Fe-based semimagnetic semiconductors with two anions

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$(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$ crystals have been studied both theoretically and experimentally. In such a system, a part of Fe^{2+} ions are located in crystal environments of a lowered symmetry. The energy level structure of these ions is substantially modified with respect to that of the Fe^{2+} ion in one-anion (ternary) crystal. Regarding magnetic properties, the most essential modification occurs when an Fe^{2+} ion is surrounded by three atoms of Te and one Se atom. Then, a doublet becomes a ground state of the magnetic ion, while, in the case of a ternary crystal, the ground state of an Fe^{2+} ion is always a nonmagnetic singlet. In consequence, for two-anion systems, we observe a Curie-like paramagnetism instead of an otherwise revealed temperature independent ($T \leqslant 10$ K) Van Vleck paramagnetism. Although, in the present work, we are concerned mostly with $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$, a similar behavior is also observed for various crystals based on zinc and mercury. The results of our photoconductivity measurements indicate that the ground energetic state of an Fe^{2+} ion can take several localizations in the band structure of the matrix crystal. A specific position depends on a configuration of nearest neighbors of an Fe^{2+} ion, i.e., if it is surrounded by four Te, or three Te and one Se, etc. Concluding, we show that doped with Fe quaternary II-VI semimagnetic semiconductors demonstrate magnetic and optical properties essentially different from that of Fe doped ternary II-VI semimagnetic semiconductors.

I. INTRODUCTION

The majority of investigations devoted to semimagnetic semiconductors (SMSC) (also referred to as diluted magnetic semiconductors) were carried out on II-VI or IV-VI semiconducting compounds containing transition metal ions (e.g., Mn, Fe, or Co) and thus forming alloys like $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$, $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Te}$, $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Se}$, etc. The observed physical (especially magnetic) properties of II-VI ternary SMSC depend, to a great extent, on the substitutional magnetic ion type and far less on the semiconductor host. This is due to the fact that, in these compounds, the electronic level scheme of the substitutional magnetic ion only slightly depends on the host material.

We present a way to change some physical properties of the chosen paramagnetic ion, i.e., Fe, by using the two-anion alloy $\mathrm{CdTe}_{1-y}\mathrm{Se}_y$ as the host material. The presence of two different types of anions in the nearest surrounding of Fe ion changes the symmetry of the ion's environment and, in consequence, modifies the energy of its ground and excited states. These changes result, in turn, in modifications of magnetic and semiconductor properties of the crystal as a whole.

In our previous papers,[1,2] we have described preliminary experimental results obtained for quaternary $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$ crystals. The present work is a more detailed study, both experimental and theoretical, of magnetic and optical properties of the same compound.

The paper is organized as follows. A brief review of selected physical properties of II-VI ternary SMSC containing Fe ions (especially $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Te}$) is given in Sec. II. Section III is devoted to our technological procedures, methods of sample preparation, and determination of the samples composition. In Sec. IV we describe the theoretical model, taking into account the crystal field of a proper symmetry, spin-orbit, and Zeeman interactions. We recall also preliminary experimental data obtained for two-anion SMSC alloys, which differ considerably from those known for one-anion (ternary) systems. The results of magnetization, Faraday rotation, and exciton magnetospectroscopy experiments are also presented in Sec. IV and theoretical fitting of the data and exchange parameters are given. In Sec. V, we discuss the experimental results, which indicate that in two-anion compounds Fe ions located in different environments introduce different energy levels into the energy gap. Conclusions are given in Sec. VI.

II. PHYSICAL PROPERTIES OF SMSC CONTAINING Fe IONS

The electronic structure of an $\mathrm{Fe}^{2+}(3d^6)$ ion in CdTe:Fe has been investigated by Low and Weger[3] and Slack and co-workers.[4] According to a Hund's rule, the ground state of an $\mathrm{Fe}^{2+}(3d^6)$ free ion is the ^5D multiplet with the orbital momentum $L=2$ and the spin $S=2$. The degeneracy of the ground level is then $(2L+1)(2S+1)=25$. This manifold is split in a tetrahedral crystal-field potential into the orbital ^5E doublet and the $^5T_2$ triplet. Under the influence of the spin-orbit interaction, the lower term ^5E splits into five levels, which, in the order of the increasing energy, are Γ_1,

Γ_4, Γ_3, Γ_5, and Γ_2 (or A_1, T_1, E, T_2, and A_2, respectively) in standard notations.

The ground state Γ_1 is a magnetically inactive singlet, hence temperature-independent Van Vleck paramagnetism. Actually, the corresponding saturation of the magnetic susceptibility at low temperatures ($T \leqslant 10$ K) was observed for various cadmium,[5,6] mercury,[6] and zinc compounds.[5] Magnetization measurements performed by Testelin *et al.*,[7] in magnetic field, B, up to 20 T and free exciton splitting (ΔE_{exc}) investigations carried out by Testelin *et al.*,[8] in $B \leqslant 7$ T provided a further evidence for the Van Vleck nature of paramagnetism of $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Te}$ crystals.[8] At magnetic fields $B \leqslant 5$ T, both M and ΔE_{exc} vary linearly as a function of B. In this field range no saturation effects appear, in contrast to the behavior observed for, e.g., Mn- or Co-based compounds.[9,10] Up to $B \leqslant 5$ T, the magnetic susceptibility $\chi = M/B$ does not depend on the magnetic field orientation, with respect to the main crystal axes. From combining $M(B)$ and $\Delta E_{\mathrm{exc}}(B)$ data acquired for the very same samples, it is possible to yield the exchange integrals for the conduction and valence bands: $N_0\alpha = 0.3 \pm 0.04$ eV and $N_0\beta = -1.27 \pm 0.08$ eV, respectively.[8]

III. SAMPLE PREPARATION AND CHARACTERIZATION

We studied the following compounds:

$$(\mathrm{Zn}_{1-x}\mathrm{Fe}_x)(\mathrm{Se}_{1-y}\mathrm{S}_y), \quad x \leqslant 0.02, \quad y \leqslant 0.06;$$

$$(\mathrm{Zn}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y), \quad x = 0.02, \quad y \leqslant 0.06;$$

$$(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y), \quad x \leqslant 0.02, \quad y \leqslant 0.20;$$

and

$$(\mathrm{Hg}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y), \quad x \leqslant 0.003, \quad y \leqslant 0.15.$$

The crystals were grown by the modified Bridgman method. In the investigated composition range, the crystals are of the zinc-blende cubic structure, which was checked by x-ray diffraction.

Samples for optical, magneto-optical, and magnetic measurements were cut from the same ingots to provide their compositions close to each other. Far infrared (FIR) absorption and Faraday rotation studies were performed on monocrystalline plates of about 1 mm thick. Since in a free exciton energy region an absorption coefficient reaches values of $10^5\ \mathrm{cm}^{-1}$, to investigate excitonic absorption, we had to use samples of a thickness less than 1 μm, prepared by etching in a 1% solution of bromine in methanol. All the magneto-optical experiments were carried out in Faraday configuration for circular light polarization, in magnetic fields up to $B = 6$ T, at $T = 1.8$ K.

The composition of our samples was determined first by an electron microprobe analysis, then by an energy dispersive x-ray fluorescence (EDXRF) method using TRACOR-5000 spectrometer, and finally by optical measurements of a free exciton energy. Figure 1 presents the dependence of the exciton absorption peak energy measured at $T = 1.8$ K on Fe and Se content, x and y, respectively, in the CdTe host (the energy gap E_g is about 10 meV greater than the exciton energy). For $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Te}$ system, $E_{\mathrm{exc}}(x)$ is described by a linear relation[8] (upper line in Fig. 1):

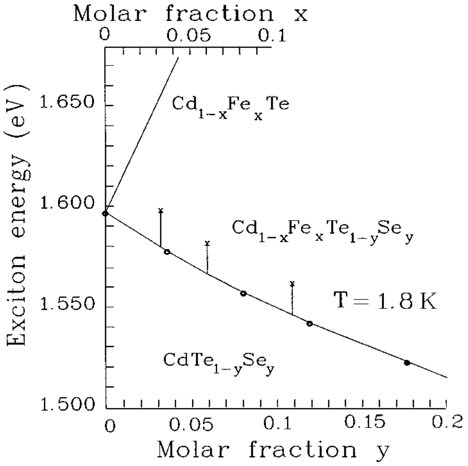

FIG. 1. The free exciton energy as a function of the alloy composition. The upper scale corresponds to $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Te}$, the lower one to $\mathrm{CdTe}_{1-y}\mathrm{Se}_y$ and $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$.

$$E_{\mathrm{exc}}(x) = (1.594 + 1.78x)\ \mathrm{eV}. \tag{1}$$

In the two-anion ternary compound $\mathrm{CdTe}_{1-y}\mathrm{Se}_y$, for $y \leqslant 0.20$, the energy gap (and the exciton energy) at $T = 1.8$ K decreases when y increases. Our data for ternary $\mathrm{CdTe}_{1-y}\mathrm{Se}_y$ samples are marked by points in Fig. 1. An analogous dependence $E_g(y)$ was observed at room temperature by Chehab and Woolley[11] and Feng *et al.*[12] The data obtained for three quaternary samples of $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$ crystals are marked by crosses in Fig. 1. For both $\mathrm{CdTe}_{1-y}\mathrm{Se}_y$ and $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$ samples, the Se content was determined with an uncertainty $\Delta y = \pm 0.002$, by the EDXRF technique. The Fe content in $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$ crystals was determined from the dependence of the exciton energy on x, see Eq. (1). The procedure took into account both the decrease of the energy gap as y increases, and its increase when x increases [see Eq. (1)]. Using this method, we evaluated the Fe molar fraction, $x = 0.009 \pm 0.0005$, in three $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$ samples. The Fe content in our quaternary crystals was also checked by the EDXRF method.

IV. SUSCEPTIBILITY, MAGNETIZATION AND FARADAY ROTATION IN TWO-ANION SYSTEM

Assuming a random distribution of anions in the quaternary $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$ crystals, we can calculate the probability b of finding a given $\mathrm{Fe}^{2+}(3d^6)$ ion in a tetrahedral surrounding of $N = 4$ nearest neighbors, consisting of m Se atoms (and $N - m$ Te atoms):

$$b = \binom{N}{m} y^m (1-y)^{N-m}, \quad 0 \leqslant y \leqslant 1. \tag{2}$$

After Pauling,[13] and van Vechten and Phillips,[14] the length of bond d_{ab} between two types of atoms is equal to the sum of the tetrahedral radii of the individual atoms $d_{ab} = l_a + l_b$. For the II-VI compounds of interest here, l_a and l_b are known from Ref. 9, and are reported in Table I. Notice that the substitution of Te by Se in

TABLE I. The tetrahedral radii of chosen group II and VI elements (after Ref. 9).

	l_a (Å)		l_b (Å)
Cd	1.405	Te	1.405
Hg	1.402	Se	1.225
Mn	1.320	S	1.127
Fe	1.260		
Zn	1.225		

$(Cd_{1-x}Fe_x)(Te_{1-y}Se_y)$ introduces a big local trigonal distortion. We expect that such a distortion modifies the energy of ground and excited states of an $Fe^{2+}(3d^6)$ ion.

A full calculation of the electronic structure of an $Fe^{2+}(3d^6)$ ion in a cation substitutional position has been performed by Mahoney *et al.*[5] for both zinc-blende and wurtzite structures. More details have been recently published by Mauger *et al.*,[15] for the $Cd_{1-x}Fe_xSe$ case. In the latter paper, the electronic structure of an Fe^{2+} ion diluted in the semiconductor matrix has been investigated within the manifold of 25 wave functions corresponding to $(3d^6)^5D$ free ion ground state configuration.

The presence of one or more foreign anions may be described by the additional crystal field potential (ACFP). In general, due to symmetry arguments,[15] this potential for an Fe^{2+} ion in the considered crystal structure may be described by two independent parameters ν and ν'. For one foreign anion, as was shown in Ref. 15, it is possible to choose these parameters in such a way that the electronic structure of an Fe^{2+} ion, in the first approximation, depends only on one of them. This is the parameter ν', the definition of which is given in Ref. 15. The dependence on ν is very weak, thus, in practical calculations, the ACFP due to a foreign atom is described by one fitting parameter. Next, for configurations with two or more foreign anions, we make the approximation that the ACFP felt by an Fe^{2+} ion is the sum of single foreign anion contributions. With such an assumption, every neighborhood configuration is described by the number of Se atoms and one parameter ν' corresponding to the difference between Se and Te atoms. The calculation procedure is standard. For every configuration we write Hamiltonian, which, in the basis of spherical harmonics, is the 25×25 matrix. Using a numerical procedure, we calculate the eigenvalues and the corresponding eigenvectors.

We limit our further considerations to the following three cases: $m=0$, $m=1$, and $m=2$. Configurations with three and four Se anions are very rare for considered compositions, thus their contribution is negligible. In our analysis, we used formulas given in Ref. 15. We assumed the required crystal-field splitting and spin-orbit parameter values equal to those obtained for pure CdTe matrix, $10Dq=-2480\ \mathrm{cm}^{-1}$ (after Ref. 4), $\lambda=-100\ \mathrm{cm}^{-1}$ (after Ref. 16). The energy level structure of an Fe^{2+} ion was calculated as a function of the distortion parameter, ν'. Figure 2(a) presents the results of our calculations for the $m=1$ configuration and Fig. 2(b), for the case $m=2$.

$\nu'=0$ obviously corresponds to the case $m=0$. Note that for ν' lower than $-175\ \mathrm{cm}^{-1}$ for $m=1$ [Fig. 2(a)], a magnetically active doublet, Γ_3, originating from split Γ_4 level, becomes the ground state of an Fe^{2+} ion. This fact is essential for the interpretation of the magnetic susceptibility behavior observed in $(Cd_{1-x}Fe_x)(Te_{1-y}Se_y)$ crystal.

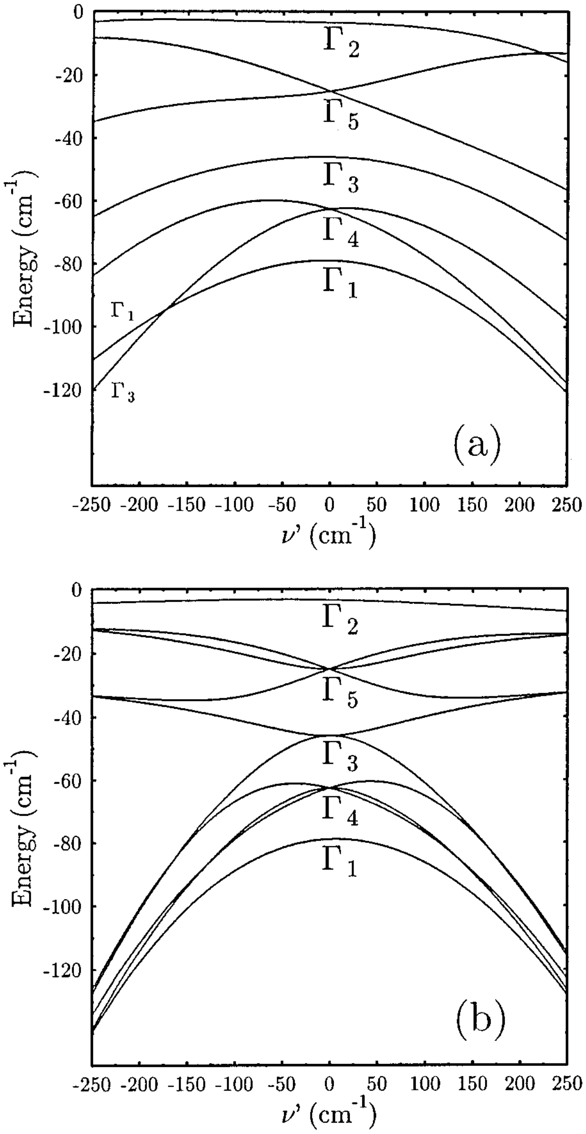

FIG. 2. The lowest set of energy levels of an Fe^{2+} ion (a) in C_{3v} symmetry, case $m=1$; and (b) in C_{2v} symmetry, case $m=2$, as a function of the distortion parameter ν'. It is worth noticing that, in the case $m=2$, the first excited level, Γ_4, is split into three distinct levels.

The low-field magnetic susceptibility, as a function of temperature, is presented in Fig. 3 (about the methods applied for susceptibility measurements see text below). In $Cd_{1-x}Fe_xTe$ and $Cd_{1-x}Fe_xSe$, Van Vleck paramagnetism is observed at low temperatures. The differences in the values of the magnetic susceptibility in these two materials are due to their different crystallographic structures and material parameters.[5] In the case of $(Cd_{1-x}Fe_x)(Te_{1-y}Se_y)$, for a small Se mole fraction $(y=0.017)$, the susceptibility resembles that found in $Cd_{1-x}Fe_xTe$. However, in a sample with $y=0.052$, in which a significant amount of Fe ions have three Te atoms and one Se atom as the nearest neighbors, χ behaves in a different way. Instead of Van Vleck, the Curie-like behavior was observed down to 50 mK. This may be explained in terms of the modification of an Fe^{2+}

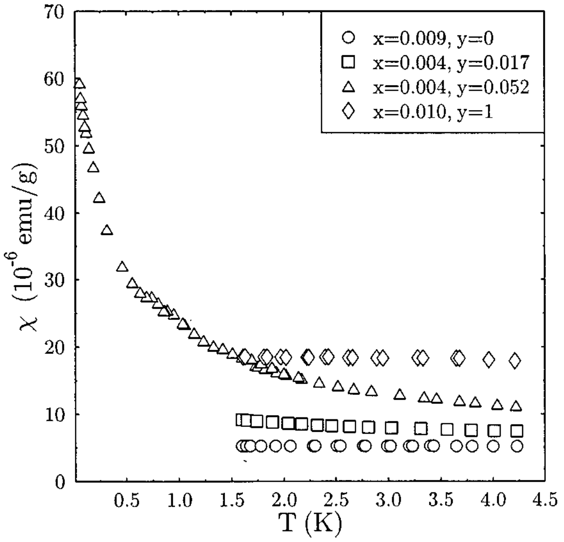

FIG. 3. Magnetic susceptibility of $(Cd_{1-x}Fe_x)(Te_{1-y}Se_y)$, as a function of temperature—experimental data.

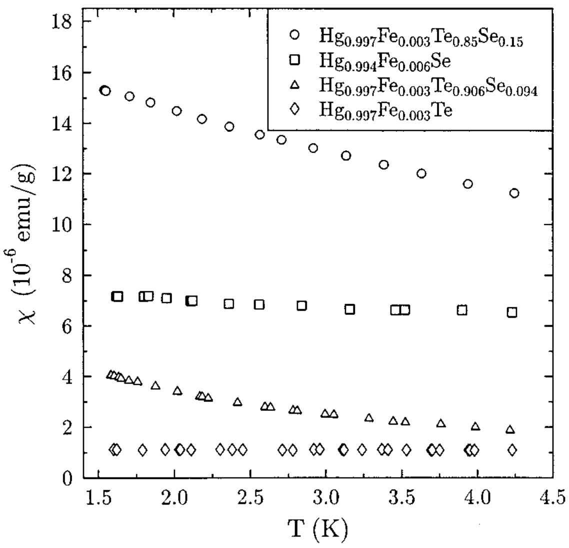

FIG. 5. Magnetic susceptibility of $Hg_{1-x}Fe_xTe_{1-y}Se_y$ at liquid helium temperatures.

ion energy level scheme (due to distortion) in such a way that the magnetically active state becomes the ground state (in the $m=1$ configuration only). Similar results were also observed for other two-anion compounds: $(Zn_{1-x}Fe_x)(Se_{1-y}S_y)$, $(Zn_{1-x}Fe_x)(Te_{1-y}Se_y)$, see Fig. 4, and $(Hg_{1-x}Fe_x)(Te_{1-y}Se_y)$, see Fig. 5.

A modification of the electronic structure of an Fe^{2+} ion, due to the changes in its nearest surrounding, should obviously affect the FIR optical properties of the crystals. In $Cd_{1-x}Fe_xTe$, optical transitions between lowest-lying electronic levels originating from an orbital ${}^5E$ doublet occur in the FIR region (see Slack *et al.*[16] and Testelin[17]). Absorption peaks at 18.6, 66, and 74 cm^{-1}, observed only at low temperature, arise from transitions between the ground state, Γ_1, and excited levels. In particular, the lowest energy peak (18.6 cm^{-1}) corresponds to $\Gamma_1 \to \Gamma_4$ internal transition within an Fe^{2+} ion, which in one-anion system is obviously surrounded tetrahedrally by four Te atoms. Figure 6 in Ref. 2 presents absorption spectra observed in the FIR region for $(Cd_{1-x}Fe_x)(Te_{1-y}Se_y)$ samples with $x=0.004$ ($\approx 7\times 10^{19}$ cm^{-3}) and $0.005 \leqslant y \leqslant 0.18$. Lowering of the 18.6 cm^{-1} peak intensity with the growing Se molar fraction, y, is related to the decrease of the number of Fe ions surrounded by four Te atoms according to formula (2). For samples with Se molar fraction exceeding $y \cong 0.1$, no absorption peak was observed in the investigated wavelength range (up to 10 cm^{-1}). This important observation indicates that the energy distance between the ground state and the first excited state remains smaller than 10 cm^{-1} (lower limit in our FIR absorption experiments, see Fig. 6 in Ref. 2). The nearest excited states are separated by about 50–60 cm^{-1}. No additional absorption peaks have been observed in low-temperature FIR investigations in the energy region 10–50 cm^{-1}. Furthermore, the evidence for the significant modification of an Fe^{2+} ion energy level structure in two-anion systems comes from magneto-optical investigations. Exciton energy splittings, ΔE_{exc} (which are proportional to the magnetization) as a function of a magnetic field are compared in Fig. 4, Ref. 1, for two-anion and one-anion systems. One can notice distinct differences in $\Delta E_{exc}(B)$ behavior observed in these two systems.

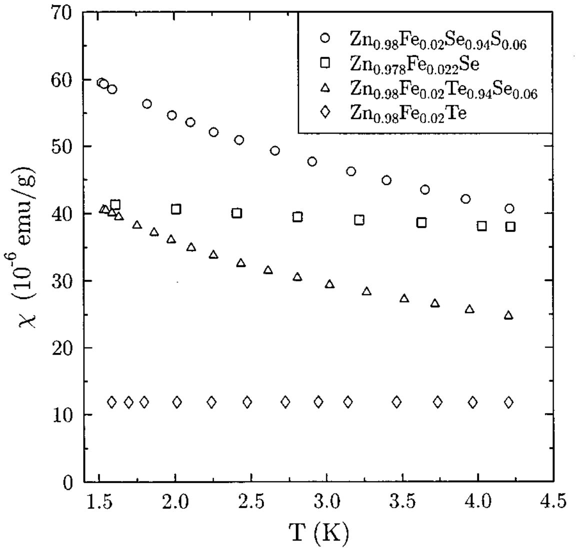

FIG. 4. Magnetic susceptibility of different SMSC containing Zn at liquid helium temperatures.

Taking into account the results of the magnetic susceptibility displayed in Fig. 3, and the optical absorption in the FIR illustrated in Fig. 6 of Ref. 2, we deduce that the value of ν', according to Fig. 2(a), should be contained in the range between -250 cm^{-1} and -175 cm^{-1} to account for both the magnetic and optical properties. For further calculations, we chose the value from the middle of this range, i.e., -215 cm^{-1}.

Let us consider the $m=1$ (3 Te 1 Se) configuration. Se atom in this configuration may be placed in four different positions, which are not equivalent if an external magnetic field is applied to the sample. For each position of the Se atom, the numerical solution of the eigenproblem enables us to calculate the susceptibility and the magnetization. Fig-

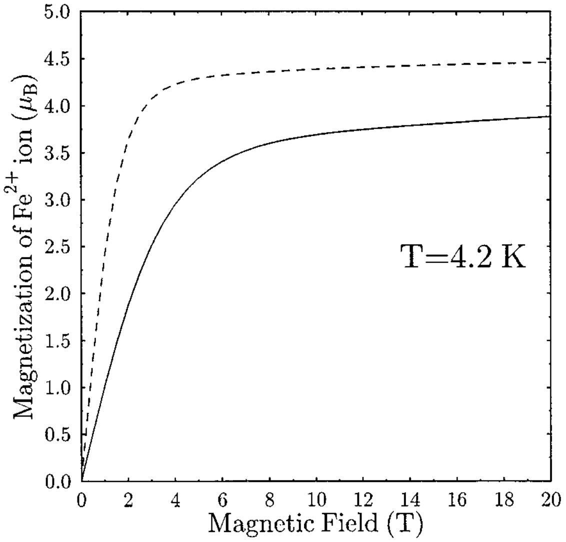

FIG. 6. Theoretical magnetization of an Fe^{2+} ion in C_{3v} symmetry, case $m=1$, obtained for various distortion orientations and for fixed external magnetic field orientation. The detailed description is given in the text.

ure 6 presents calculated magnetizations as a function of magnetic field for the $m=1$ configuration. The direction of the magnetic field is along the [111] direction and the two curves correspond to different positions of the Se atom. The broken curve represents magnetization for the case in which the Se atom is placed along the [111] direction and the continuous line corresponds to one of the other possible positions of selenium (along $[\bar{1}11]$, $[11\bar{1}]$, $[1\bar{1}1]$ directions) that are equivalent for this particular direction of the magnetic field. The difference between these two curves is quite prominent. Now we can imagine a situation in which the Fe-Se bonds are directed mostly along the [111] direction. Although we have no argument in favor of this preferential occupation, it cannot be precluded. If this is the case, we should observe in experiments an anisotropic behavior of the samples due to relevant percentage of $m=1$ configuration [see Eq. (2)]. However, for the investigated range of selenium content, we have never noticed any sign of an anisotropy neither of the magnetic susceptibility nor of the magnetization of the samples, so we conclude that the four positions of the Se atom in $m=1$ configuration are equally probable. Thus, it is quite natural to define the susceptibility $\chi_{m=1}(T)$ for the Fe^{2+} ion as the arithmetic average of the four susceptibilities calculated for these four positions of selenium. In the same way, we define the magnetization $M_{m=1}(H,T)$. The analogous procedure has been applied to compute $\chi_{m=2}(T)$ and $M_{m=2}(H,T)$ (of course the number of nonequivalent positions is six in this case). It turns out that after such an averaging procedure, the quantities defined above practically become isotropic, or more precisely, the calculated anisotropy becomes so small that it is impossible to detect it using our experimental setup. In our fitting procedure for the low-field magnetic susceptibility, we consider the temperature interval 1.5–4.2 K. In this interval, the calculated $\chi_{m=0}(T)$ is constant which reflects the fact that the ground state of Fe^{2+} in the tetrahedral environment is the magnetically inactive singlet and the distance to the first exited level is about 18 cm^{-1}, much larger than the thermal activation energy in this temperature range. As a consequence, we obtain the Van Vleck type of susceptibility.

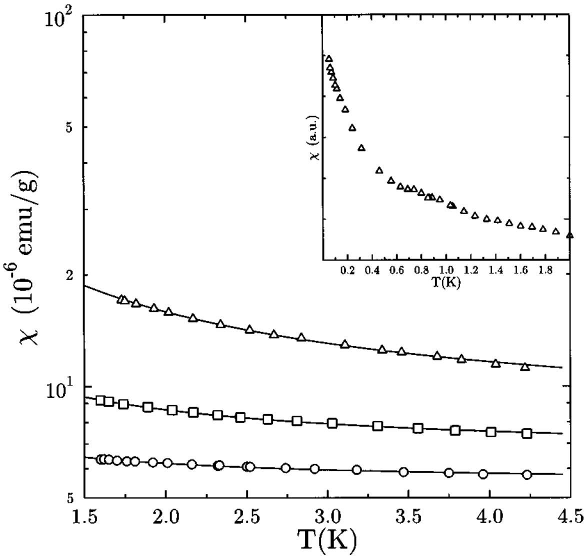

FIG. 7. Magnetic susceptibility of $(Cd_{0.996}Fe_{0.004})(Te_{1-y}Se_y)$ crystals, $y=0.008$ (circles), $y=0.017$ (squares), $y=0.052$ (triangles). Lines represent our theory. The details of calculations are given in the text. The susceptibility data for temperatures in the range 50 mK–2 K are presented in the inset.

For $m=1$, the scheme of the energy levels [Fig. 2(a)] shows that, for $\nu' < -175$ cm^{-1}, the ground state of the ion becomes a doublet. For $\nu' < -180$ cm^{-1}, the distance between this doublet and the first excited level is large in comparison to the thermal energy kT, thus, $\chi_{m=1}(T) \propto T^{-1}$ and this Curie type of behavior is practically ν' independent.

The behavior of $\chi_{m=2}(T)$ is different. For $\nu' < -180$ cm^{-1}, the energy distance between the ground state and the exited levels is comparable with the thermal energy [Fig. 2(b)]. As a consequence, we obtain neither Van Vleck nor Curie type of behavior for the susceptibility, and moreover $\chi_{m=2}(T)$ is strongly ν' dependent. We have not found any simple analytical formula for $\chi_{m=2}(T)$ having transparent physical meaning.

Let us now turn to the experimental results. For low Se content ($y=0.008$, 0.017, 0.052), from statistical distribution [Eq. (2)], we obtain that the probability of $m=2$ configuration is less than 0.015 for $y=0.052$ (for $y=0.008$, 0.017 it is of course much smaller). Therefore, having in mind the above analysis concerning the magnetic susceptibilities in different environments, we postulate the following formula $\chi_{\mathrm{exp}}=(A+B/T)10^{-6}$ emu/g (where the temperature T is in Kelvins) to describe the experimental susceptibility data. It consists only of two contributions, one being of the temperature-independent Van Vleck type and the other one of the Curie type, characteristic of the $m=0$ and $m=1$ configurations, respectively. Indeed, this simple expression fits the experimental data (see Fig. 7). The values of the constants A and B for three different Se quantities are collected in Table II.

The inset in Fig. 7 presents the results of the susceptibility

TABLE II. The values of coefficients A, B describing the experimental data for the susceptibility for different Se compositions, y. The calculated concentration x of Fe atoms and the fraction of $m=1$ configuration are compared to the results of the microprobe analysis $x_{\mu p}$ and to the binomial distribution b_{stat} (see the text for more explanation).

y	A	B	x	b	$x_{\mu p}$	b_{stat}
0.008	5.44	1.50	0.0040	0.025	0.0040	0.031
0.017	6.45	4.398	0.0049	0.060	0.0040	0.065
0.052	7.40	17.2	0.0064	0.178	0.0040	0.177

measurements performed in the dilution refrigerator on one of the samples. The measurements in the interval 1.5–4.2 K provided us with the absolute values of the susceptibility. In this temperature range, we used a standard mutual inductance technique. The absolute values of the susceptibility per unit mass were obtained by comparison with the standard paramagnetic Er_2O_3 sample. In our dilution refrigerator, one measures only changes of the susceptibility relative to the susceptibility at a certain temperature ($T=2$ K). Due to large apparatus noise in the interval 1.5–2.0 K, it is difficult to connect univocally the results obtained from the dilution refrigerator measurements with those obtained for higher temperatures. This is the reason why we are not able to give any absolute value of the susceptibility in the inset and we do not make a comparison between the theory and the experiment in this temperature interval. Despite the fact that the results presented in the inset in Fig. 7 have only qualitative character, they are very important, because they clearly indicate that the susceptibility grows up when the temperature decreases and even for the lowest temperatures we do not observe any sign of deviation from the Curie-like type of behavior. This is an important indication that the ground state of the ion is magnetically active.

Within our model, the theoretical susceptibility is described by the formula $\chi_{\mathrm{theory}}=1.4\times10^{-3}x(1-b)+1.5\times10^{-2}xb/T$ emu/g, where x is the Fe quantity and b is the fraction of Fe^{2+} ions in $m=1$ environment. Having A and B, it is easy to obtain x and b. For comparison, we have also reported in Table II the composition $x_{\mu p}$ known from microprobe analysis and b_{stat} calculated according to the Eq. (2). The agreement between these two sets of data is quite good, which supports the validity of the assumption of the binomial distribution of the Se atoms for the considered range of compositions.

In our previous publications,[1,2] we proposed the concept of the chemical preference. It was introduced because the fitted value of the parameter b differed considerably from the value of b_{stat}. It seemed to us that the Fe and Se atoms ‘‘tried to be’’ the nearest neighbors, thus the number of $m=1$ configurations was increased. This concept was qualitatively confirmed by the unexpectedly fast decay of the absorption peak (FIR) with increasing of the Se content (see Fig. 6 in Ref. 2). The previously obtained discrepancy between b and b_{stat} was caused by the wrong choice of experimental points to the fitting procedure. The old fitting procedure took into account the whole temperature interval, i.e., down to 50 mK. However, as we discussed above, the results for the lowest temperatures have rather qualitative meaning (the Curie-like type of behavior of the susceptibility), and cannot be taken for a quantitative comparison with the theory.

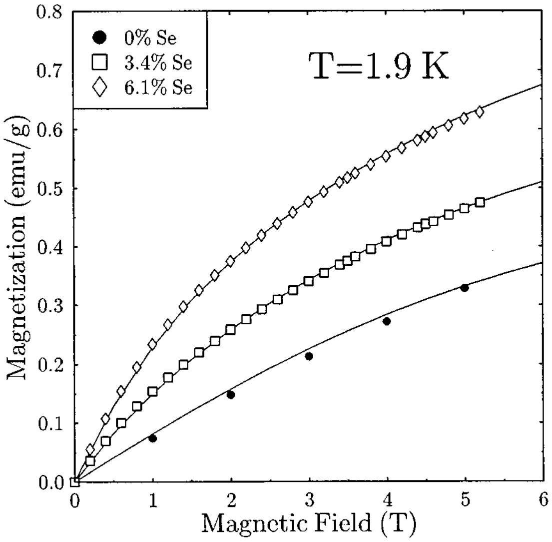

FIG. 8. Magnetization of $(Cd_{1-x}Fe_x)(Te_{1-y}Se_y)$ crystals, $x=0.009$, $0\leqslant y\leqslant0.11$ (points—experiment, lines—theory). The description is given in the text.

Let us now turn to the magnetization measurements. The points at Fig. 8 represent the experimental data and the lines are theoretical, according to the formula $M(H,T)=(1-b_{\mathrm{stat}})xM_{m=0}(H,T)+b_{\mathrm{stat}}xM_{m=1}(H,T)$, where $M_{m=0}(H,T)$ and $M_{m=1}(H,T)$ are calculated numerically.

In the case of SMSC, key parameters are the exchange integrals describing the strength of magnetic interactions $N_0\alpha$, $N_0\beta$, between magnetic ions and band carriers: at the bottom of the conduction band and at the top of the valence band, respectively. The coefficient N_0 is the number of unit cells in the unit volume. Both parameters can be determined using the method originally employed for wide-gap SMSC containing Mn^{2+} ions,[18,19] i.e., by combining exciton splitting and magnetization values. Within the virtual crystal and mean field approximations, the exciton splitting is proportional to the thermal average of an Fe^{2+} ion spin along the external magnetic field $\langle S_z\rangle$, and the magnetization is proportional to the magnetic moment of a single Fe^{2+} ion $\langle L_z+2S_z\rangle$. Therefore, a combination of the exchange parameters $N_0(\alpha-\beta)$ can be determined from the formula:[8]

$$\frac{\Delta E_1}{M}=N_0(\alpha-\beta)\frac{m(x)}{\mu_B N_A}\frac{\langle S_z\rangle}{\langle L_z+2S_z\rangle}, \tag{3}$$

where M represents the macroscopic magnetization per unit mass, $m(x)$ denotes the molar mass, N_A is the Avogadro number, and μ_B is the Bohr magneton.

Since we observed only two exciton absorption peaks, one for each component (σ^+, σ^-) of the circular polarization, we can deduce only the combination of the exchange parameters. The results of magneto-optical experiments: the free exciton Zeeman splitting ΔE_1, and the Faraday rotation as a function of a magnetization are plotted in Fig. 9 for two samples of $(Cd_{1-x}Fe_x)(Te_{1-y}Se_y)$, both with $x=0.009\pm0.0005$, and with $y=0.061$ and $y=0.11$. One can

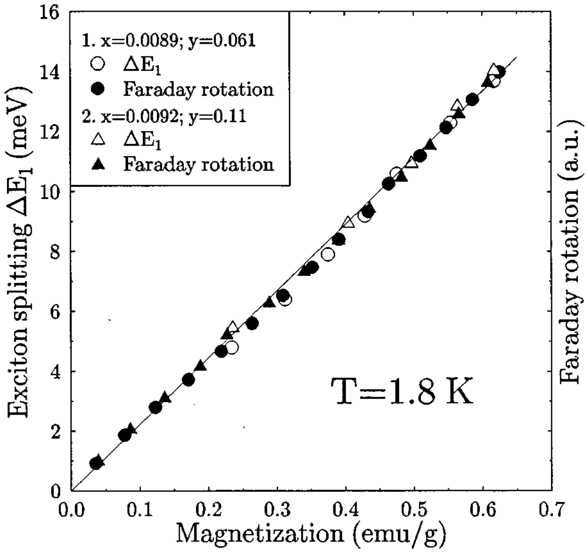

FIG. 9. Energy splitting ΔE_1 and Faraday rotation as a function of magnetization. The straight line represents the least square fit.

see that both studied quantities depend linearly on the macroscopic magnetization, M. The data for both samples lay along a single straight line. From its slope, and taking $\langle L_z+2S_z\rangle/\langle S_z\rangle=2.29$ after Ref. 8, we obtained $N_0(\alpha-\beta)=1.20\pm0.05$ eV. One can compare this value with those obtained for the one-anion SMSC (Table III).

V. PHOTOCONDUCTIVITY AND TEMPERATURE DEPENDENCE OF CONDUCTIVITY OF Cd(Te,Se):Fe

The photoconductivity spectra of $\mathrm{CdTe}_{1-y}\mathrm{Se}_y$ crystals doped with Fe are dominated by the photoionization transitions:

$$\mathrm{Fe}^{2+}+h\nu \rightarrow \mathrm{Fe}^{3+}+\text{ free electron.} \tag{4}$$

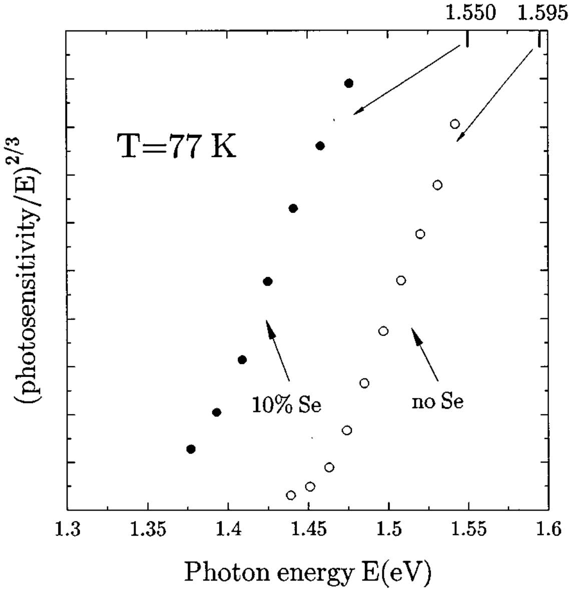

FIG. 10. Fe-related photoconductivity threshold for $\mathrm{CdTe}_{0.9}\mathrm{Se}_{0.1}$:Fe and CdTe:Fe at 77 K. The values of the energy gap are 1.550 eV and 1.595 eV, respectively.

In the region of the photoionization threshold, the photoconductivity spectrum of a thin sample represents the spectrum of the optical cross section of the Fe^{2+} centers for the photoionization transitions. In Fig. 10, the photoconductivity spectrum of $\mathrm{CdTe}_{0.9}\mathrm{Se}_{0.1}$:Fe is compared with the spectrum of CdTe:Fe. As the photoionization cross section (σ) from the d-shell is known[20] to follow the expression

$$\sigma \propto E(E-E_0)^{3/2},$$

(E—photon energy, E_0—threshold energy), a suitable ordinate is used to show the threshold. For CdTe (Refs. 21–23), this threshold is at 1455 meV at $T=77$ K (the Fe^{2+} level lies 140 meV above the top of the valence band). For $\mathrm{CdTe}_{0.9}\mathrm{Se}_{0.1}$:Fe, the Fe^{2+} ionization transitions occur at lower energies, and the threshold seems to be shifted more than 80 meV down. We should bear in mind, that the energy gap of $\mathrm{CdTe}_{0.9}\mathrm{Se}_{0.1}$ is only 45 meV (see Fig. 1) smaller than that of CdTe. One might argue that the ionization energy of the regular Fe^{2+} center, surrounded by 4 Te atoms is, for some unknown reason, lowered in $\mathrm{CdTe}_{0.9}\mathrm{Se}_{0.1}$ by 80 meV, but we think that the lower ionization energy corresponds to those Fe^{2+} centers, which are surrounded by 3 Te atoms and 1 Se atom (more than 29% of the Fe^{2+} centers are in this situation in $\mathrm{CdTe}_{0.9}\mathrm{Se}_{0.1}$:Fe). In other words: in $\mathrm{CdTe}_{0.9}\mathrm{Se}_{0.1}$:Fe, beside the regular Fe^{2+} level, we can see a second (upper) level corresponding to the Fe^{2+} centers in a different anion environment (3 Te atoms and 1 Se atom). It may be useful to recall the meaning of a ‘‘donor level’’ in the case of the multielectron center: ‘‘Fe^{2+} donor level’’ is a visualization of the minimum energy E_I required for the ionization process (4), when the Fe^{2+} center is in the ground ^5E state. By definition, the Fe^{2+} donor level is placed at the distance E_I below the conduction band edge. We do not distinguish between the optical and the thermal ionization energy, because the lattice relaxation energy is very small for Fe in CdTe.[23]

TABLE III. The s,p-d exchange parameters of various one-anion cadmium compounds and of $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$.

Compound	$N_0(\alpha-\beta)$ (eV)	Reference
$\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$	1.10 ± 0.05	18
$(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$	1.20 ± 0.05	This work
$\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Te}$	1.57 ± 0.05	8
$\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Se}$	1.89 ± 0.05	19

The presence of the second level is also seen in transport measurements. The conductivity of both CdTe:Fe and $\mathrm{CdTe}_{0.9}\mathrm{Se}_{0.1}$:Fe is of p type, due to residual acceptor impurities. But, since the Fe^{2+} donor level is close to the valence band and the concentration of iron is high, the Fermi level is pinned to the Fe^{2+} level, and the concentration of holes is governed by the distance between the Fe^{2+} level and the valence band. We have found that the activation energy of the conductivity for $\mathrm{CdTe}_{0.9}\mathrm{Se}_{0.1}$:Fe is more than 70 meV higher than for CdTe:Fe. We think that, in this case, the Fermi level is pinned to the upper Fe^{2+} level.

VI. CONCLUSIONS

We show that the presence of two different types of anions in $(A^{\mathrm{II}}_{1-x}\mathrm{Fe}_x)(B^{\mathrm{VI}}_{1-y}C^{\mathrm{VI}}_y)$ system significantly modifies physical properties of the compound. The temperature-independent Van Vleck paramagnetism characteristic of II-VI SMSC containing Fe ions is replaced by a Curie-type paramagnetism. This was established by both low-temperature magnetic susceptibility measurements of two-anion systems based on cadmium, zinc, and mercury and the magnetization study of $(\mathrm{Cd}_{1-x}\mathrm{Fe}_x)(\mathrm{Te}_{1-y}\mathrm{Se}_y)$ crystals. Theoretical calculations performed by us explain the experimental results and provide a good description of magnetic properties of investigated compounds.

Optical properties in the FIR range and magneto-optical properties in exciton energy region are also altered. The results of our photoconductivity measurements suggest that the ground state of an Fe^{2+} ion can take several different positions in the energetic band structure of the host material, depending on a composition of a group of atoms constituting the nearest neighbors.

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