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Electrical properties of $Cd_{1-x}Fe_xSe$

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We present results of resistivity and Hall-effect measurements performed on *n*-type as-grown $Cd_{1-x}Fe_xSe$ crystals with $0<x\leq 0.07$ in the temperature range 1.7–300 K. For $T<80$ K, activated behavior in conductivity is observed. We found that E_1 (the energy required to raise electrons from the donor center to the conduction band) and E_3 (the activation energy in hopping conduction) vary strongly with composition x. These results are discussed in the framework of both Anderson localization (produced by substitutional disorder) and random fluctuations in composition and central-cell potentials.

In diluted magnetic semiconductors (DMS), where magnetic ions are randomly distributed in the host II-VI compound, the exchange interaction between the charged carriers and localized spins leads to strong magneto-optical and magnetotransport effects. These effects have been widely studied and understood for Mn-based DMS, in which the magnetic ions have permanent moments, such as for $Cd_{1-x}Mn_xSe$ and $Zn_{1-x}Mn_xTe$.[1] Recently, much interest has been attracted to wide-gap DMS such as $Zn_{1-x}Fe_xTe$, $Zn_{1-x}Fe_xSe$, and $Cd_{1-x}Fe_xSe$.[2] These alloys, in which the Fe^{2+} ions have only field-induced magnetic moments in the ground state, are expected to exhibit novel interesting effects. So far, no investigations concerning electrical properties of these new DMS has been reported. In this Brief Report we report the Hall-coefficient and resistivity data obtained on as-grown *n*-type $Cd_{1-x}Fe_xSe$ crystals.

Single crystals of this alloy were grown by the modified Bridgman method and were not intentionally doped. Their composition x was checked by neutron-activation and chemical analysis. We measured the resistivity and Hall effect for single-crystal samples with $0<x\leq 0.07$ in the temperature (T) range $1.7\leq T\leq 300$ K. The CdSe-FeSe system forms a single-phase solid solution of the wurtzite structure for $0\leq x\leq 0.15$. We checked that the results of our measurements do not depend on the relative orientation of the c axis and magnetic field.

Figure 1 shows the resistivity as a function of inverse temperature for various samples of $Cd_{1-x}Fe_xSe$ with different composition. The inverse-temperature dependence of the Hall coefficient is shown in Fig. 2 for the same samples. The resistivity and Hall-coefficient data show clearly three regions: (a) a high-temperature range which shows the onset of saturation, where all impurities are ionized and the carrier concentration is independent of T ($T>200$ K), (b) a region corresponding to freezing-out of electrons on impurity levels, between about 80 and 20 K, where the temperature dependence of the electrical conductivity is almost entirely due to a rapid decrease in the free electron concentration, and (c) a hopping range, for $T<6$ K, which corresponds to activated conduction in the impurity band. The maxima observed in the Hall data are characteristic of the transition from band to impurity conduction.

The resistivity dependence for $T\lesssim 70$ K can be, with good accuracy, approximated by the expression

$$\rho^{-1}(T)=\rho_1^{-1}\exp\left[-\frac{E_1}{kT}\right]+\rho_3^{-1}\exp\left[-\frac{E_3}{kT}\right], \tag{1}$$

where the first term corresponds to band conduction and the second to hopping conduction. In the samples studied the equation for carrier concentration in that region

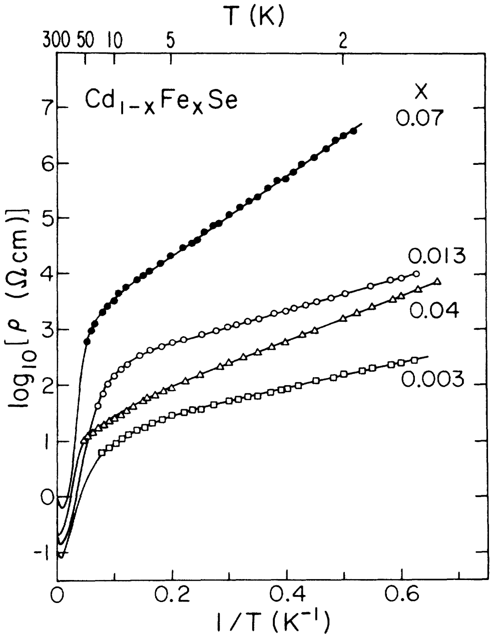

FIG. 1. Variation of resistivity with reciprocal temperature for $Cd_{1-x}Fe_xSe$ samples with $x=0.003$, 0.013, 0.04, and 0.07. At the leftmost part of the figure no experimental points are shown. There are too many of them. Each solid line shown stands for about 500 data points for $1/T\lesssim 0.1$.

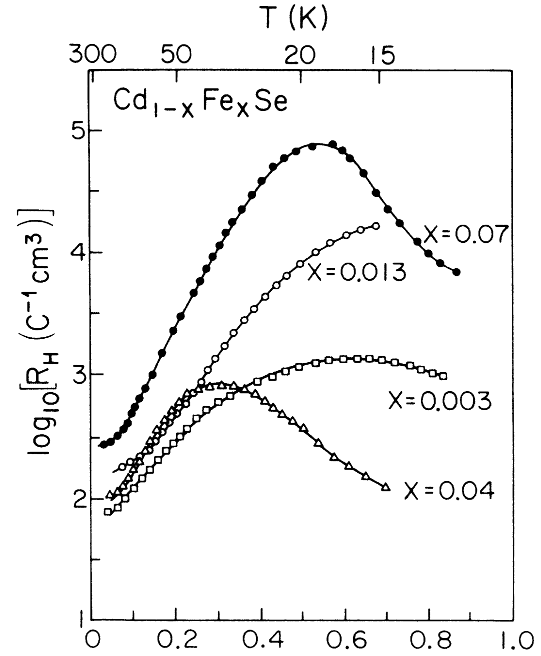

FIG. 2. Variation of the Hall coefficient with reciprocal temperature for $Cd_{1-x}Fe_xSe$ samples with different x. The solid lines are guides to the eye.

which corresponds to the first term can be written as the following:[3]

$$n(T)=\frac{N_D-N_A}{1+2(N_A/N_C)\exp(E_1/kT)}\ , \tag{2}$$

where N_D and N_A are the donor and acceptor concentrations, respectively, and N_C is the density of states in the conduction band (proportional to $T^{3/2}$). This expression reduces to $n=[(1-K)/2K]N_C\exp(-E_1/kT)$ for low temperatures, therefore we may estimate the value of $K=N_A/N_D$ from a plot of $\ln(n/T^{3/2})$ versus $1/T$. The high temperature values of $n(T)$ give N_D-N_A, from which we obtain the values of N_D and N_A, which are given in Table I for the samples studied. We used the value of $0.13m_0$ for the effective mass of electrons in the conduction band.[4] It follows from Table I that the values of K are close to 0.4 for all compositions and $N_D\approx(0.5-1.3)\times10^{17}$ cm^{-3}. This assures us that (a) we are in a light doping region, where $N_Da^3\ll1$ (a is the characteristic wave-function size, which may be taken as equal to the effective donor Bohr radius) and (b) that we are consequently below the critical Mott concentration $n_c\approx(0.25/a)^3$, which is about 3×10^{17} cm^{-3} for our samples. The donor Bohr radius ($=\hbar^2\kappa/e^2m^*$) is about 40 Å in $Cd_{1-x}Fe_xSe$, using CdSe value of 9.3 for the dielectric constant κ.

TABLE I. $Cd_{1-x}Fe_xSe$ parameters deduced from experimental data.

Composition x	N_D (cm^{-3})	$K=N_A/N_D$
0.003	1.3×10^{17}	0.39
0.013	7.0×10^{16}	0.40
0.04	1.28×10^{17}	0.45
0.07	4.5×10^{16}	0.43

The curves of $\log\rho$ versus $1/T$ have constant slopes for 20 K $<T<$ 80 K which give E_1—the activation energy required to raise electrons from donor centers to the conduction band. Similarly, E_3 follows from the values of the observed constant slopes for $T\lesssim6$ K. The values of E_1 are shown in Fig. 3 as a function of iron concentration in the samples studied. An extrapolation of E_1 versus x to $x=0$ gives $E_1\approx7$ meV which is considerably smaller than the donor binding energy for CdSe calculated using the hydrogenic model (≈20 meV). We cannot account for this difference, but note that a value of E_1 (≈9 meV) not far from our extrapolated value follows from the ρ versus $1/T$ dependence reported for CdSe (Ref. 4) with $N_D\approx1\times10^{17}$ cm^{-3}. We also plot the values of E_3—the activation energy for the hopping conduction in Fig. 3. A strong dependence of both activation energies on x is observed. We will first try to explain the variation of E_1 with sample composition.

For this purpose, we notice that in $Cd_{1-x}Fe_xSe$ alloys the Fe^{+2} ions are randomly distributed throughout the lattice, so they give rise to static potential fluctuations. This disorder leads to band tailings and also to the appearance of a mobility-edge energy (E_C) within the bands, below which electrons are localized.[5] The mobility edge shifts towards higher energies with increasing disorder (x). Thus, the observed monotonic increase of the activation energy E_1 with x might be explained by this model. In our case, $E_1=E_C+E_0$, where E_0 corresponds to the position of the donor level in CdSe. Similar behavior of E_1 was observed in $V_{1-x}Nb_xO_2$ and was also inter-

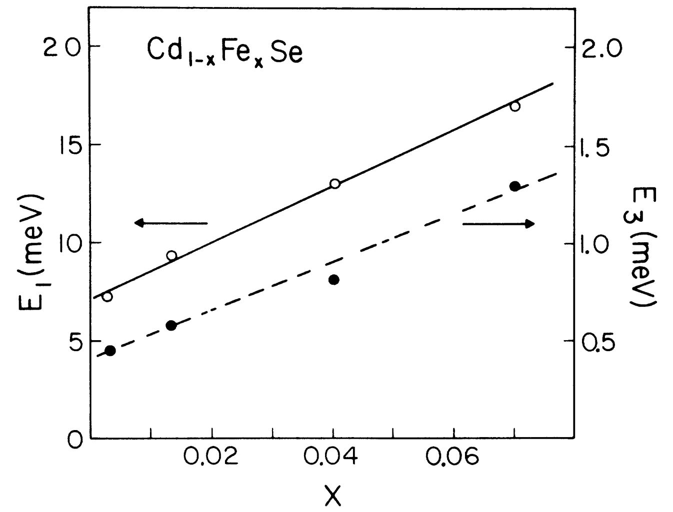

FIG. 3. Variation of the activation energy E_1 (right scale) and E_3 (left scale) with composition in $Cd_{1-x}Fe_xSe$. The solid straight lines are guides to the eye.

preted as the onset of Anderson localization resulting from disorder.[6]

An alternative explanation for the increase of the activation energy E_1 with x may be based on the idea of formation of bound magnetic polarons,[7] since mixed crystals of $Cd_{1-x}Fe_xSe$ contain a paramagnetic ion Fe^{+2}. From our measurements of magnetic susceptibilities performed on some samples, we estimate the characteristic energy of a bound magnetic polaron as ≈ 0.05 meV, at $T=4$ K, for $x=0.04$. Therefore, the effect of the exchange contribution to the binding energy of a donor is too small in the materials studied. This is in agreement with recent optical measurements performed on the same alloys.[8]

We now consider the low-temperature region ($T<6$ K), in which the activated behavior for hopping of the form $\rho=\rho_3\exp(E_3/kT)$ is observed. From Figs. 1 and 3 it is seen that E_3 and ρ_3 vary considerably as the Fe content increases. For lightly doped samples, $\ln\rho_3 = 1.73/(N_D^{1/3}a)$.[9] This expression fits our experimental data well for all samples, if the values of the localization radius a are 1.5 to 2 times larger than the values given by the relation $a=\hbar/(2mE_0)^{1/2}$. The need for such a factor is not surprising, for this expression is not likely to be accurate: much larger values for a were obtained previously for CdSe with similar concentration of donors.[4] Such numerical deviations from the estimated value of a are not as relevant as the fact that $\ln\rho_3 \propto N_D^{-1/3}$ agrees with our data. E_3 depends weakly on N_D, so the variation of $E_3(x)$ is smoother. The value of E_3 corresponding to $x=0$ is about 4×10^{-4} eV and increases almost linearly with x. At intermediate values of compensation K, a composition independent contribution to E_3 should be of the order of the Coulomb interaction E_D $(=e^2N_D^{1/3}\kappa)$ between carriers and ionized impurities. The experimental values for E_3 found in different materials with $K\approx0.5$ are always much smaller than E_D. This is also the case of our samples, in which E_D (≈ 5 meV) is much larger than E_3 $(x=0)$. Theoretical calculations which take into account correlations[10] and electron-electron interaction[11] in one-electron hopping, corresponding to the activated regime, give a significant reduction to E_D, but still the theoretical results for E_3 are larger than the observed values.

To explain the increase of E_3 with increasing x we need, in addition to the Coulomb interaction, some other mechanism which (a) contributes to disorder energies in the impurity band and (b) depends on composition. Following Gelmont *et al.*,[12] we suggest two altertnaive mechanisms to explain the data obtained on $Cd_{1-x}Fe_xSe$. Consider first distribution of impurity levels, caused by fluctuations in the composition. The contribution of random large-scale fluctuations in composition to E_3 goes like $\alpha(x/Na^3)^{1/2}$, where N is the number of cation lattice sites per unit volume and α $(=dE_{CB}/dx)$ is the variation of the bottom of the conduction band with x. If we assume that a $(=\hbar/(2mE_0)^{1/2}\approx 80$ Å) does not depend on composition and that $\alpha=1.44$ eV,[8] then we get a contribution to E_3 of 1.4 meV for $x=0.7$. This value is too large since the experimental value of the activation energy rises by 0.9 meV between $x=0$ and 0.07. A larger value of a (as observed in CdSe with similar donor concentration[4]) would however bring down the estimated contribution to E_3, in better agreement with the data. Thus, our data are reasonably consistent with this mechanism. However, different (from $x^{1/2}$) x dependences (e.g., linear) cannot be ruled out, because the range of the data is not extensive enough.

The second mechanism considered by Gelmont *et al.*, fluctuations of the central-cell potential, give a contribution to E_3 proportional to $8\times\Delta$, where Δ is a phenomenological parameter which measures the energy shift of an impurity level produced by variations in the configuration of nearest neighbors. To fit our results we need $\Delta\approx2$ meV, which is a reasonable value.

In conclusion, both disorder mechanisms, random fluctuations in composition and fluctuations in central-cell potential, give equally good agreement with the observed variation of the hopping activation energy with x in $Cd_{1-x}Fe_xSe$. Our data do not allow us to discriminate between these two mechanisms.

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