

# Low-temperature specific heat of the diluted magnetic semiconductor mercury cadmium iron selenide

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## Low-temperature specific heat of the diluted magnetic semiconductor $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$

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The specific heat of the diluted magnetic semiconductors  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$  has been measured for temperatures below 25K. The excess specific heat ( $C_m$ ) has been extracted by scaling of non-magnetic lattice contributions. The resulting  $C_m$  of these systems reveals a broad maximum at  $T \approx 10$  K, whereas for low temperatures a Schottky-type exponential decay of  $C_m$  can be observed. These phenomena can be fairly well understood on the basis of a simple crystal-field model and a random distribution of  $\text{Fe}^{2+}$ . On the other hand, no drastic effect of the energy gap is clearly reflected by our data and therefore we suggest that only  $\text{Fe}^{2+}$  states involving the valence bands dominate the antiferromagnetic  $d$ - $d$  interactions, analogously to the  $\text{Mn}^{2+}$  case.

### INTRODUCTION

Diluted magnetic semiconductors (DMS) or semimagnetic semiconductors are currently attracting considerable attention because of their interesting transport, magneto-optical, and magnetic properties.<sup>1</sup> So far, research has been focused mainly on DMS containing  $\text{Mn}^{2+}$  ions. The magnetic behavior of these systems can be understood on the basis of a random array of localized Mn ions coupled by long-ranged isotropic antiferromagnetic exchange interactions<sup>1-3</sup> which are mediated by the carriers. It has been shown that the dominant microscopic mechanism causing  $d$ - $d$  exchange interaction between the Mn ions is probably superexchange (at least for the nearest neighbors). However, the relation to the band structure, as well as the nature of and the driving force behind, the observed phase transitions and the role of anisotropy are still somewhat obscure, and subject to further investigations.<sup>2,3</sup>

In a way, the substitutional  $\text{Mn}^{2+}$  with its degenerate  $^6A_1$  spin-only ground state, represents a rather simple, although theoretically attractive case, since all the phenomena which involve the orbital momentum are absent. In contrast, substitutional iron  $\text{Fe}^{2+}$  ( $d^6$ ) can serve as a much more general case, since it possesses both spin and orbital momenta ( $S=2$  and  $L=2$ ). Moreover, the  $d$ - $d$  exchange is intimately related to the location of the magnetic ion levels with respect to the band structure.<sup>1</sup> Therefore, substitution of Fe instead of Mn might affect the character and strength of these interactions, since the  $\text{Fe}^{2+}$   $d^6$  level may be located far above the valence band in contrast to the  $\text{Mn}^{2+}$  levels. The properties of Fe-based DMS are, however, still relatively unexplored,<sup>4</sup> although recently some optical and magnetic data were reported for some DMS.<sup>4-10</sup> The optical properties and, in particular, the band splitting of Fe-based DMS (which follow macroscopic magnetization<sup>9</sup>) show a similar behavior as the analogous quantities for the Mn-type materials and in that sense seem not very sensitive to the orbital momentum.

On the other hand, the magnetic properties are expect-

ed to be substantially different from Mn-type DMS. This difference can be ascribed to the different energy scheme of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  ions. Substitutional  $\text{Fe}^{2+}$  has a  $d^6$  electronic configuration. The ground state of the  $\text{Fe}^{2+}$  free ion ( $^5D$ ) is split by a tetrahedral crystal field into a  $^5E$  orbital doublet and a higher lying  $^5T$  orbital triplet (separated from  $^5E$  by  $10Dq$ , where  $Dq$  is the crystal-field parameter). Spin-orbit interaction splits the  $^5E$  term into a singlet  $A_1$ , a triplet  $T_1$ , a doublet  $E$ , a triplet  $T_2$ , and a singlet  $A_2$  (the energy separation between these states is approximately equal to  $6\lambda^2/10Dq$ , where  $\lambda$  is the spin-orbit parameter).<sup>11,12</sup> Thus the ground state is magnetically inactive singlet  $A_1$  resulting in Van Vleck-type paramagnetism.<sup>12,13</sup> Moreover, isolated  $\text{Fe}^{2+}$  ions contribute to the specific heat even in the absence of a magnetic field, in contrast with isolated  $\text{Mn}^{2+}$  ions, where only Mn-Mn pairs and larger clusters can contribute to the specific heat for  $B=0$ .

So far some experimental data reported on  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ ,<sup>6,14</sup> as well as  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ ,<sup>10,15</sup> seem to corroborate this model of Fe-based DMS. Reported data on the zero-gap DMS  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  (Ref. 8) are, however, at variance with such a model, since the specific heat was reported to be much smaller than for  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$  and the low-temperature susceptibility reveals a rather typical Brillouin-type paramagnetic behavior instead of Van Vleck behavior. It was suggested<sup>8</sup> that this behavior of  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  results from the specific location of the Fe  $d^6$  level in relation to the HgSe bands (in this material the Fe level is situated 0.2 eV above the bottom of the conduction band, whereas in wide gap materials like ZnSe or CdSe it is located in the gap between conduction and valence band<sup>5</sup>).

Very recently it was suggested that some of these discrepancies between wide and zero-gap materials mentioned above, might be removed by a more careful analysis of the specific-heat data<sup>16</sup> and by taking into account the contribution of the  $\text{Fe}^{3+}$  ions, which are always present in  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  crystals,<sup>17</sup> to the susceptibility. In view of this we thought it worthwhile to investigate the magnetic properties of open as well as zero-gap Fe

containing DMS in a more detailed way. As we will see later these results will allow us to estimate the nearest-neighbor interactions between  $\text{Fe}^{2+}$  ions.

### EXPERIMENTAL

The samples of  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ ,  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$  (cubic), and  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$  (hexagonal) investigated in the present paper are listed in Table I. They were grown by a modified Bridgman technique, and their concentration and homogeneity was checked by microprobe analysis. The specific heat ( $C_p$ ) was measured by a standard heat-pulse method in the temperature range 1.5–25 K and in the absence, as well as in the presence, of a magnetic field (up to  $B=2.75$  T). The specific-heat results for  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ ,  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$ , and  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$  are shown in Figs. 1, 2, and 3, respectively. The magnetic contribution to the total specific heat can be well observed in low temperatures. We notice that  $C_p$  for all the compounds is practically field independent (at least for  $B < 3\text{T}$ ), which is exemplified in Fig. 4 for  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ . This suggests a singlet ground state for Fe ions for all the compounds. At higher temperatures,  $C_p$  is dominated by the lattice contribution. In the case of  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ ,  $C_p$  of pure HgSe exceeds  $C_p$  for the diluted system with iron for sufficiently high  $T$ . Such a situation was observed earlier by us<sup>16</sup> and was also reported for  $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ .<sup>18</sup>

If the magnetic contribution  $C_m$  is estimated by subtraction of the undiluted lattice, i.e.,

$$C_m(\text{Hg}_{1-x}\text{Fe}_x\text{Se}) = C_p(\text{Hg}_{1-x}\text{Fe}_x\text{Se}) - C_p(\text{HgSe}), \quad (1)$$

this would lead to the physically unacceptable situation of negative magnetic specific heat at higher temperatures. This situation is extreme for  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  but not unique. Moreover, for  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ , with 8% of Fe, the magnetic specific heat obtained by Eq. (1) can become negative at high  $T$ .

Such a situation results from the fact that substitution of heavy Hg or Cd atoms by relatively light Fe atoms changes the lattice vibrational modes considerably, and, consequently, the lattice specific heat of the mixed or diluted system differs significantly from that of the nondiluted system. This may be well observed in Fig. 5, where we show the specific heat of pure ZnSe (as a close approximation of FeSe), CdSe, HgSe, and a mixed compound  $\text{Hg}_{0.51}\text{Cd}_{0.49}\text{Se}$ . The increasing difference in atomic mass

TABLE I. Materials used in experiment.

Material	$x$ (Fe)	$y$ (Cd)	$1-x-y$ (Hg)
$\text{Hg}_{1-x}\text{Fe}_x\text{Se}$	0.015	0	0.985
	0.024	0	0.976
	0.045	0	0.955
$\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$	0.01	0.43	0.56
	0.044	0.446	0.51
$\text{Cd}_{1-x}\text{Fe}_x\text{Se}$	0.008	0.992	0
	0.034	0.966	0
	0.080	0.920	0

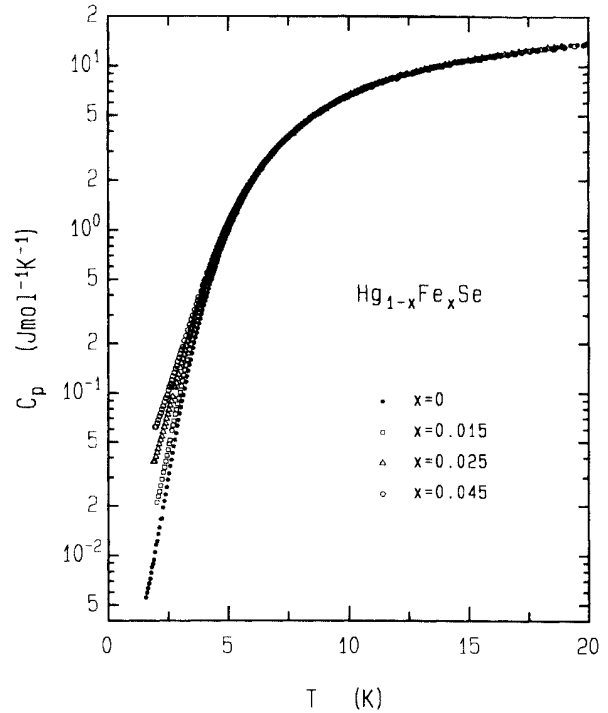


FIG. 1. Specific heat ( $C_p$ ) of  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ , for several concentrations  $x$ .

of Zn, Cd, and Hg as compared to Fe, which in the Debye approach yields an increasing difference in  $\Theta_D$ , is clearly reflected in  $C_p$ . It is obvious that for  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ , and to a lesser extent for  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ , a more realistic procedure of extracting the magnetic contribution from the total specific heat should be used.

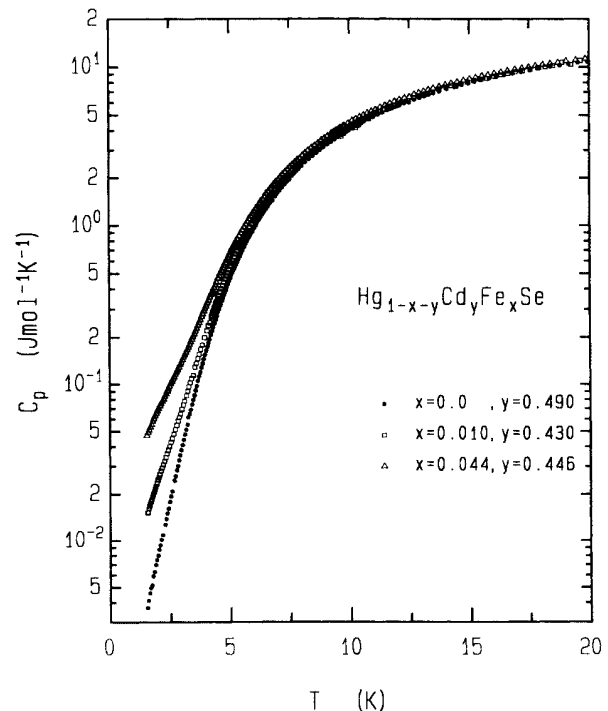


FIG. 2. Specific heat ( $C_p$ ) of  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$ , for several concentrations.

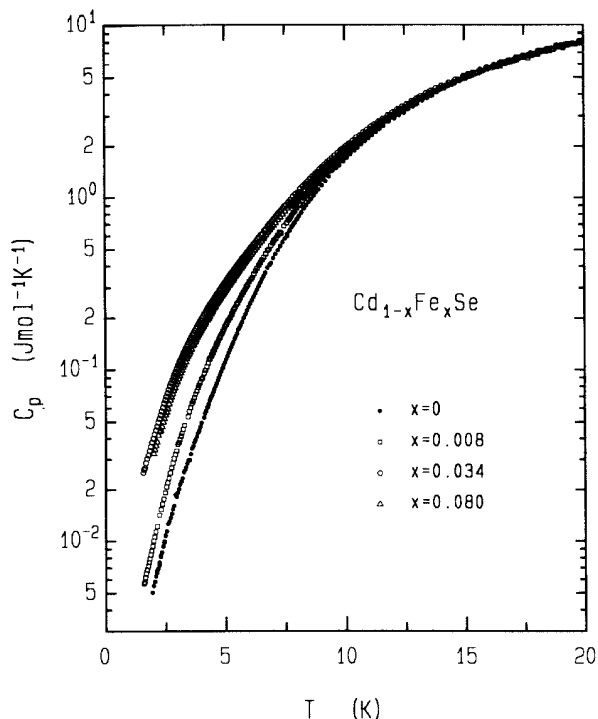


FIG. 3. Specific heat ( $C_p$ ) of  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ , for several concentrations  $x$ .

There are several possible procedures of simulating the lattice heat capacity of an actual crystal. We have tested some of them (based mainly on the Debye approach or linear interpolation of nonmagnetic lattices), and we have found that the validity of all of them is rather limited to

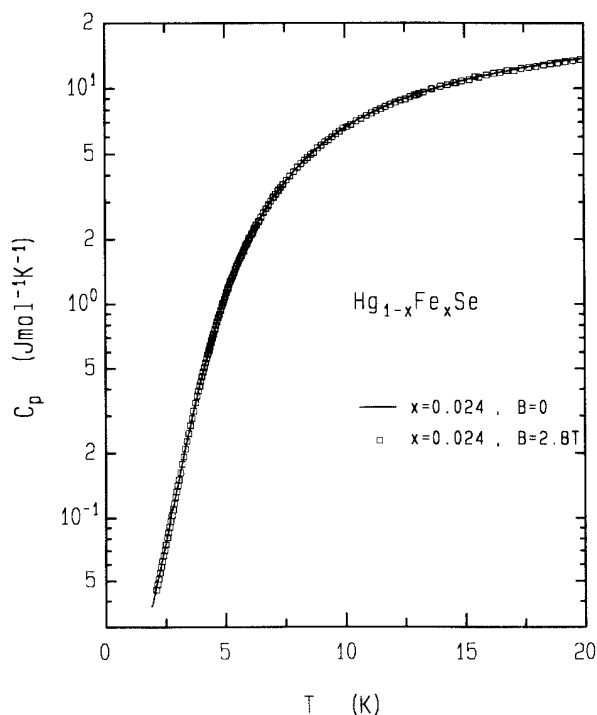


FIG. 4. Specific heat ( $C_p$ ) of  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  ( $x=0.024$ ), for  $B=0$  and  $B=2.8$  T.

the temperature range where the magnetic contribution is somehow comparable to the lattice  $C_p$ . At higher temperatures where  $C_m \ll C_p$ , simulation of lattice  $C_p$  requires very accurate information about the crystal composition. Such accuracy can hardly be obtained for the systems like  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  or  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$  with the help of standard microprobe or chemical analysis. Finally, whatever procedure was used, we were not able to obtain as fine high-temperature results as were found for  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ . We should stress that the low-temperature data, which provided the most important physical information, are reliable for all the compounds.

With respect to the aforementioned remarks, we decided to use simple phenomenological interpolation procedure for the lattice simulation (PLS):

$$C_p^{\text{latt}}(\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}, T) = AC_p(\text{HgSe}, T) + BC_p(\text{CdSe}, T) + xC_p(\text{ZnSe}, T), \quad (2)$$

where the prefactors  $A$ ,  $B$ , and  $x$  are chosen in accordance to the actual  $x$  and  $y$  concentration (Table I).

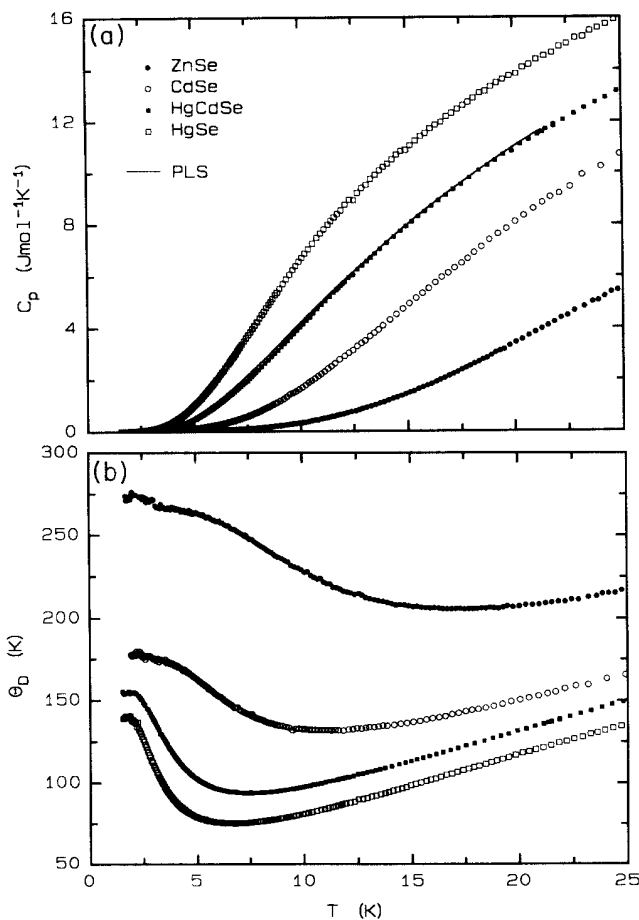


FIG. 5. (a) Specific heat of  $\text{ZnSe}$ ,  $\text{CdSe}$ ,  $\text{Hg}_{0.51}\text{Cd}_{0.49}\text{Se}$ , and  $\text{HgSe}$ ; the solid line represents calculations within PLS (see the text). (b) The corresponding Debye temperatures [ $\Theta_D(T)$ ] of the nonmagnetic lattices.

In order to test this procedure we calculated the specific heat of  $\text{Hg}_{0.51}\text{Cd}_{0.49}\text{Se}$  using the experimental data on the  $\text{HgSe}$  and  $\text{CdSe}$  lattice. The results of these attempts are shown in Fig. 5(a) together with the actual experimental data. Our procedure, although it has no physical background, seems to provide a very reasonable approximation for the lattice specific heat of the mixed crystal. The results obtained for  $C_m$  are given in Figs. 6 ( $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ ) and 7 ( $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ ), where  $C_m/x$  is displayed as a function of temperature. For completeness, in Fig. 8 the results for  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$  (Ref. 14) are given, obtained by a simple lattice subtraction [Eq. (1)] which is equivalent to PLS for this compound. Due to the delicate dependence of  $C_p$  on the actual composition of  $\text{Hg}$  and  $\text{Cd}$  for the quaternary compound  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$ , we could not obtain the reliable  $C_m$  data in this case. Therefore, this compound will not be analyzed quantitatively. We only note that the overall behavior of  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$  heat capacity is the same as that of the other systems (cf. Figs. 1–3).

It can be observed that the overall shape of  $C_m$  is similar for all Fe-based DMS and the magnetic specific heat calculated per one Fe ion ( $C_m/x$ ) generally decreases with increasing iron concentration. However, there is practically no magnetic field dependence of  $C_m$  for  $B < 3$  T (see Figs. 4, 6, and 7). From this behavior one may conclude that the major contribution to  $C_m$  originates from  $\text{Fe}^{2+}$  ions in a singlet ground state as we showed earlier.<sup>14</sup>

In that case one could also expect roughly the same absolute values of  $C_m$  at the maximum, which is apparently not observed. These large differences may only partially result from the fact that our procedure of simulating the lattice is not perfect. On the whole, however, it seems rather well established that the absolute value at the maximum of the magnetic specific heat of  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$  is

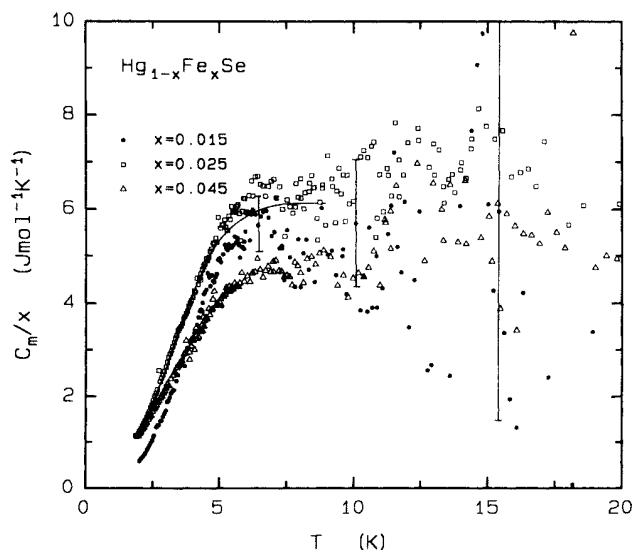


FIG. 6. Magnetic specific heat per mole Fe ( $C_m/x$ ) of  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ , using PLS [Eq. (2)]. The solid line shows  $C_m/x$  for  $x=0.025$  at  $B=2.8$  T.

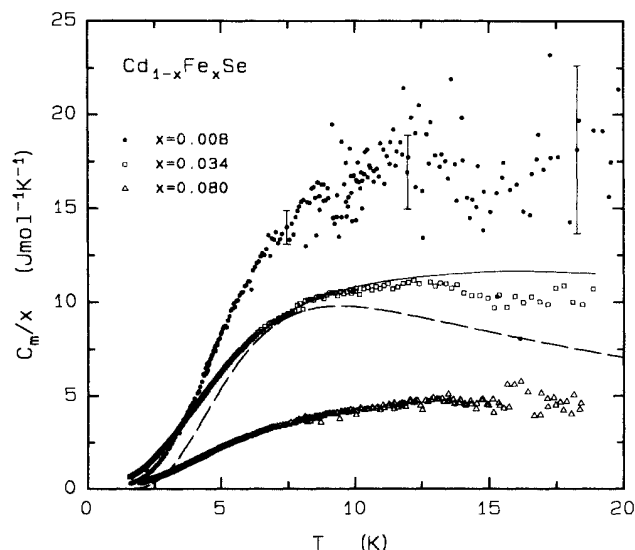


FIG. 7. Magnetic specific heat per mole Fe ( $C_m/x$ ) of  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ , using PLS [Eq. (2)]. The solid line shows  $C_m/x$  for  $x=0.034$  at  $B=2.8$  T. The dashed line displays the calculated  $C_m/x$  (Refs. 21–26) assuming no interaction between Fe ions.

much higher than that of  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ . We return to this point later.

In order to visualize the exponential onset of the magnetic specific heat, we plotted the low-temperature data of  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$  (Fig. 9),  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$  (Fig. 10), and  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  (Fig. 11) as  $\ln(C_m T^2)$  versus  $T^{-1}$ . The specific ordinates are chosen in accordance to the low-temperature behavior of a Schottky anomaly originating from a singlet ground state and a threefold degenerate first excited state at  $\Delta E$ , which schematically represents the lowest levels of the  $\text{Fe}^{2+}$  ion in a cubic crystal field with spin-orbit interaction.<sup>12</sup>

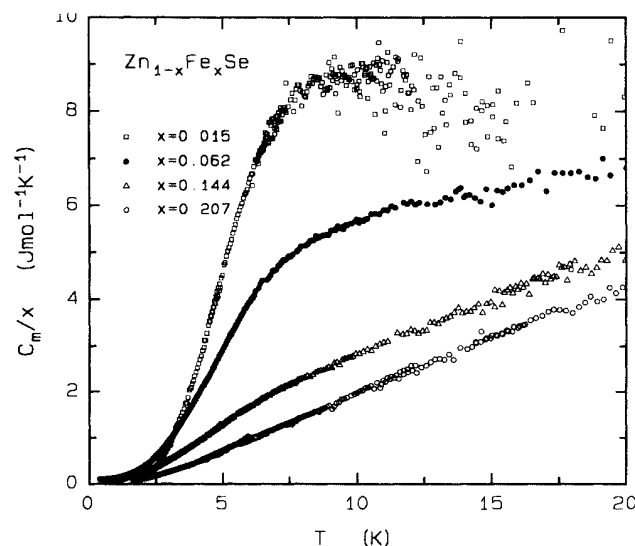


FIG. 8. Magnetic specific heat per mole Fe ( $C_m/x$ ) of  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ ; see Ref. 14.

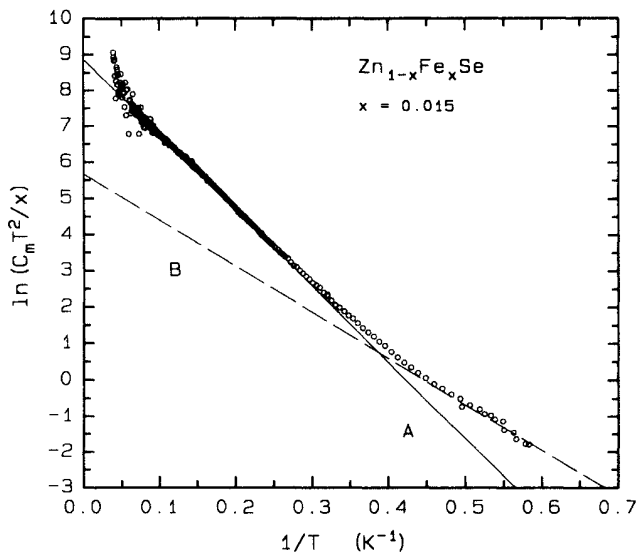


FIG. 9. Magnetic specific heat per mole Fe ( $C_m/x$ ) of  $Zn_{1-x}Fe_xSe$ , plotted as  $\ln(C_m T^2/x)$  vs  $T^{-1}$ ; the lines are described in the text. Line *A* yields  $\Delta E_{\text{single}}=21$  K and line *B*  $\Delta E_{\text{pair}} < 13$  K.

$$C_{\text{Sch}}(T) = xR \left( \frac{g_1}{g_0} \right) \left[ \frac{\Delta E}{kT} \right]^2 \exp \left( \frac{-\Delta E}{kT} \right) \quad (3)$$

with  $g_1/g_0=3$ . Within the framework of this simplified model a straight line should be obtained below the maximum of  $C_m$  with a slope determined by  $\Delta E$ . Extrapolation to  $T=\infty$  will yield the value for  $g_1/g_0$ . Detailed calculations for the real energetical structure of an isolated Fe ion (i.e., five levels<sup>12</sup>) reveal a similar linear behavior of  $\ln(C_m T^2)$  versus  $T^{-1}$  (Fig. 12).

The data for the various compounds indeed show a linear part below  $C_{\text{max}}$  yielding, for low-Fe concentrations where Eq. (8) should apply,  $\Delta E$  in the range 20–25 K, in accordance with data from spectroscopic experiments, and  $g_1/g_0$  in the range 2–4. The deviations at extremely low temperatures (see Figs. 9–11) result from the fact that in our crystals we are dealing not only with isolated Fe ions [to which Eq. (8) applies], but also with Fe-Fe pairs as well as larger clusters. We recall that for  $x=0.015$  only 83% of the Fe ions can be regarded as isolated in the sense that they have no magnetic nearest neighbor (NN). It was shown<sup>7,14</sup> that the energetical structure of a Fe-Fe pair, coupled by exchange interaction, yields a situation essentially similar to that of an isolated Fe ion: the pair ground state is a singlet, however, the energy gap between the ground and the first excited states is strongly reduced [typically by a factor of 2 (Ref. 7 and 14)]. Therefore, if Fe-Fe pairs are present in the crystal, one may expect an additional contribution to the  $C_m$  which will be dominant at low temperatures since only the first excited pair states will be thermally populated. This pair contribution can be observed in Fig. 12, where we plotted the calculated  $C_m$  assuming only NN interactions and a statistical distribution of Fe ions in the crystal (for details of the calculations we refer to Refs. 7 and 14). We note that although our model calculations result from a rather simple Hamiltonian describing Fe-Fe pairs and single ions,<sup>7,14</sup> the behavior of the real experimental data can be well recovered. It is also apparent that plotting  $\ln(C_m T^2/x)$  versus  $T^{-1}$  enables one to estimate energy gaps for an isolated Fe ion as well as for the Fe-Fe pair from the appropriate linear parts of the plot. In the present case the temperature is still somewhat too high to restore the linear part in the pair contribution completely. Therefore the “pair” straight lines in Figs.

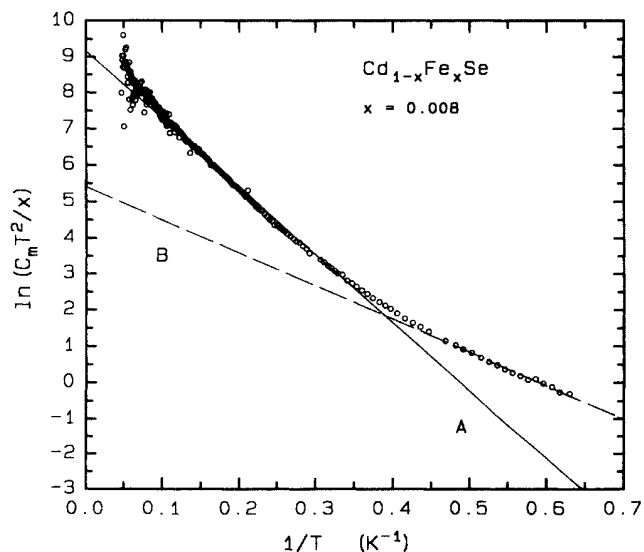


FIG. 10. Magnetic specific heat per mole Fe ( $C_m/x$ ) of  $Cd_{1-x}Fe_xSe$ , plotted as  $\ln(C_m T^2/x)$  vs  $T^{-1}$ ; the lines are described in the text. Line *A* yields  $\Delta E_{\text{single}}=19$  K and line *B*  $\Delta E_{\text{pair}} < 9$  K.

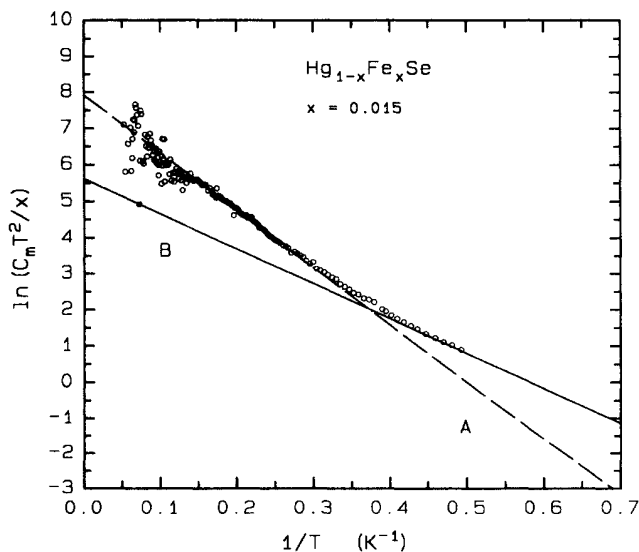


FIG. 11. Magnetic specific heat per mole Fe ( $C_m/x$ ) of  $Hg_{1-x}Fe_xSe$ , plotted as  $\ln(C_m T^2/x)$  vs  $T^{-1}$ ; the lines are described in the text. Line *A* yields  $\Delta E_{\text{single}}=16$  K and line *B*  $\Delta E_{\text{pair}} < 10$  K.

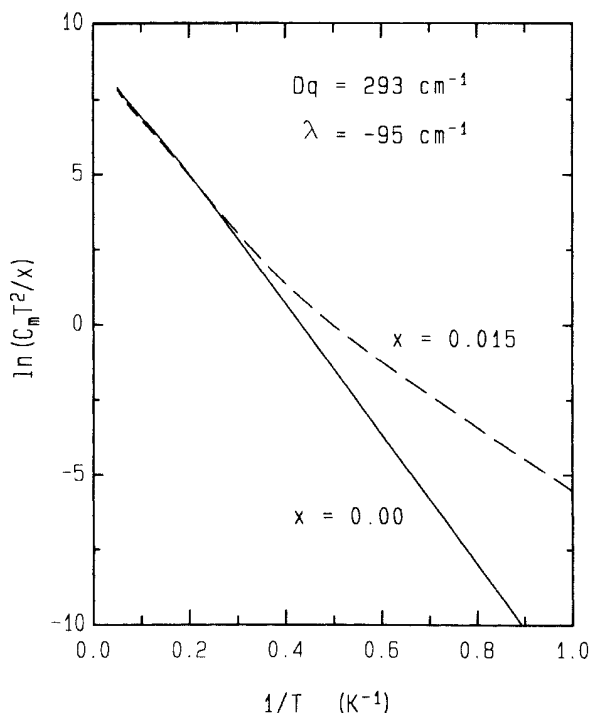


FIG. 12. Calculated magnetic specific heat per mole Fe ( $C_m/x$ ), plotted as  $\ln(C_m T^2/x)$  vs  $T^{-1}$  ( $Dq=293 \text{ cm}^{-1}$ ,  $\lambda=-95 \text{ cm}^{-1}$ ,  $J_{\text{NN}}=-22 \text{ K}$ ). The line for  $x=0.00$  corresponds to the case of noninteracting Fe ions.

9–11 give only an estimate of the upper limit for the pair energy gap. Actually, we find a reduction of the pair energy gap by a factor 1.6–2 (in respect to the isolated Fe ion energy gap) instead of 2.44 resulting from the calculations (assuming exchange interaction between nearest neighbors of the order of  $-20\text{K}$ ).

For completeness we would like to add that the contributions resulting from nuclear hyperfine interaction, the presence of paramagnetic impurities in our crystals (mainly  $\text{Mn}^{2+}$  with concentrations  $n=10^{17}-10^{19} \text{ cm}^{-3}$ ) and the linear term in  $C_m$  brought about by the free carriers ( $n < 10^{19} \text{ cm}^{-3}$ ) are too small to be observed in this specific experiment.

## DISCUSSION

From the experimental data presented we conclude the following.

(i) The magnetic contribution to the specific heat of our crystals is fairly large at low temperatures, whereas at higher temperatures it is only a small fraction of the lattice contribution. Therefore, the high-temperature  $C_m$  of some materials is very sensitive to the extraction method and in some cases ( $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$ ) reliable data cannot be obtained (at least not without a separate study of the  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Zn}_x\text{Se}$  lattice specific heat). However, the most important physical information results from the low-temperature data, where there are no problems with extracting  $C_m$  from the total heat capacity.

(ii) The magnetic contribution to the specific heat shows similar overall behavior for all the Fe-type DMS investigated so far (in spite of some uncertainty in the absolute value).

(iii) The exponential low-temperature increase of  $C_m$  clearly indicates an energy gap between the ground state and the excited states, of the order of 20 K.

(iv) The very weak field dependence of  $C_m$  strongly indicates that the ground state of the Fe ion is a singlet one.

(v) The decrease of the magnetic specific heat per one Fe ion ( $C_m/x$ ) with increasing concentration, suggests an antiferromagnetic  $d-d$  exchange interaction between Fe ions in all cases.

These observations are in agreement with our “crystal-field” model developed recently for Fe-based DMS.<sup>7,14</sup> We recall briefly that in this model we factorized the whole magnetic system into pairs coupled by (principally) long-range exchange interaction [so-called extended nearest-neighbors pair approximation<sup>19,20,3</sup> (ENNPA)]. The basic element in this model is based on the numerical solution of an Fe-Fe pair, where the crystal field (cubic or hexagonal), spin-orbit interaction, magnetic field, and the Heisenberg-type exchange interaction are taken into account simultaneously. It was shown<sup>7</sup> that the ground state of both an isolated Fe ion and an Fe-Fe pair is a singlet with a first (excited) threefold degenerate state at about 10–20 K, leading to a Shottky-type specific heat, which is very weakly magnetic field dependent, in accordance with the experimental evidence.

However, this model also predicts a similar maximal absolute value of the specific heat (practically independent of crystal-field and spin-orbit interaction parameters), whereas our experimental maximal values differ largely in magnitude. In Fig. 7 we show the calculated specific heat  $C_m/x$  for  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$  assuming no interaction between Fe ions, which is the upper limit for  $C_m/x$ .<sup>21–26</sup> Inspection of Fig. 7 shows that the maximal specific heat of  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$  is apparently consistently too large irrespective of the specific procedure used to estimate the lattice<sup>27</sup>.

In order to substantiate this fact we calculated the total entropy contained in the experimental specific heat. The data in the temperature range  $0 < T < 1.5 \text{ K}$  were approximated by a linear extrapolation, whereas for  $T > 20 \text{ K}$  a high-temperature  $T^{-2}$  approximation was used. The recovered experimental entropy is always 50–60% larger than expected for a  $\text{Fe}^{2+}$  ten-level system:  $S = R \ln 10$ .<sup>28</sup> This suggests that in fact we are dealing with more than the ten levels contained in the  ${}^5E$  multiplet. Since the term structure of Fe is rather well established for both  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$  and  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$  from the  ${}^5E \rightarrow {}^5T$  optical transition,<sup>5,25</sup> the only mechanism which can supply additional energy levels seems inclusion of electron-phonon interaction, i.e., Jahn-Teller effect.<sup>29</sup>

The Jahn-Teller effect on the  ${}^5E$  term of  $\text{Fe}^{2+}$  has been studied by several authors.<sup>30–33</sup> Generally speaking, modifications of the  ${}^5E$  energy structure due to electron-phonon interaction depend on the coupling phonon energy. If the phonon interaction is larger than the spin-orbital splitting of the  ${}^5E$  term, the main effect of the Jahn-Teller effect is a reduction of the energy intervals

between the  ${}^5E$  term levels.<sup>32</sup> This reduction, however, can be accounted for by a small change in the crystal-field and spin-orbit parameters and is thus not very apparent. Only if the phonon energy is small enough (in practice smaller than spin-orbital splitting of the  ${}^5E$  term), this electron-phonon coupling can modify the energy levels seriously.<sup>30</sup> In particular, new energy levels appear in the energy spectrum as a result of coupling 0,1,2, . . . phonons to the electronic levels.<sup>30</sup> For crystals like ZnS or ZnSe, phonons which can couple to the electronic states [TA(L)] have sufficiently high energies<sup>34</sup> and produce no noticeable effects. The far-infrared spectroscopic data for ZnS:Fe and  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$  can be satisfactorily described by considering only the crystal-field and spin-orbit interaction.<sup>35</sup> On the other hand, in CdTe, the TA(L) phonon has an energy small enough ( $35\text{ cm}^{-1}$ ) to modify the energetical structure and optical selection rules considerably.<sup>30</sup> The reported TA phonon energy for CdSe is  $43\text{ cm}^{-1}$ ,<sup>36</sup> which is a considerably smaller value than the total splitting of the  ${}^5E$  term, suggesting that the Jahn-Teller effect should be taken into account for this material. To our knowledge nothing is known about electron-phonon coupling for the  ${}^5E$  term in  $\text{Hg}_{1-x}\text{Cd}_x\text{Se}$  or HgSe. Only very recently it was suggested from Mössbauer experiments<sup>37</sup> that a Jahn-Teller distortion might be expected for  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$ . Since no Jahn-Teller calculations have been reported for CdSe:Fe (in particular, taking into account its hexagonal structure), we performed a simple calculation to demonstrate the influence of "phonon replica" energy levels on the specific heat. We considered five equally spaced Fe electronic levels,<sup>11</sup> to which up to ten phonons of energy  $h\omega$  can be coupled. For simplicity we assumed no coupling between these vibronic levels, i.e., no true Jahn-Teller effect. The resulting specific heat is shown in Fig. 13 for different phonon energies. As conjectured, the maximal value of the specific heat increases with decreasing phonon energy, i.e., with increasing number of vibronic levels which can be thermally populated. Although the phonon energies,

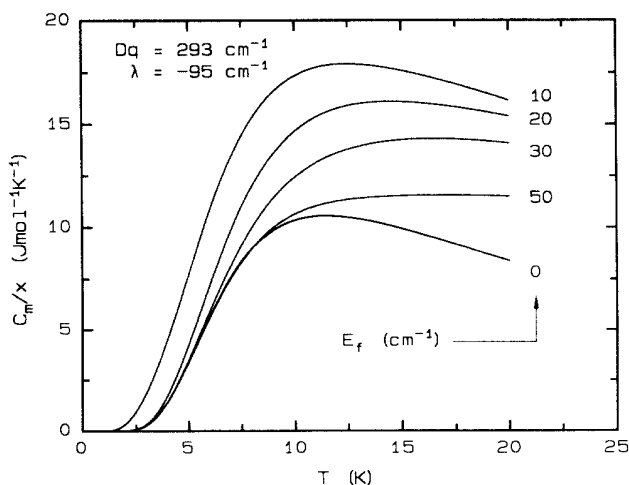


FIG. 13. Influence of additional "phonon-replica" energy levels (simulating the Jahn-Teller effect) on the specific heat in the crystal-field model, using  $Dq = 293\text{ cm}^{-1}$ ,  $\lambda = -95\text{ cm}^{-1}$ .

which produce a substantial increase of  $C_m$ , are apparently too low as compared to the reported Brillouin-zone-edge TA phonon [ $43\text{ cm}^{-1}$  (Ref. 36)], one cannot exclude the possibility that phonons over a considerable range inside the entire Brillouin Zone contribute to electron-phonon coupling, which may result in smaller "effective phonon" energy. We should stress, however, that these calculations should be regarded only as an illustration suggesting a possible source of the anomalous high specific-heat values. A detailed discussion of this problem requires precise calculations of the  $\text{Fe}^{2+}$  energy levels with crystal-field, spin-orbit, and Jahn-Teller interactions taken into account. One can, however, expect that for the Fe-Fe pair, such calculations would lead to rather large Hamiltonian matrices.

Summarizing the remarks listed, we notice that no essential differences are observed for the specific heat for the  $\text{Hg}_x\text{Fe}_{1-x}\text{Se}-\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}-\text{Cd}_{1-x}\text{Fe}_x\text{Se}$  series. The general behavior of  $C_m$  ( $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$ ) is also similar to that found for  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ .<sup>14</sup> Recent analysis of the magnetic susceptibility of  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  (Ref. 17) shows that the reported Brillouin-type behavior in Ref. 8 is mainly due to the presence of  $\text{Fe}^{3+}$  ions in all the investigated  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  crystals: a result of self-ionization of  $\text{Fe}^{2+}$  ions.<sup>4</sup>  $\text{Fe}^{3+}$  ions have a  $d^5$  electronic configuration (the same as  $\text{Mn}^{2+}$  ions) resulting in a Curie-type susceptibility. Although the concentration of  $\text{Fe}^{3+}$  ions is small ( $n = 5 \times 10^{18}\text{ cm}^{-3}$  constant for all  $x > 0.01$  (Refs. 4 and 5)), their contribution to the total susceptibility may be dominant at low temperatures ( $T < 3\text{ K}$ ) and may completely mask the Van Vleck-type temperature-independent susceptibility of  $\text{Fe}^{2+}$  ions. In Ref. 17 it was shown that below 3–4 K, the temperature-dependent susceptibility is independent of the Fe concentration and can be well described as the Curie-type susceptibility of  $n = 5 \times 10^{18}\text{ cm}^{-3}$   $\text{Fe}^{3+}$  ions. A similar effect was also reported in  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ ,<sup>9</sup> although in that case the paramagnetic ions were impurities in the material used for crystal growing (mainly  $\text{Mn}^{2+}$  as detected by electron paramagnetic resonance experiments.<sup>9</sup>)

Summarizing our discussion on the results of specific-heat and susceptibility data so far, we are tempted to conclude that these data do not reveal any anomalous behavior which can be related to the location of the  $\text{Fe}^{2+}$  energy level relative to the band structure. This does not exclude, in principle, hybridization of the resonant  $\text{Fe}^{2+}$  level with the conduction band,<sup>8</sup> but the effect of such a hybridization does, in our opinion, not manifest itself in the present data. This weak Fe-level dependence may be understood on the basis of recent calculations of the  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  energy structure.<sup>38</sup> In Fig. 14 we reproduce a schematic diagram for the  $d$  levels in II-VI semiconductors.<sup>38</sup> In the case of Mn-type DMS ( $d^5$ ), the five electrons of Mn occupy  $e_+$  and  $t_+$  orbitals ( $e_+^2 t_+^3$  configuration) located deeply in the valence band. For Fe-type materials ( $d^6$ ), the additional sixth electron must occupy an  $e_-$  orbital, yielding a  $e_+^2 t_+^3 e_-^1$  configuration. The reported variation of the Fe level position with Cd content in  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$  (Ref. 5) concerns precisely electrons from the  $e_-$  orbital. However,  $e$  orbitals in tetrahedral crystals hybridize very weakly with  $p$ -type



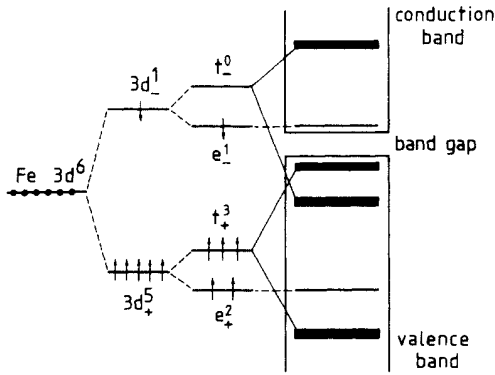


FIG. 14. Schematic representation of the electronic Fe levels within the band structure of a II-IV semiconductor, based on recent calculations on the Mn containing CdTe (Ref. 38).

bands: They do not form strong  $\sigma$ -type bonds; only weak  $\pi$ -type bonding is formed. Therefore, no first-order effects are expected with a variation of the Fe level position relative to the band structure.<sup>39</sup> Consequently, we feel confident to assume that the description of the magnetic properties of all the Fe-based DMS investigated so far, can be based in first approximation on a simple "crystal-field model"<sup>7</sup> (eventually augmented by electron-phonon interaction).

In that respect one can now estimate the  $d$ - $d$  exchange interaction parameters for the series  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$ . This can be done using the high-temperature expansion series for the magnetic susceptibility developed recently<sup>40</sup> based on the "crystal-field model" of Fe-based DMS. In this model the Curie-Weiss temperature determined from high-temperature susceptibility data, can be expressed as<sup>40</sup>

$$\Theta(x) = \frac{\langle M_z^2 \rangle_\infty \langle E \rangle_\infty - \langle M_z^2 E \rangle_\infty}{\langle M_z^2 \rangle_\infty k_B} + \frac{2 \langle M_z S_z \rangle_\infty^2}{\langle M_z^2 \rangle_\infty} x \sum_p z_p (J_p / k_B), \quad (4)$$

where  $\langle \dots \rangle$  denotes average values of the energy ( $E$ ), magnetic-moment ( $M$ ), and spin ( $S$ ) operators.  $J_p$  is the exchange integral for the  $p$ th coordination sphere and  $z_p$  is the coordination number. Assuming that the possible electron-phonon interaction does not significantly

TABLE II. Parameters for the crystal-field model.

Material	$Dq$	$\lambda$	$\nu$	$\nu'$
$\text{Hg}_{1-x}\text{Fe}_x\text{Se}$	293	-85, 0, -95	0	0
$\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$	280	-80	0	0
$\text{Cd}_{1-x}\text{Fe}_x\text{Se}$	257	-93.8	31	38
$\text{Zn}_{1-x}\text{Fe}_x\text{Se}$	293	-95	0	0(14)

influence the average values in Eq. (9), and using parameters from Table II, we calculated the nearest-neighbor exchange integrals for the mixed  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$  systems from the reported  $\Theta(x)$  values.<sup>8,41</sup> The results are tabulated in Table III.

We should stress that, although crystal-field and spin-orbit parameters for  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  and  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$  are not provided by spectroscopic experiments as in the case of  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ ,<sup>21-25</sup> changing these parameter values results only in a very small variation of  $J_{\text{NN}}$  (significantly smaller than the errors given by the experimental inaccuracy of the Curie-Weiss temperature). Inspection of Table III shows that the  $d$ - $d$  exchange interaction for the Fe-type DMS is of the same sign (AF) but stronger than the exchange observed in Mn-type materials. The interaction strength is of the same order of magnitude for all the Fe-DMS, although a general trend of increasing interaction while passing from HgSe to ZnSe is found.

Considering the different possible mechanisms we notice that the dipole-dipole interaction can be effective only at mK temperatures. A Ruderman-Kittel-Kasuya-Yosida interaction<sup>46</sup> is also ineffective because the concentration of free carriers in Fe-type DMS is too low (similarly as for Mn-type materials). The Bloembergen-Rowland mechanism<sup>47,48</sup> would yield a strong dependence of exchange on the energy gap of the crystal. In contrast, we observe practically the same strength of exchange in the series  $\text{Hg}_{1-x}\text{Fe}_x\text{Se}$  (zero-gap material),  $\text{Hg}_{1-x-y}\text{Cd}_y\text{Fe}_x\text{Se}$  (narrow-gap material),  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ , as well as  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$  (both wide-gap crystals) (Table III). Therefore, it seems very likely that for an Fe-ion system, superexchange<sup>49,50</sup> is the dominant mechanism of exchange (at least for NN), as was well established in Mn-type DMS.<sup>45,51</sup> This hypothesis is further supported by the fact that for both Fe- and Mn-ion systems, the major contribution to the exchange comes from the same electrons (Fig. 14).

If superexchange produces the major contribution to the interaction, then the "three-level model" developed

TABLE III. Curie-Weiss temperatures and  $d$ - $d$  interaction strength for II-VI Fe-containing DMS; a comparison is made with Mn compounds.

Material	$\Theta$ (K)	$J_{\text{NN}}$ (K)	$J_{\text{NN}}$ (Mn) (K)
$\text{Hg}_{0.99}\text{Fe}_{0.01}\text{Se}$	-9±5(8)	-18±2	-11(45), -6(42)
$\text{Hg}_{0.95}\text{Fe}_{0.05}\text{Se}$	-38±5(41)		
$\text{Hg}_{0.54}\text{Cd}_{0.41}\text{Fe}_{0.05}\text{Se}$	-35±5(8)	-18±2	
$\text{Cd}_{0.95}\text{Fe}_{0.05}\text{Se}$	-36(8)	-18.8±2	-9(43)
$\text{Zn}_{1-x}\text{Fe}_x\text{Se}$		-22±2(40)	-13(44)

for Mn-type DMS (Ref. 51) can be also adopted for Fe-type materials giving some insight in chemical trends observed in Table III. The "three-level model" is based on kinetic superexchange<sup>49,51</sup> and simplifies the actual situation by considering only three levels: the valence band (at energy  $E_v$ ), the six-electron occupied  $d$  level ( $E_d$ ), and an unoccupied level to which electron from the valence band can be transferred. Such an electron transfer results in an increase of the correlation energy, so a seven-electron configuration has energy  $E_d + U$ . Thus, the analytic expression for  $J$  can be written as<sup>51</sup>

$$J = -2V_{pd}^4 [(E_d + U - E_v)^{-2} U^{-1} + (E_d + U - E_v)^{-3}] f(R), \quad (5)$$

where  $V_{pd}$  is the hybridization parameter describing the probability of a valence band electron hopping to the Fe  $d$  level;  $f(R)$  describes the dependence on the Fe-Fe distance. The parameter  $V_{pd}$  may be related to the  $s$ - $d$  exchange constant for the valence band  $N_0\beta$ :<sup>51</sup>

$$N_0\beta = -2V_{pd}^2 [(E_d + U - E_v)^{-1} - (E_d - E_v)^{-1}]. \quad (6)$$

At the moment knowledge about the parameters occurring in Eqs. (5) and (6) is rather poor. In particular,  $N_0\beta$  is known only for  $Zn_{1-x}Fe_xSe$  (Ref. 9) and  $Cd_{1-x}Fe_xSe$  (Ref. 52). For these materials one finds that  $N_0\beta$  is larger in  $Zn_{1-x}Fe_xSe$  by a factor of 1.3 in respect to  $Zn_{1-x}Mn_xSe$  (1.5 in the case of CdSe).<sup>9,53</sup> Assuming that this increase of  $N_0\beta$  results mainly from a stronger hybridization, one can expect a larger  $d$ - $d$  exchange parameter by a factor of 1.7 (2.1 for CdSe), which compares favorably with the experimental  $J$  value [ $J_{NN}(Zn_{1-x}Fe_xSe) = -22 \text{ K} \approx 1.7 \times J_{NN}(Zn_{1-x}Mn_xSe)$ ;  $J_{NN}(Cd_{1-x}Fe_xSe) = -19 \text{ K} \approx 2.1 \times J_{NN}(Cd_{1-x}Mn_xSe)$ ]. The higher  $J_{NN}$  values obtained for HgSe and  $Hg_{1-x}Cd_xSe$  with iron suggest a similar situation also for the  $Hg_{1-x-y}Cd_yFe_xSe$  series. Detailed analysis of the chemical trends in the  $d$ - $d$  and  $s$ - $d$  exchange interaction

in these materials awaits further study. Magneto-optical experiments providing information about  $N_0\beta$  and ultra-violet photoemission studies determining  $E_d$  would also be very useful.

## CONCLUSIONS

In the present study of the specific heat of  $Hg_{1-x-y}Cd_yFe_xSe$  DMS we found that all the Fe-types DMS investigated so far demonstrate generally similar magnetic properties, which suggest that the ground state of both the isolated Fe ion and Fe-Fe pair is a singlet (separated from the excited states by at about  $20 \text{ cm}^{-1}$  for an isolated ion and  $10 \text{ cm}^{-1}$  for the Fe-Fe pair). Antiferromagnetic coupling between Fe ions is observed. No experimental evidence was found that the magnetic properties of narrow-gap DMS differ from those of the wide-gap materials and, consequently, no Fe-level position dependence could be deduced. A simple crystal-field model (eventually complemented by electron-phonon interaction) seems to be sufficient to describe the magnetic properties of all the Fe-type DMS. The  $d$ - $d$  exchange parameters for the  $Hg_{1-x-y}Cd_yFe_xSe$  systems are substantially larger than those of  $Hg_{1-x-y}Cd_yMn_xSe$ , in agreement with the situation encountered for  $Zn_{1-x}Fe_xSe$  and  $Zn_{1-x}Mn_xSe$ .

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- <sup>21</sup>The "crystal-field" model for hexagonal materials has been recently reported (see Ref. 22) with a relatively simple form of the hexagonal term in the Hamiltonian. In this paper we used basically the same model, however, expressing hexagonal distortion in a way more common in the literature (see Ref. 23):  $H_1 = -\frac{2}{3}B_4(O_4^0 + 20.2 O_4^2) + B_2^0 O_2^0 + B_4^0 O_4^0$  and the  $z$  axis was chosen along [111] direction (i.e., parallel to crystal  $c$  axis). The presence of trigonal distortion in the Hamiltonian causes splitting of triplets  $T_1, T_2$  into singlets and doublet ( $T_1 - A_2, E$  and  $T_2 - A_1, E$ ) (Ref. 13). Since the Hamiltonian matrix is parametrized by material constants  $Dq$  (describing cubic crystal field),  $\nu, \nu'$  (both describing hexagonal distortion), and  $\lambda$  (spin-orbit interaction), the obtained energies can be used for the estimation of these parameters for  $Cd_{1-x}Fe_xSe$ . We used very recent measured energies of optical transition  $A_1 \rightarrow A_2$  [ $13 \text{ cm}^{-1}$  (Ref. 24)],  $A_1 \rightarrow E$  [ $17.6 \text{ cm}^{-1}$  (Ref. 24)], as well as zero-phonon line energy for  ${}^5E \rightarrow {}^5T$  transition [ $2375 \text{ cm}^{-1}$  (Ref. 25)]. The best fit was found for  $Dq = 257 \text{ cm}^{-1}$ ,  $\lambda = -93.8 \text{ cm}^{-1}$ ,  $\nu = 31 \text{ cm}^{-1}$ , and  $\nu' = 38 \text{ cm}^{-1}$ .
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- <sup>27</sup>One should not be confused by the data for higher Fe concentrations, which compare reasonably with the calculations. The calculated specific heat shown in Figs. 6–8 corresponds to the very dilute limit, in which interactions between Fe ions can be neglected. For higher  $x$ , AF interactions between Fe ions results in lowering of  $C_m/x$ .
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