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Magnetic susceptibility of iron-based semimagnetic semiconductors: High-temperature regime

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The high-temperature magnetic susceptibility of random, diluted magnetic systems is discussed for magnetic ions having not only spin momentum but also nonvanishing orbital momentum. In particular, the magnetic susceptibility of $Zn_{1-x}Fe_xSe$ (Fe^{2+}, $S=2$, $L=2$) is reported in the temperature range 2–300 K. The nearest-neighbor Fe-Fe exchange interaction is estimated as $J_{NN}/k_B = -22$ K for $Zn_{1-x}Fe_xSe$ and $J_{NN}/k_B = -17.8$ K for $Cd_{1-x}Fe_xSe$.

I. INTRODUCTION

Semimagnetic semiconductors (SMSC's) or diluted magnetic semiconductors[1] are materials based on the well-known II-VI or II-V compounds in which some cations are substituted for by magnetic ions. The concentration of magnetic ions can be controlled in a very wide range (from doped to mixed crystals) which allows one to study in one material both the very dilute and high concentrated regimes. Because of that, these alloys have attracted considerable attention during the last decade, and interesting magnetooptical and magnetic properties were reported.[1] The strong s-d exchange interaction between band electrons and localized d electrons of the magnetic ions results in effects like giant free-exciton Zeeman splitting or formation of magnetic polarons. On the other hand, due to the antiferromagnetic d-d interaction between magnetic ions, various magnetic phases (paramagnetic, spin-glass, and antiferromagnetic) were found, depending on the concentration and temperature range.

So far, most of the studies were devoted to manganese-based SMSC's such as $Cd_{1-x}Mn_xTe$, $Hg_{1-x}Mn_xTe$, or $Zn_{1-x}Mn_xSe$. From a magnetic point of view these materials are particular since Mn^{2+} has a d^5 electronic configuration resulting in a spin-only ground state since the orbital momentum is zero. Only recently, more attention has been focused on iron-based SMSC's ($Hg_{1-x}Fe_xSe$, $Zn_{1-x}Fe_xSe$, or $Cd_{1-x}Fe_xSe$),[2] which can be considered examples of a more general magnetic situation, because Fe^{2+} possesses both spin and orbital momenta ($S=2$ and $L=2$).[3-5]

Although some attempts to understand the magnetic behavior of these compounds were already reported,[6-8]

crucial information about the Fe-Fe interaction (strength and range) is still lacking. The only estimate for the nearest-neighbor interaction (J_{NN}) is derived from high-temperature susceptibility[8] assuming $L=0$. We therefore thought it worthwhile to study the $L\neq0$ case more carefully in order to be able to evaluate the d-d exchange parameters more reliably. We also report in this paper new results of magnetic susceptibility of $Zn_{1-x}Fe_xSe$ in the temperature range 2–300 K. Finally, we reexamine previous results[8] for $Cd_{1-x}Fe_xSe$.

II. DERIVATION OF THE HIGH-TEMPERATURE SUSCEPTIBILITY FOR $L\neq0$

In this section we calculate the high-temperature expansion (HTE) of the static magnetic susceptibility following the method applied in Ref. 9 for the spin-only case ($L=0$). We obtain a Curie-Weiss law for the general case of magnetic ions with both $S\neq0$ and $L\neq0$, resulting in a relationship between macroscopic parameters such as the Curie constant, the Curie-Weiss temperature, the magnetic ion concentration x, and d-d exchange integrals. Assuming that magnetic ions interact isotropically with each other via spin momenta, the Hamiltonian for a random, dilute system can be expressed in the following way:

$$\mathcal{H} = -\frac{1}{2}\sum_{i,j} 2J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j\xi_i\xi_j + \mu_B B_z \sum_i (L_{zi}+gS_{zi})\xi_i$$
$$+ \sum_i H_{cfi}\xi_i + \sum_i \lambda\mathbf{L}_i\cdot\mathbf{S}_i\xi_i , \tag{1}$$

where sums over i and j run over all lattice sites ($i\neq j$), and ξ_i is 0 or 1, depending on whether the cation site is

occupied by a nonmagnetic (Zn, Cd, or Hg) or a magnetic ion, respectively. S_i and L_i are the atomic-spin and orbital-momenta operators, respectively. The first term in Hamiltonian (1) describes the d-d exchange interaction (J_{ij} is the exchange integral), the second the influence of the magnetic field, the third the crystal-field splitting, and the last the spin-orbit interaction. A given sequence $\{\xi_i\}$ determines a specific distribution of magnetic ions on the lattice sites. The static susceptibility per unit volume is defined by

$$\chi_v = -\frac{1}{V}\left[\frac{\partial^2 F}{\partial B_z^2}\right]_T , \tag{2}$$

where V is the volume of the system and F is its free energy, given by

$$F = -k_B T \sum_{\{\xi\}} P(\{\xi_i,\ldots,\xi_N\})\ln \mathrm{Tr}e^{-\beta H} = -k_B T\,\overline{\ln Z} . \tag{3}$$

In this expression $P(\{\xi_i,\ldots,\xi_N\})$ is the probability distribution of a given sequence $(\xi_1,\xi_2,\ldots,\xi_N)$, Tr denotes

trace, Z is the partition function for a particular configuration $\{\xi_1,\ldots,\xi_N\}$, $(\overline{\cdots})$ means averaging over configurations, and $\beta = 1/k_B T$.

In the high-temperature regime the partition function Z can be expanded as follows:

$$Z = \mathrm{Tr}e^{-\beta H} \simeq \mathrm{Tr}(1-\beta H + \tfrac{1}{2}\beta^2 H^2 - \tfrac{1}{6}\beta^3 H^3) . \tag{4}$$

Performing double derivation of free energy (3), one finds

$$\chi = \frac{kT}{V}\left[\frac{1}{Z}\frac{\partial^2 Z}{\partial B_z^2} - \left[\frac{1}{Z}\frac{\partial Z}{\partial B_z}\right]^2\right] \tag{5}$$

and

$$\frac{\partial Z}{\partial B_z} = -\beta\,\mathrm{Tr}M + \beta^2\mathrm{Tr}(MH) - \tfrac{1}{2}\beta^3\mathrm{Tr}(MH^2) , \tag{6}$$

$$\frac{\partial^2 Z}{\partial B_z^2} = \beta^2\mathrm{Tr}(M^2) - \beta^3\mathrm{Tr}(M^2 H) , \tag{7}$$

where we introduced $M \equiv \partial H/\partial B_z$ and used the relation $\mathrm{Tr}(ABC)=\mathrm{Tr}(BCA)=\mathrm{Tr}(CAB)$. Substituting (6) and (7) into (5) yields, to first order in H,

$$\chi = \frac{\beta}{V}\left[\frac{\mathrm{Tr}(M^2)}{\mathrm{Tr}1} + \beta\frac{\mathrm{Tr}(M^2)\,\mathrm{Tr}(H)}{\mathrm{Tr}1\,\mathrm{Tr}1} - \beta\frac{\mathrm{Tr}(M^2 H)}{\mathrm{Tr}1} - \left[\frac{\mathrm{Tr}M}{\mathrm{Tr}1}\right]^2 - 2\beta\frac{\mathrm{Tr}M}{\mathrm{Tr}1}\left[\frac{\mathrm{Tr}(M)\mathrm{Tr}(H)}{\mathrm{Tr}1\mathrm{Tr}1} - \frac{\mathrm{Tr}(MH)}{\mathrm{Tr}1}\right]\right]$$

$$= (\beta/V)\overline{(\langle M^2\rangle_\infty + \beta\langle M^2\rangle_\infty\langle H\rangle_\infty - \beta\langle M^2 H\rangle_\infty - \langle M\rangle_\infty^2 - 2\beta\langle M\rangle_\infty^2\langle H\rangle_\infty + 2\beta\langle M\rangle_\infty\langle MH\rangle_\infty)} , \tag{8}$$

where $\langle A\rangle_\infty = \mathrm{Tr}(A)/\mathrm{Tr}1$ means the statistical average taken at infinite temperature. The advantage of using $\langle\cdots\rangle_\infty$ is that as $T\to\infty$ magnetic moments on different sites $(i\neq j)$ can be regarded as independent and averages $\langle\cdots\rangle_\infty$ in (8) can be expressed by single-ion averages. Noting that $\langle M\rangle\to 0$ as $B\to 0$ and $T\to\infty$, we finally obtain the high-temperature, zero-field susceptibility:

$$\chi = (\beta/V)\overline{(\langle M^2\rangle_\infty + \beta\langle M^2\rangle_\infty\langle H\rangle_\infty - \beta\langle M^2 H\rangle_\infty)} . \tag{9}$$

One can now evaluate the traces in (9) and get

$$\langle M^2\rangle = \sum_{i,j}\delta_{ij}\langle M_{zi}^2\rangle_\infty\xi_i ,$$

$$\langle M^2\rangle\langle H\rangle = \sum_{i,j}\left[\delta_{ij}\langle M_{zi}^2\rangle_\infty\left[\langle E_i\rangle_\infty\xi_i\right.\right.$$
$$\left.\left. + \sum_{k\neq i}\langle E_k\rangle_\infty\xi_k\right]\right] , \tag{10}$$

$$\langle M^2 H\rangle = \sum_{i,j}\left\{\delta_{ij}\left[\langle M_{zi}^2 E_i\rangle_\infty\xi_i\right.\right.$$
$$\left.+ \langle M_{zi}^2\rangle_\infty\left[\sum_{k\neq i}\langle E_k\rangle_\infty\xi_k\right]\right]$$
$$\left. + 2J_{ij}\xi_i\xi_j\langle M_{zi}S_{zj}\rangle_\infty^2\right\} ,$$

where $E_i = \lambda L_i S_i + H_{cfi}$ is the single-ion crystal-field and spin-orbit operator, and $M_{zi} = L_{zi} + gS_{zi}$ is the single-ion

magnetic moment operator. It follows from (10) and (9) that

$$\chi = (\mu_B^2/k_B TV)$$
$$\times\sum_{i,j}\{\delta_{ij}[\langle M_{zi}^2\rangle_\infty + \beta(\langle M_{zi}^2\rangle_\infty\langle E_i\rangle_\infty - \langle M_{zi}^2 E_i\rangle_\infty)\xi_i]$$
$$+ 2\beta J_{ij}\xi_i\xi_j\langle M_{zi}S_{zi}\rangle_\infty^2\} . \tag{11}$$

Performing an averaging over configurations yields

$$\chi = (\mu_B^2/k_B TV)xN\left[\langle M_z^2\rangle_\infty\right.$$
$$+ \beta(\langle M_z^2\rangle_\infty\langle E\rangle_\infty - \langle M_z^2 E\rangle_\infty)$$
$$\left. + 2\beta\langle M_z S_z\rangle_\infty^2 x\sum_p J_p z_p\right] , \tag{12}$$

where z_p is the number of cations in the pth coordination sphere and we inserted a random arrangement of magnetic ions, yielding

$$\overline{\xi_i\xi_j} = \begin{cases}\overline{\xi_i^2} = \overline{\xi_i} = x & \text{for } i = j, \\ \overline{\xi_i}\,\overline{\xi_j} = x^2 & \text{for } i\neq j.\end{cases} \tag{13}$$

Equation (12) can be expressed as follows:

$$\chi = \frac{\mu_B^2}{k_B T V} x N \langle M_z^2 \rangle_\infty \left[1 + \frac{\langle M_z^2 \rangle_\infty \langle E \rangle_\infty - \langle M_z^2 E \rangle_\infty}{\langle M_z^2 \rangle_\infty} \right.$$

$$\left. + \frac{2 \langle M_z S_z \rangle_\infty^2 x}{\langle M_z^2 \rangle_\infty} \sum_p J_p z_p \right] \qquad (14)$$

and for high temperatures can be expanded as a Curie-Weiss law $C(x)/[T - \Theta(x)]$ with Curie constant

$$C(x) = \frac{\mu_B^2 N \langle M_z^2 \rangle_\infty}{k_B V} x = C_0 x \qquad (15)$$

and a Curie-Weiss temperature

$$\Theta(x) = \frac{\langle M_z^2 \rangle_\infty \langle E \rangle_\infty - \langle M_z^2 E \rangle_\infty}{\langle M_z^2 \rangle k_B}$$

$$+ \frac{2 \langle M_z S_z \rangle_\infty^2}{\langle M_z^2 \rangle_\infty} x \sum_p z_p (J_p / k_B)$$

$$= A + \Theta_0 x , \qquad (16)$$

which reduces to a standard HTE (Ref. 9) for $L = 0$. If the distribution of magnetic ions is truly random [Eq. (10)], then both the Curie constant and the Curie-Weiss temperature are a linear function of temperature. However—in distinction from the spin-only case[9]—the Curie-Weiss temperature may be nonzero even for $x \to 0$ (noninteracting ions). The values of averages in (12) and (13) can be evaluated for a particular ion in a particular crystal field if the ion eigenfunctions are known. We will return to this point for Fe^{2+} in the discussion.

III. EXPERIMENTAL RESULTS

We have measured the magnetic susceptibility per unit mass X_m [related to Eq. (2) by $X_m = X_v / \rho$, ρ being density of the crystal] of $Zn_{1-x}Fe_x Se$, with $x = 0.022 \pm 0.002$, 0.049 ± 0.003, 0.057 ± 0.003, and 0.072 ± 0.005 as checked by microprobe analysis. X_m was studied in the temperature range 2–300 K, in two stages. Below 77 K we used a standard ac mutual inductance method, whereas above 77 K the Faraday method was applied. In the latter case the magnetization M_m of the samples was measured, which was found to depend linearly on the magnetic field up to 1 T. The susceptibility was obtained from the relation $X = M_m / B$. All the data were corrected for the diamagnetic susceptibility of ZnSe $(X_d = -0.32 \times 10^{-6}$ emu/g).[10]

The results are shown in Fig. 1, where the inverse susceptibility is plotted versus temperature. For clarity of the figure the low-temperature part (below 77 K) is shown only for $x = 0.022$ and 0.072. At high temperatures all the samples reveal a typical Curie-Weiss behavior with a negative Curie-Weiss temperature. These temperatures $\Theta(x)$, as determined from extrapolation of X_m^{-1} versus T, are tabulated in Table I. Below ~ 70 K a well-pronounced downward bending of X_m^{-1} can be observed. This bending—as distinct from Mn-based materials[11]—changes its slope as $T \to 0$, although even at the lowest measured temperatures no temperature-independent X_m^{-1} is observed (i.e., typical Van Vleck–type behavior is ab-
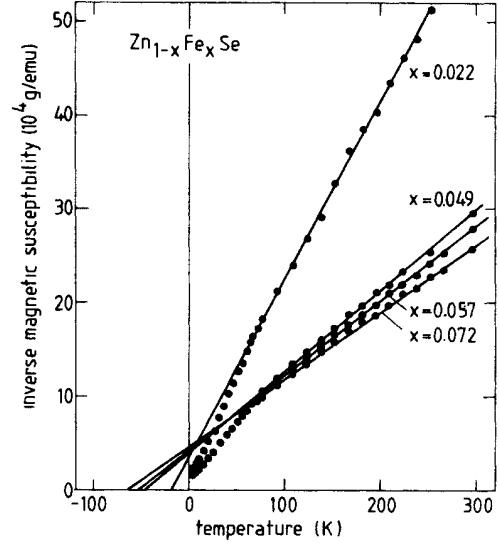

FIG. 1. Inverse magnetic susceptibility of $Zn_{1-x}Fe_x Se$ as a function of temperature. Straight lines show Curie-Weiss law with parameters according to Table I.

sent). This is in agreement with our previous results[12] and is probably due to paramagnetic impurities present in the source iron material used for crystal growing.[12] The deviation from Van Vleck–type behavior in the low-temperature range seems to be proportional to the iron content, which corroborates such an assumption.

IV. DISCUSSION

A. High-temperature susceptibility

The behavior of the experimental data presented above as $X_m(T)$ in the range of high temperatures may be compared with the result of HTE as derived in Sec. I. In Fig. 2, $\Theta(x)$ and $C(x)$ are shown as functions of x. Both quantities are proportional with concentration x, in agreement with Eqs. (15) and (16). Moreover, the Curie-Weiss temperature tends to zero (within experimental accuracy) as $x \to 0$ suggesting that parameter A from Eq. (16) vanishes in our case. The detailed fit of the data presented in Fig. 2 by Eqs. (15) and (16) yields the following values: $C_0 = (212 \pm 40) \times 10^{-4}$ emu K/g ($\langle M_z^2 \rangle = 7.6$), $A = +0.85 \pm 2.7$ K, and $\Theta_0 = -920 \pm 54$ K. A negative value of Θ_0 indicates a negative d-d exchange integral J, i.e., antiferromagnetic coupling.

In order to obtain more detailed information from the evaluated parameters, one has to calculate averages $\langle \cdots \rangle_\infty$ present in Eqs. (15) and (16). We performed these calculations, using the Fe^{2+} single-ion wave functions as proposed by Slack et al.[4] with the parameters obtained[5] for ZnSe:Fe, crystal-field splitting $10Dq = 2930$ cm^{-1} and spin-orbit coupling $\lambda = -85$ cm^{-1}.

The summation in the average $\langle \cdots \rangle_\infty$ is performed over all states originating from the ground ^5E term. The other states originating from the first-excited term (^5T) can be omitted since the separation from the ground state is 4000 K (Fig. 3). The regime we are considering is therefore a high-temperature regime relative to the (split)
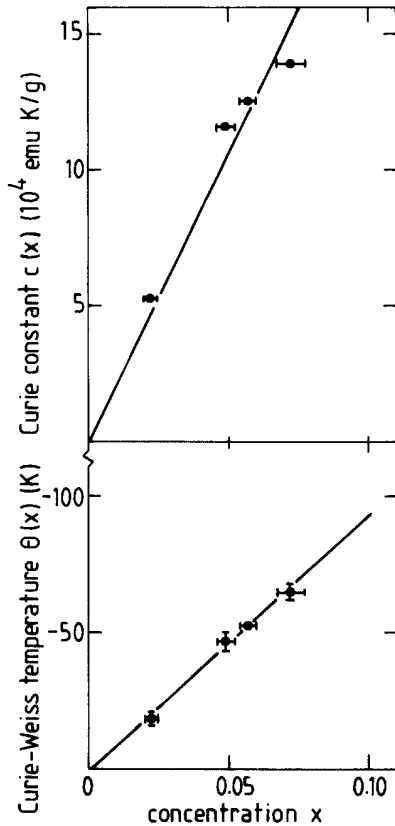
FIG. 2. Concentration dependence of the Curie constant $C(x)$ and the Curie-Weiss temperature $\Theta(x)$ of $Zn_{1-x}Fe_xSe$. Solid lines represent $C_0 = 212 \times 10^4$ emu K/g and $\Theta(x) = +(0.85-920 \text{ K})x$.
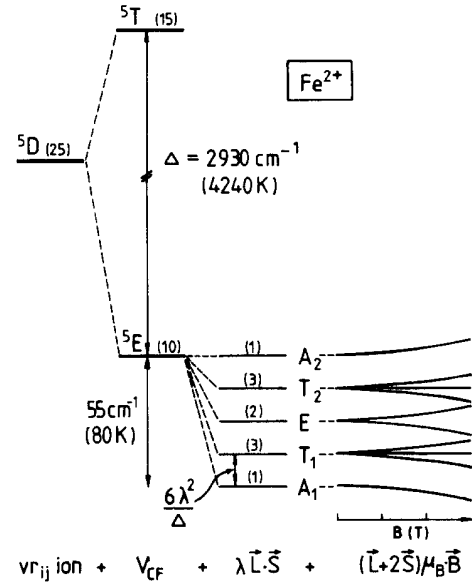

FIG. 3. Energy-level diagram for an isolated Fe^{2+} ion. Effects of crystal field, spin-orbit interaction, and magnetic field are shown (not to scale).

^5E ground state and, at the same time, a low-temperature regime in respect to crystal-field splitting. We obtained the following values:

$$\langle M_z^2 \rangle_\infty = 10.89 \; ,$$

$$\langle E \rangle_\infty = -11.71\lambda^2/10Dq$$

(is the mean energy of the ^5E term)   (17)

$$\langle M_z^2 E \rangle_\infty = -130.76\lambda^2/10Dq \; ,$$

$$\langle M_z S_z \rangle_\infty = 4.22 \; .$$

We first notice that the calculated $\langle M_z^2 \rangle_\infty$ value is larger than that obtained from experimental Curie constant. Such an effect is not unique for $Zn_{1-x}Fe_xSe$ and

was observed previously also in Mn^{2+} based SMSC's.[13] Although this reduction can be attributed to some physical mechanisms[13,9] it may also be due to the simplicity of our model. In particular, one should remember that we assumed infinite temperature deriving Eqs. (12)–(16). Although the experimental Curie-Weiss temperatures are smaller than our temperature range, they are not negligible even compared to the highest temperatures at which X_m was obtained (cf. Table I). One can therefore expect that spins in different lattice sites are not completely independent, which means that the average $\langle M_{zi}M_{zj} \rangle_\infty$, which defines the Curie constant, is smaller than $\langle M_{zi}^2 \rangle_\infty$. This effect should increase with increasing concentration of magnetic ions. Inspection of Table I seems to reveal such a tendency. The question now arises whether this mismatch also may affect the reliability of the values which can be obtained for J_p and A, in which averages like $\langle M_z^2 \rangle_\infty$ also play a role [see Eqs. (15) and (16)]. One has to recall, however, that J_p and A (through Θ_0) are given by ratios like $\langle M_z^2 E \rangle_\infty / \langle M_z^2 \rangle_\infty$ or $\langle M_z S_z \rangle_\infty^2 / \langle M_z^2 \rangle_\infty$. It seems likely that these ratios, since they contain similar expectation values in both nominator and denominator, are less sensitive for these deviations. This is demonstrated by the fact that parame-

TABLE I. Relevant parameters for $Zn_{1-x}Fe_xSe$ and $Cd_{1-x}Fe_xSe$.

Material	x	C (10^4 emu K/g)	Θ (K)	$\langle M_z^2 \rangle$
$Zn_{1-x}Fe_xSe$	0.022	5.25±0.1	−18.5±2.1	9.2
	0.049	11.60±0.1	−46.5±3.5	9.1
	0.057	12.53±0.1	−52.2±1.3	8.4
	0.072	13.93±0.2	−64.5±2.5	7.4
				$g^2 S_{eff}(S_{eff}+1)/3$
$Cd_{1-x}Fe_xSe$	0.05		−36±6	10.6 (Ref. 8)
	0.15		−102±8	10.1 (Ref. 8)

ter A resulting from (16) ($A = +1.07$ K) is indeed very small, in agreement with the experimental observation ($A = +0.85 \pm 2.7$ K). Combining now the experimental Curie-Weiss temperature Θ_0 with (16) and (17), one is able to determine the d-d exchange constant:

$$\sum_p z_p J_p / k_B = -281 \pm 17 \text{ K} , \qquad (18)$$

which gives the upper estimate of the nearest-neighbor interaction $|J_{NN}/k_B| < 23.5$ K. Assuming the same distance dependence of the interaction as observed in $Zn_{1-x}Mn_xSe$ and related compounds,[14] $J_p = J_{NN}/R_p^{6.8}$, where R_p is the radius of pth coordination sphere (in units of R_{NN}), we find that

$$\sum_p z_p J_p / k_B = (z_{NN} J_{NN}/k_B) 1.09 ,$$

which results in $J_{NN}/k_B = -22 \pm 1$ K. This is a much higher value than was found[15] for $Zn_{1-x}Mn_xSe$ ($J_{NN}/k_B = -12.6$ K).

A similar analysis can be performed for the other Fe-based SMSC's, in particular for $Cd_{1-x}Fe_xSe$, for which susceptibility data are available[8] (see Table I). $Cd_{1-x}Fe_xSe$ crystallizes in hcp structure, which results in lowering of the cubic symmetry, and, consequently, the threefold degeneracy of T_1 and T_2 levels is removed. In order to account for this effect, we completed single-ion crystal-field Hamiltonian H_{CF} by the trigonal distortion term $Cp(z^2 - 1/3r^2)$. Assuming[5] for $Cd_{1-x}Fe_xSe = -81$ cm^{-1}, $10Dq = 2680$ cm^{-1}, and[16] $Cp = 30$ cm^{-1}, we obtain

$$\langle M_z^2 \rangle_\infty = 10.95$$

[to be compared with the experimental value $g^2 S_{eff}(S_{eff} + 1)/3$ from Table I],

$$\langle E \rangle_\infty = -11.71\lambda^2/10Dq ,$$

$$\langle M_z^2 E \rangle_\infty = -132.48\lambda^2/10Dq , \qquad (19)$$

$$\langle M_z S_z \rangle_\infty = 4.24 .$$

In this case the calculated value for $\langle M_z^2 \rangle_\infty$ is in perfect agreement with experimental data (cf. Table I). However, we believe this agreement may be rather accidental especially for $x = 0.15$, for which the reported Curie-Weiss temperature is -102 K, since the experimental temperature range from which the data were obtained cannot be considered as the high-temperature limit.

It follows in this case from (19) that $A = 1.4$ K, which results in $\sum_p z_p J_p / k_B = -228 \pm 37$ K. Assuming again the relation $J_p = J_{NN}/R_p^{6.8}$, one obtains $J_{NN}/k_B = -17.8 \pm 3$ K for $Cd_{1-x}Fe_xSe$, which is also appreciably higher than reported[9] for $Cd_{1-x}Mn_xSe$ (-10.6 K).

In a previous analysis the value for the integral in $Cd_{1-x}Fe_xSe$ was reported[8] to be $J_{NN}/k_B = -11$ K. The difference between our result and this value is a direct consequence of using the *spin-only* high-temperature-series expansion in the latter case, where it is not applicable. The smaller value for J_{NN} obtained by this procedure may be understood by the following reasoning. While using the spin-only model,[9,8] one usually rewrites

Eq. (15) in the form

$$C(x) = (\mu_B g)^2 S_{eff}(S_{eff} + 1) N x / 3 k_B V , \qquad (20)$$

where S_{eff} is the so-called effective spin and is derived from the experimental value $C(x)$. Thus the factor $g^2 S_{eff}(S_{eff} + 1)/3$ plays the same role as $\langle M_z^2 \rangle_\infty$, and $g S_{eff}$ can be regarded as an effective magnetic moment. This magnetic moment, furthermore, is used to determine the exchange integrals [from relation (16) substituting S_{eff} for S and $L = 0$]. Roughly speaking, one implicitly assumes in such a procedure that the magnetic ions interact via the total magnetic momenta and not by the spins only [cf. Eq. (1)]. In that respect the lower value of J produced by the spin-only model can be understood: Since the susceptibility is a response of the magnetic moments to the experiencing magnetic field [Eq. (9)], a weaker interaction is needed between magnetic moments (composed of both spin and orbital momenta) than between spins only to obtain the same effect on the susceptibility (Curie-Weiss temperature).

It should be stressed, however, that although we prefer ion-ion interaction via spin momenta instead of full magnetic momenta, the Heisenberg Hamiltonian used in (1) is one of the simplest possibilities to describe the magnetic interactions. Further experiments are needed to confirm our assumption or to establish a proper Hamiltonian.

B. Low-temperature susceptibility

Having determined the d-d exchange integral, one can describe the high-temperature as well as the low-temperature susceptibility by applying the method proposed recently by us for iron-type SMSC's.[7] This method is based on solving numerically the Fe-Fe pair eigenproblem [i.e., Hamiltonian (1) with $i,j = 1,2$], which allows one to calculate the Fe-Fe-pair partition function and the susceptibility. The susceptibility of the whole crystal is calculated in extended nearest-neighbor pair approximation (ENNPA),[13,14,17] which is an approximative calculation method, particularly useful for random, diluted alloys with long-range interaction. This method is based on the assumption that the partition function of the system can be factorized into contributions of pairs of ions. In ENNPA each ion is considered to be coupled by an exchange interaction J_L only to its nearest *magnetic* neighbor, which may be located anywhere at the distance R_L from a reference site. The statistical weight $[P_L(x)]$ of pair configurations with various R_L is assumed to be determined by the random distribution of the ions. Knowing the susceptibility of an Fe pair, coupled by an exchange integral J_L, one can evaluate the susceptibility of the whole crystal as

$$X = \sum_L X_L(J_L) P_L(x)/2 ,$$

where summation is performed until 98% of the pairs are included. For more details of the calculations refer to Ref. 7.

Results of our calculations for $Zn_{1-x}Fe_xSe$ ($x = 0.022$ and 0.072) are shown in Fig. 4. Fairly good agreement between the experimental and calculated susceptibility is
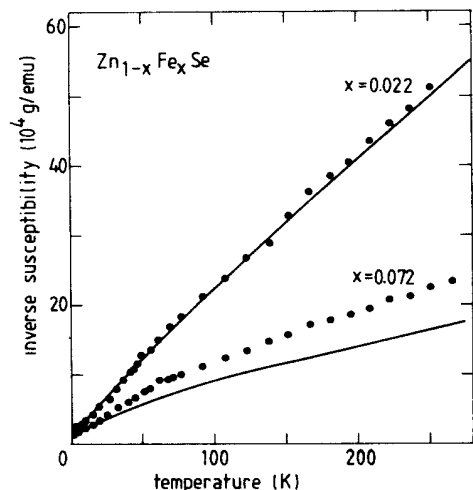
FIG. 4. Inverse magnetic susceptibility of $Zn_{1-x}Fe_xSe$ as a function of temperature. Solid lines represent ENNPA calculations with the parameters $J_{NN} = -22$ K, $J_p = J_{NN}/R_p^{6.8}$, $10Dq = 2930$ cm^{-1}, and $\lambda = -85$ cm^{-1}.

observed for $x = 0.022$, whereas a substantial discrepancy exists for $x = 0.072$. We should stress, however, that for $x = 0.072$, the dilute limit as considered in ENNPA may not be approached. In fact, in all the cases when ENNPA was applied for SMSC's, a reasonable description of the experimental data was obtained only for low

concentrations $(x < 0.05)$.[13,14] We therefore find the situation presented in Fig. 4 quite satisfactory.

V. CONCLUSIONS

We generalized the high-temperature expansion of the magnetic susceptibility of SMSC's for the case of magnetic ions with nonvanishing orbital momenta. We obtained a Curie-Weiss law with Curie constant and Curie-Weiss temperature linearly dependent on the concentration of the magnetic ions. This result is in agreement with high-temperature experimental data for $Zn_{1-x}Fe_xSe$ and $Cd_{1-x}Fe_xSe$. From the Curie-Weiss temperature we estimated the exchange integrals $J_{NN}/k_B = -22$ K for $Zn_{1-x}Fe_xSe$ and $J_{NN}/k_B = -17.8$ K for $Cd_{1-x}Fe_xSe$, which are both systematically higher than those observed in the corresponding Mn compounds. Using these exchange constants, we were able to fit susceptibility in the whole temperature range by applying the ENNPA.

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