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Magnetoresistance of $Cd_{1-x}Fe_xSe$: Electron-correlation effects

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Large positive magnetoresistance has been observed at low temperatures for *n*-type $Cd_{1-x}Fe_xSe$ in the insulating phase. This effect is difficult to explain by existing theory. We show that the most relevant features of the data can be accounted for by the *s-d* interaction between Fe^{2+} spins and spins of impurity electrons *and* by electron intrastate correlations.

In diluted magnetic semiconductors (DMS)'s, where magnetic ions are randomly distributed in the host matrix, the exchange interaction between the spins of charge carriers and localized spins leads to strong magneto-optical and magnetotransport effects.[1] The interaction of the spin of a charge carrier in a bound state with neighboring localized spins produces a bound magnetic polaron. It has been shown[2] that the bound magnetic polaron dominates the transport properties of Mn-based DMS's in the insulating regime at low temperatures, leading to large positive and negative magnetoresistance effects. Recently, much interest has been shown in DMS's containing Fe^{2+} ions in II-VI compounds such as $Cd_{1-x}Fe_xSe$. The ground state of Fe^{2+} in these alloys is a singlet state with zero magnetic moment leading to Van Vleck paramagnetism.[3]

The main purpose of this communication is to report for the first time a large positive magnetoresistance (MR) in Fe-based DMS's. This effect seems to be too large to be produced either by bound magnetic polarons or by redistribution of electrons between the two spin subbands in these substances. Instead, an explanation based on the effect of intrasite electron correlations in the hopping regime is proposed.

The present work was carried out on as-grown $Cd_{1-x}Fe_xSe$ samples with $0.003 \leq x \leq 0.07$. All samples were *n*-type single crystals not intentionally doped. Their composition was checked by chemical and neutron-activation analysis. The resistivity ρ and Hall coefficient R_H were measured by the Van der Pauw method. Ohmic contacts were prepared by ultrasonic soldering of indium.

Figure 1 exhibits resistivity of $Cd_{1-x}Fe_xSe$ as a function of the inverse temperature in magnetic fields $H=0$ and $H=5$ T. The activated behavior of ρ at low temperature indicates that all samples are in the hopping conduction regime. At zero magnetic field, $\rho=\rho_3\exp(\varepsilon_3/kT)$ below 6 K, which describes phonon-assisted hopping between nearest-neighbor impurity sites. The value of ε_3 depends on composition: it increases almost linearly with x from the value of 0.45 meV for $x=0.003$ to the value of 1.3 meV for $x=0.07$. At $H=5$ T the experimental points fit better a $\rho \propto \exp(T_0/T)^n$ law with $\frac{1}{4} \leq n \leq 1$. From Hall coefficient data in the range 20–80 K (corresponding to freezing out of electrons on impurity levels) we found $N_A/N_D \approx 0.4$ in the samples studied (N_D and N_A are donor and acceptor concentrations, respectively).[4] The room-temperature values of $1/R_H$ give N_D-N_A: we found

$$N_D \approx (0.5-1.3)\times 10^{17}\ \text{cm}^{-3}$$

in our samples. The transverse and longitudinal MR for $T \leq 4.2$ K was measured in fields up to 7 T; some of these data (with c axis of crystal perpendicular to H) are shown in Figs. 2 and 3 for different compositions. We found a small magnetic anisotropy in our MR measurements.

Figure 2 shows $\rho(H)/\rho(0)$ for $Cd_{1-x}Fe_xSe$ samples with $x=0.003$ and 0.013. It is seen that ρ increases

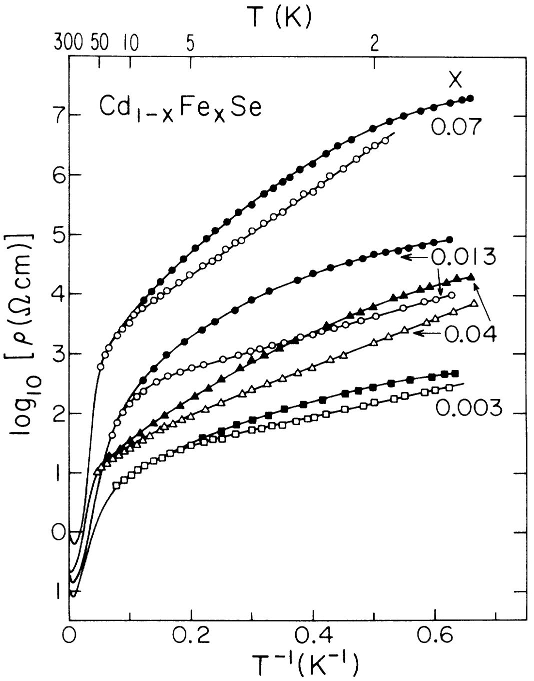

FIG. 1. Resistivity of $Cd_{1-x}Fe_xSe$ as a function of inverse temperature in magnetic fields $H=0$ (open symbols) and $H=5$ T (closed symbols).

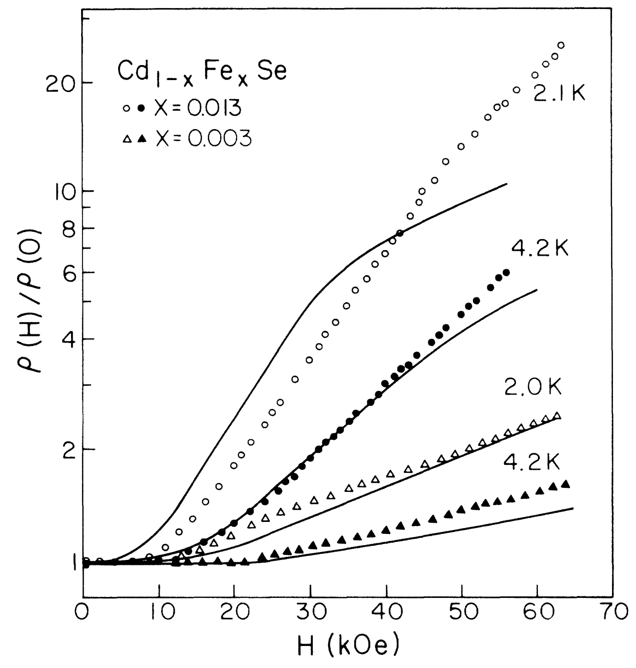

FIG. 2. Normalized transverse magnetoresistance for $Cd_{1-x}Fe_xSe$ with $x=0.003$ and 0.013 as a function of magnetic field at two different temperatures. The solid lines are numerical fits to the experimental data.

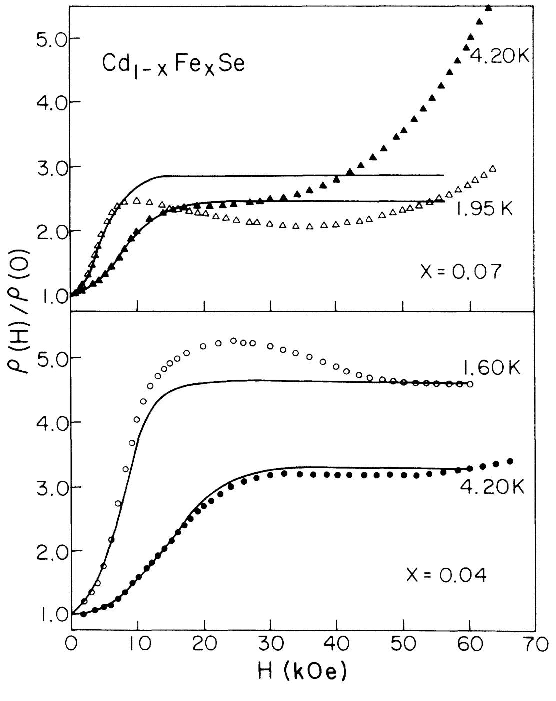

FIG. 3. Normalized transverse magnetoresistance of $Cd_{1-x}Fe_xSe$ with $x=0.04$ and 0.07 as a function of magnetic field at two different temperatures. The solid lines are numerical fits to the experimental data.

monotonically with H at high fields and that this rise is steeper as T is lowered or x increased. The positive MR effect in these samples is much larger than in pure CdSe with comparable donor concentration.[5] At low fields, a small negative MR is observed. The $\rho(H)$ dependence in compounds with higher Fe content is more complicated. Figure 3 shows that, in $x=0.04$ and 0.07 samples, ρ first rises with increasing H, goes through a maximum, then decreases slightly but increases again at high magnetic fields. As the temperature is lowered, the maximum rises and its position shifts to lower H as x is increased. We have observed these qualitative features in other samples studied with $x>0.02$. The observed MR in $Cd_{1-x}Fe_xSe$ is large—in several samples, relatively small fields produce changes of more than an order of magnitude in ρ.

We note that the behavior of the magnetoresistance in n-type $Cd_{1-x}Mn_xSe$ is markedly different from the one we observe in $Cd_{1-x}Fe_xSe$. In the insulating phase the MR in these materials is positive at low fields (with a magnitude of the positive MR comparable to that found in our samples) but, at higher fields, is much strongly negative.

To interpret the data obtained, we notice that the characteristic wave function size $a\ (=\hbar\sqrt{2m^*E_1}$, where E_1 is the impurity ionization energy and m^* is the electron effective mass), which is about 40–70 Å in the samples studied,[4] is much smaller than the magnetic length $\lambda\ [=(c\hbar/eH)^{1/2}]$ for all applied fields. Thus, the system is in the weak magnetic field regime, where H produces only a small correction to the electronic wave function. First, we consider the effect of the magnetic field on the donor wave function. For H such that $\lambda^2/a \gg N_D^{-1/3} \gg a$ (which is satisfied in our samples) percolation calculations in the hopping regime predict[6]

$$\ln[\rho(H)/\rho(0)] \approx A(a/N_D)H^2 ,$$

where

$$A \approx 8\times10^{-4}\ (\mathrm{cm}^{-4}\mathrm{T}^{-2}) .$$

Clearly, fields of up to tens of Teslas would be needed to produce the observed effects. Therefore, some other mechanism must be behind the large MR in $Cd_{1-x}Fe_xSe$ in low fields. In high fields, however, the rise of ρ, which is roughly the same as that observed in CdSe for similar values of N_D and T (Ref. 5), may be attributed to the diamagnetic shrinking (induced by the magnetic field) of the donor wave function, which leads to a decrease in the hopping conduction. For n-type CdSe this effect has been quantitatively analyzed by Finlayson *et al.*[5]

We next discuss briefly models which may possibly account for the low-field MR and argue that the relevant features of MR in $Cd_{1-x}Fe_xSe$ can be explained by the s-d interaction between Fe^{2+} spins and the spins of impurity electrons *and* by electron correlation effects.

The s-d exchange interactions in DMS's produce a large spin splitting of s electrons in the presence of magnetic fields. Its effect on the transport properties of DMS's in the insulating regime has been previously studied for $Cd_{1-x}Mn_xSe$ samples.[2] The MR, which is positive in small fields and negative for higher fields, was explained in Ref. 2 by a model of hopping of bound magnetic polarons. Such an analysis does not however apply to $Cd_{1-x}Fe_xSe$, which is Van Vleck–type DMS. The existence of the bound magnetic polaron was shown in $Cd_{1-x}Fe_xSe$, but that is a quantum effect whose magnitude is very small compared to usual magnetic polaron effect in Mn-based compounds;[7] its contribution to transport in $Cd_{1-x}Fe_xSe$ is consequently negligible.

Consider, for a possible alternative explanation a redistribution of electrons between two spin subbands.[8] This produces a change of the density of states at the Fermi level and leads to an increase of the screening radius in the Thomas-Fermi approximation. Consequently, Coulomb potential fluctuations are enhanced, what leads to the positive MR. However, estimates of this effect suggest that it is too weak to account for the large MR observed in $Cd_{1-x}Mn_xSe$.[9] This conclusion holds also in the case of $Cd_{1-x}Fe_xSe$, where the spin splitting is even smaller.

Fluctuations of alloy composition and its effect on spin splitting can also affect the magnetoresistance of DMS's in the insulating regime. The band gap of $Cd_{1-x}Fe_xSe$ varies strongly with x.[10] The random distribution of Fe atoms in the cation sublattice produces a Gaussian broadening of the impurity band,[4,6] which depend on magnetic field. However, an estimation of this effect[11] with the available data shows that its contribution is negligible. A similar conclusion can be drawn about the influence of the thermodynamic fluctuations of the magnetization on the hopping conduction in DMS's.[2]

Our interpretation of the present MR data follows basically the idea of Kurobe and Kamimura[12] who have shown that the intrastate electron correlation in hopping in the intermediate impurity concentration regime leads to positive MR which saturates above a certain magnetic-field value. In this scheme, unoccupied (UO), singly occupied (SO) as well as double occupied (DO) impurity states are allowed. Consequently, there are four different kinds of hopping processes between two of these impurity states (neglecting spin-flip transitions): (1) from a SO to an UO state, (2) from a SO to a SO state, (3) from a DO to an UO state and (4) from a DO to a SO state. Note that the final states have doubly occupied sites in processes 2 and 4. The magnetic field suppresses processes involving states with spins antiparallel to it. The number of transitions from SO to UO impurity states is not much affected. On the other hand, the number of transitions from SO to SO states is cut down drastically since one of the two electrons must have its spin antiparallel to the field (recall that only no spin-flip processes are considered). The SO to SO and DO to UO transitions are the ones strongly suppressed by the magnetic field—leading to a positive MR effect. At high enough fields, when all electrons are in the up-spin subband, only transitions from DO to SO and from SO to UO states contribute to the hopping conduction, and, consequently, MR saturates. In the $Cd_{1-x}Fe_xSe$ system the electronic effective magnetic moment (μ^*) is large (because of the *s-d* interaction). Large μ^* produce large spin splittings, which, in addition to the possibility of double occupancies of localized states (corresponding to a *finite* correlation energy), gives rise to unusually strong MR effects in $Cd_{1-x}Fe_xSe$ at relatively small fields.

A crucial assumption of this model is that the correlation energy (intrasite electron repulsion) is smaller than the width of the impurity band. It follows then that singly and doubly occupied states can coexist at the Fermi level. There is some experimental support for this seemingly speculative assumption. The conductivity measurements in insulating CdSe and $Cd_{1-x}Fe_xSe$ samples,[4,5] as well as the results of the cyclotron resonance experiments for $Cd_{1-x}Mn_xSe$,[13] indicate the existence of electrons with $a \gg a_B$ at the Fermi level apart from states with $a \approx a_B$ (a is the localization length of electron and a_B the effective donor Bohr radius). It is also known that the correlation energy, U, which, for isolated impurities is roughly the ionization energy, decreases as a increases.[14] Furthermore, U is reduced by impurity-impurity interaction and also is expected to decrease with increasing N_D and screening.[14] Consequently, one may expect the presence of SO and DO states in the samples studied.

We calculated, numerically, the conductivity in the model described above. The four different types of transitions were taken into account with proper expressions for electron occupation probabilities[15] and intrinsic hopping rate.[16] We assume that the correlation energy is the same for all donor sites and that the localizations lengths for DO states (a_2) and for SO states (a_1) do not depend on the energy of the corresponding states.[17] For the density of states in the impurity band, we used the Gaussian form with an adjustable variance E_0.

The values of the following parameters are needed in order to perform a numerical fit to the observed change of resistivity with magnetic field $[\rho(H)/\rho(0)]$: N_D, N_A, $\mu^*(x)$, E_0, U, a_2/a_1, and R_{ij}/a_2 (R_{ij} is a distance between the i and j localized states). The values of N_D and N_A have previously been obtained from Hall coefficient data.[4] The effective magnetic moment and its dependence on x has been obtained from the magnetization and photoconductivity measurements performed on the same samples.[10] Since ε_3 turns out to be constant in all samples at $H=0$, it follows that $\ln(\rho_3) \propto 2R_{ij}/a_2$ at $H=0$.[6] Therefore, the value of R_{ij}/a_2 may be estimated from the intercept [with the $\ln(\rho)$ axis] of the $\ln(\rho)$ versus $1/T$ plot (extrapolated from low temperatures). We performed our calculations–to fit the data in Figs. 2 and 3–with three adjustable parameters: E_0, U and a_2/a_1.

The results of our numerical calculations are shown by solid lines in Figs. 2 and 3 for each composition. We found that the value of H at which th MR saturates depends on E_0 and U, while the amplitude of the MR effect is very sensitive to the value of a_2/a_1. Since our fits were performed for two different temperatures for each sample, we were able to discriminate between different values of E_0, U, and a_2/a_1. The best values for the adjustable parameters turned out to be: $E_0 \approx \varepsilon_3(H=0)$; $a_2/a_1 \approx 1.5$ for $x=0.0003$, 0.013, and 0.04 and $a_2/a_1 \approx 1.1$ for $x=0.07$. In all cases $U \approx E_0/2$, which corresponds to values between 5 and 10 K in our samples. From Ref. 14 $U \approx 0.15E_1$ for $x=0.003$ and 0.04; for $x=0.013$, $U \approx 0.5E_1$.

We have tried out values of $U \gg E_0$ in our calculations. The positive MR effect was then wiped out in our numerical results, which shows the relevance of intrastate correlations in the system studied. Note, however, that a value of U much lower than that which is usually assigned to it must be used in our model.

In conclusion, we have measured low-temperature magnetoresistance of insulating $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Se}$ in fields up to 7 T for various compositions. We observe large positive MR values in relatively small fields. They can be accounted for neither by a hopping of bound magnetic polaron, redistribution of electrons between spin subbands nor by fluctuations of magnetization. We show that the intrastate electron correlations in this material, where the *s-d* interaction leads to large spin splittings in magnetic fields, can produce the observed effects. The same effect might also show up in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$, where the spin splitting is even larger than in $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Se}$; however, sizable magnetic polarons in this system may mask it.

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