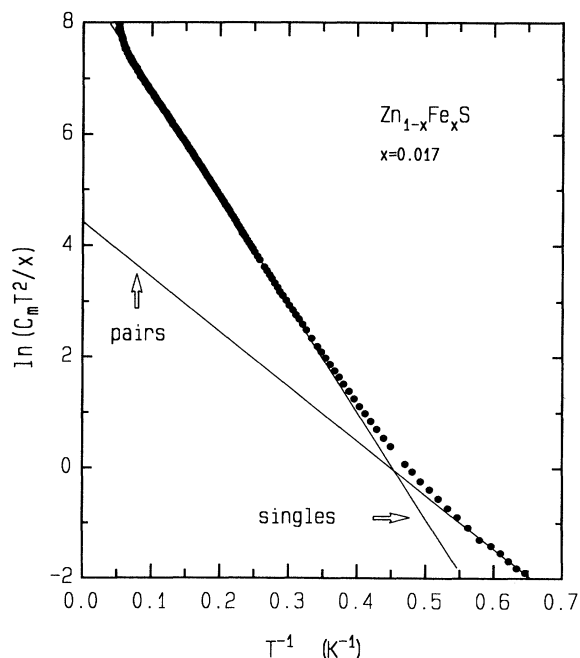


FIG. 7. Magnetic specific heat of $\text{Zn}_{0.983}\text{Fe}_{0.017}\text{S}$ plotted as $\ln(C_m T^2/x)$ vs $1/T$, indicating the contribution of isolated ions and pairs.

TABLE I. Energy gap Δ (in K) for the isolated ion and Fe-Fe pair as well as nearest-neighbor interaction for Fe-Fe and Mn-Mn pairs.

Material		Zn-Fe-S	Zn-Fe-Se	Cd-Fe-Se	Hg-Fe-Se
Δ , isolated Fe ion	C_m	20	21	19	16
	FIR	21 ^a	23 ^b	19 ^c	
Δ , Fe-Fe pair	C_m	< 9.5	< 13	< 9	< 10
	HTE ^d		10.5	13	8.6
$ J_{NN} $	Fe pair	> 23	22 ^e	19 ^f	18 ^f
	Mn pair	16 ^g	13 ^g	8.7 ^h	11 ⁱ
				7.9 ^j	6 ^k

^aReference 24.

^bReference 25.

^cReference 20 and 26.

^dReference 27.

^eReference 8.

^fReference 10.

^gReference 28.

^hReference 29.

ⁱReference 30.

^jReference 31.

^kReference 32.

It is worthwhile to mention that this analysis of the specific heat provides the first experimental evidence of the reduction of the pair energy gap (no FIR spectroscopy data for the Fe-Fe pair were reported so far). It seems that the low-temperature specific heat in this particular case may serve as a useful tool for the energy-structure determination (even in the case that FIR spectroscopy cannot be used because of selection rules). We should also note that no information about material parameters (such as the crystal-field parameter Dq or the spin-orbit constant λ) is necessary for the estimation of the single-ion or pair energy gap.

However, for a detailed calculation of the magnetic properties, estimates of the values of these parameters are necessary. The crystal-field parameter Dq and spin-orbit constant λ , which determine the single-ion energy structure, can be evaluated from the spectroscopic data. FIR transitions within the 5E term; $A_1 - T_1$ [transition energy 14.6 cm^{-1} (Ref. 24)] and $A_1 - T_2$ [transition energy 45.1 cm^{-1} (Ref. 24)], as well as IR transition ${}^5E - {}^5T_2$ [so-called zero phonon line with transition energy 2947 cm^{-1} (Ref. 33)], were used for adjusting Dq and λ . The best fit was found for $Dq = 315.75 \text{ cm}^{-1}$ and $\lambda = -94.75 \text{ cm}^{-1}$ (calculated energies are 14.2, 45.6, and 2947.5 cm^{-1} , respectively).

For the pair calculations the value of the NN interaction constant (J_{NN}) is necessary. This value was not evaluated so far in contrast to the other Fe DMS's.^{8,10} The estimation of the upper limit of the pair energy gap (Table I) can be used for this. In Fig. 9 we show the vari-

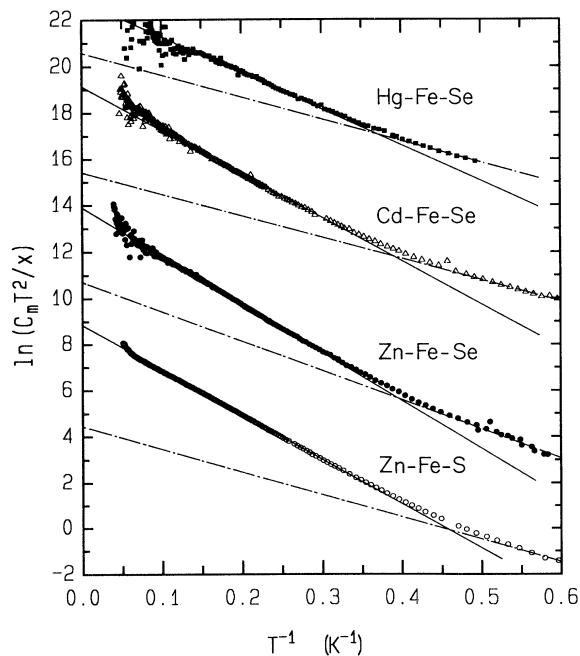


FIG. 8. Specific heat of Zn-Fe-S ($x=0.017$), Zn-Fe-Se ($x=0.015$), Cd-Fe-Se ($x=0.008$), and Hg-Fe-Se ($x=0.015$) plotted as $\ln(C_m T^2/x)$ vs $1/T$ (plots are shifted in vertical scale over 5 units for Zn-Fe-Se, 10 units for Cd-Fe-Se, and 15 units for Hg-Fe-Se).

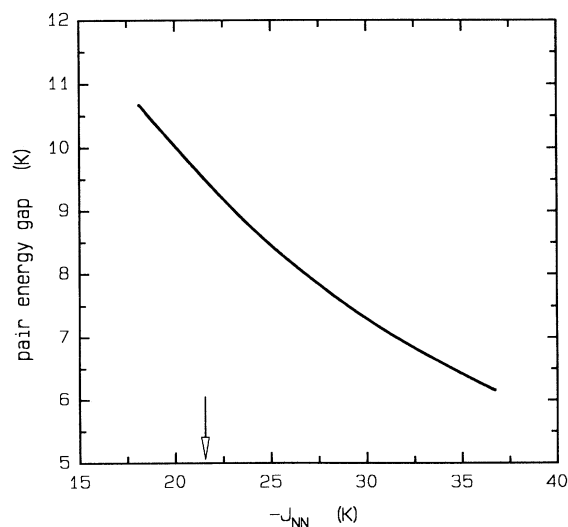


FIG. 9. Calculated Fe-Fe pair energy gap (Refs. 7 and 13) as a function of the NN exchange interaction integral J_{NN} ($Dq = 315.75 \text{ cm}^{-1}$, $\lambda = -94.75 \text{ cm}^{-1}$). The arrow indicates the lower limit for $-J_{NN}$.

ation of the pair energy gap with J_{NN} for the Zn-S host lattice and the parameter values quoted above. We note that $|J_{\text{NN}}|$ must be larger than 22 K to produce an energy gap smaller than 9.5 K as observed (Table I). Although this value is only a lower bound for $|J_{\text{NN}}|$, we can conclude that the interaction between Fe ions in Zn-Fe-S is stronger than for the other Fe DMS's (Table I). This is in agreement with the general trend observed for exchange interactions of Mn-based DMS's.^{1,5}

For the calculations we have adopted the value $J_{\text{NN}} = -25$ K.³⁴ The results for the specific heat are plotted in Fig. 2 for $x = 0.017$ and 0.024 and show a reasonable agreement with the experimental data. In particular, the maximum value of C_m is well recovered. For higher Fe concentrations our basic assumption that the ion system can be factorized solely into isolated ions and pairs is no longer valid.^{19,18}

IV. CONCLUSIONS

The data for Zn-Fe-S are compatible with the reported magnetic properties of the other Fe-based DMS's, and therefore we may state that all the Fe DMS's known up to now show the same magnetic behavior. This fact implies the same physical mechanism behind this behavior, and consequently the same model should describe magnetic properties of these crystals. It seems that the basic features of the specific heat are described reasonably well by our simple crystal-field model.

We have shown that the low-temperature specific heat provides experimental evidence of the reduction of the energy gap between the ground and excited states due to the exchange interaction between Fe ions. Moreover, the Fe-Fe pair energy gap can be determined from the specific-heat data obtained in the temperature range $1 < T < 2$ K.

Although the basic magnetic properties of the paramagnetic phase of Fe DMS's are understood, some problems still exist. The possible existence of the spin-glass phase, as suggested by low-temperature susceptibility, should be checked by studying crystals with a broader Fe concentration range. This, however, depends on the progress in technology of these compounds. Thin layers of Fe DMS's can be helpful in this respect. Another problem concerns the origin of the permanent magnetic moments discussed above and in the Appendix. It appears that a precise electron paramagnetic (EPR) study would be very helpful in solving this problem.

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APPENDIX

In this appendix we discuss the amount and possible origin of the permanent magnetic moments (PMM's) in our crystals.

Assuming that PMM's reveal a Curie-type susceptibility and that the Fe^{2+} contribution to the susceptibility is constant at sufficiently low temperatures [we assumed that for $T < 3$ K (Ref. 15)], one can estimate the concentration of PMM's. We have done this for Zn-S, Zn-Se, Cd-Se and Hg-Se. The results are tabulated in Table II. We note that for $x < 0.1$ the PMM concentration increases with increasing Fe^{2+} content and amounts roughly to 1–2 % of the actual x . Only for Hg-Fe-Se the PMM concentration is rather constant (accuracy is of the order of 50–100 % in this case) and corresponds to the concentration $N = 2 \times 10^{18} \text{ cm}^{-3}$.

The PMM's present in our crystals should contribute to the specific heat at nonzero magnetic field. In fact, the low-temperature increase of C_m observed for $\text{Zn}_{0.983}\text{Fe}_{0.017}\text{S}$ (not resolved in Fig. 3) can be accounted for the presence of PMM's in this sample. For $\text{Zn}_{0.74}\text{Fe}_{0.26}\text{S}$, C_m slightly decreases with magnetic field at the lowest temperatures, which is compatible with the observed susceptibility of this sample (Fig. 6).

Hypothetical PMM's in our crystals could originate from (1) residual paramagnetic impurities (such as Mn, Co) or could be an inherent property of Fe DMS crystals and results from (2) Fe^{3+} (d^5) ions which, from magnetic point of view, are equivalent to Mn^{2+} , (3) Fe^{2+} ions at interstitial, octahedrally coordinated sites, which have a magnetically active ground state,³⁶ or (4) large clusters

TABLE II. Estimated concentration of permanent magnetic moments (PMM's). PMM's are assumed to contribute to the susceptibility in Curie-type way: $\chi = (x/m)(g\mu_B)2S(S+1)/(3k_B T)$, where we have chosen $S = \frac{5}{2}$. For $x > 0.1$ no excess susceptibility at low temperatures was observed.

Material	x	x_{PMM} (10^{-4})	x_{Mn} (EPR) (10^{-4})
Zn-S	0.017	0.9	0.3
	0.033	4	0.1
	0.08	16	<0.01
	0.26		
Zn-Se ^a	0.014	1.4	
	0.04	3.2	
	0.06	13.6	
	0.16		
	0.22		
Cd-Se ^b	0.011	1.4	
	0.038	3.2	
	0.049	6.3	
	0.15		
Hg-Se ^c	0.003	1.2	
	0.01	1.4	
	0.02	1.4	
	0.05	0.8	
	0.1		

^aReference 17.

^bReference 35.

^cReference 16.

formed of Fe^{2+} ions. Clusters larger than Fe-Fe pairs were not investigated so far,^{13,5} and in principle one cannot exclude the possibility that there could exist clusters with the multiplet ground state. However, by extrapolating the results obtained for pairs,¹³ such a situation would be rather unlikely. Finally, they could originate from (5) exchange-interaction-induced magnetic moments associated with magnetic polarons.²⁶

To check for the impurities in our crystals, we performed EPR experiments and found indeed some isolated Mn^{2+} (Table I). However, the concentration of these ions is too small to recover the entire low-temperature increase of susceptibility. On the other hand, the concentration of PMM's estimated for Hg-Fe-Se compares favorably with the concentration of Fe^{3+} ($N=4 \times 10^{18}$, x independent for $x > 0.005$) always present in this material

as a result of selfionization of Fe^{2+} .⁴ This fact strongly suggests that large Fe clusters contribute negligibly to the low-temperature susceptibility; otherwise, the PMM concentration for Hg-Fe-Se should be much larger and should increase with increasing x (reflecting the increasing number of large clusters). This conclusion can be extended for other Fe DMS's since there is no reason for different Fe-ion statistics in these crystals.

Although we believe we can rule out large clusters for all the crystals, we are not able to conclude about the origin of PMM's. Therefore, the existence of PMM's is still hypothetical, except for the Hg-Fe-Se case. An open question still remains why Hg-Fe-Se differs so much from wide-gap materials (Cd-Fe-Se, Zn-Fe-Se, and Zn-Fe-S) in this respect.

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