Technical saturation and magnetization steps in diluted magnetic semiconductors: Predictions and observations

Y. Shapira and S. Foner
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

D. H. Ridgley, K. Dwight, and A. Wold
Department of Chemistry, Brown University, Providence, Rhode Island 02912
(Received 16 April 1984)

A model for the high-field magnetization of II-VI semimagnetic compound semiconductors at low temperatures is presented. It applies for low Mn concentrations. The model explains quantitatively and without adjustable parameters the magnetization of $Cd_{1-x}Mn_xTe$, $Cd_{1-x}Mn_xSe$, $Cd_{1-x}Mn_xS$, $Zn_{1-x}Mn_xSe$, and $Zn_{1-x}Mn_xS$ near 100 kOe for $T < 2$ K. At higher magnetic fields, magnetization steps are predicted. The first step is observed in $Cd_{1-x}Mn_xSe$ and $Zn_{1-x}Mn_xSe$, and is used to determine the nearest-neighbor exchange constant. The results support a random distribution of Mn ions.

Diluted magnetic semiconductors (or semimagnetic semiconductors) are of great current interest.[1] They are ideal for studying the magnetic properties of dilute magnetic systems, and the influence of the s-d exchange interaction on semiconducting properties. The most extensively studied materials are II-VI semiconductor compounds in which a fraction x of the cations have been replaced by manganese, e.g., $Cd_{1-x}Mn_xSe$. The magnetic behavior of these materials has been the focus of many investigations. Nevertheless, several fundamental problems remain. Among them are the question of whether the Mn ions are randomly distributed in the crystal, and discrepancies between results for the Mn-Mn exchange constant.[2] In this paper we present a model which describes quantitatively and without adjustable parameters the magnetization of many II-VI compounds with $x < 0.1$, in high magnetic fields ($H \gtrsim 10^5$ Oe) and at low temperatures ($T < 2$ K). This model also predicts the existence of magnetization steps, which are observed in the present work, and which yield directly the dominant Mn-Mn exchange constant. The experimental results support a random distribution of the Mn ions.

We use a cluster model similar to that which was used to interpret low-field susceptibility data.[3] Specifically, we make the following assumptions: (1) the Mn ions are distributed randomly over the cation sites; (2) each Mn ion has spin $S = \frac{5}{2}$ and a g factor $g = 2$; (3) the exchange constant J between nearest-neighbor (NN) Mn ions is negative (antiferromagnetic), and its magnitude is typically $J/k \cong -10$ K, where k is the Boltzmann constant; (4) all other exchange constants J_i', between next-nearest neighbors (NNN's) or more-distant neighbors, are much smaller in magnitude, i.e., $|J_i'/k| \lesssim 0.5$ K typically; (5) for magnetic fields $H \gtrsim 100$ kOe ($g\mu_B H/k \gtrsim 13.4$ K, where μ_B is the Bohr magneton) all exchange interactions other than between NN's can be ignored. This last assumption is not valid when $T \lesssim 4$ K and $H \ll 100$ kOe,[3] but is expected to hold for $H \gtrsim 100$ kOe because the Zeeman energy overwhelms the weak exchange interactions with $|J_i'/k| < 0.5$ K. Some of the justification for these assumptions will be given later, after the consequences of the model are presented.

Assuming NN exchange interactions only, the magnetization for Mn concentrations $x \lesssim 0.05$ is well approximated by the sum of the magnetizations of four types of NN clusters: isolated Mn ions (singles), pairs, open triangles (OT), and closed triangles (CT).[3,4] The probabilities that a Mn ion belongs to each of these clusters are[5]

$$P_1 = (1-x)^{12} \tag{1}$$

for singles,

$$P_2 = 12x(1-x)^{18} \tag{2}$$

for pairs,

$$P_3 = 18x^2(1-x)^{23}(7-5x) \tag{3}$$

for OT's,

$$P_4 = 24x^2(1-x)^{22} \tag{4}$$

for CT's, where a zinc-blende structure is assumed. For II-VI materials with the wurtzite structure the probabilities are the same, except for P_4. The difference for P_4 is, however, numerically insignificant for $x < 0.1$.

The energy-level scheme for the various clusters was discussed by Nagata and co-workers.[4] For a pair the energy is

$$E = -J[S_T(S_T+1) - 35/2] - g\mu_B mH \ , \tag{5}$$

where S_T is the total spin for the pair, and $m = -S_T, -S_T+1, \ldots, S_T$. For $J < 0$ the ground state at $H = 0$ is nonmagnetic, with $S_T = 0$. It remains the lowest state in fields $g\mu_B H < 2|J|$. Thus, for $|J/k| \geq 10$ K the pair magnetization is negligible if $H < 100$ kOe and $T < 2$ K. (In some materials $|J/k|$ might be as low as 6 or 7 K, and the field range where the pair magnetization is negligible is somewhat smaller.) For closed triangles the ground state at $H = 0$ has $S_T = \frac{1}{2}$ and is two-fold degenerate ($m = \pm\frac{1}{2}$). The state with $m = \frac{1}{2}$ remains the lowest for $g\mu_B H < 3|J|$. Therefore, the magnetization of a CT at 100 kOe and for $T < 2$ K corresponds to $m = \frac{1}{2}$, or $\frac{1}{15}$ of the saturation magnetization for three singles. For open triangles the state with $S_T = m = \frac{5}{2}$ has the lowest energy in the range $0 < g\mu_B H < 7|J|$, and the magnetization per triangle at 100

kOe and for $T < 2$ K is $\frac{1}{3}$ of the saturation magnetization for three singles.

Experimental results in II-VI materials with $x \leq 0.1$ show that the magnetization M for $T \lesssim 4$ K and $H \lesssim 100$ kOe obeys the phenomenological equation[6-11]

$$M = M_s B_{5/2}(5\mu_B H/k(T+T_0)) \ , \tag{6}$$

where $B_{5/2}$ is the Brillouin function for $S = \frac{5}{2}$, and M_s and T_0 are phenomenological parameters which are nearly temperature independent in this range. For $T < 2$ K the magnetization near 100 kOe is nearly H independent, and is very nearly equal to M_s. This M_s, which we call the technical saturation value, is lower than the true saturation value M_0 for concentration x with $S = \frac{5}{2}$ and $g = 2$. Often, one defines an effective Mn concentration $\bar{x}$ by the relation $\bar{x}/x = M_s/M_0$. Physically, $\bar{x}$ is that concentration which would have given rise to a magnetization M_s if the Mn spins were fully aligned.

Based on our results for the magnetization of the various NN clusters at 100 kOe and for $T < 2$ K we predict that

$$\bar{x}/x = M_s/M_0 = [P_1 + (P_3/3) + (P_4/15)] \ . \tag{7}$$

This equation is represented by the solid curve in Fig. 1. Also shown are experimental results for $Cd_{1-x}Mn_xTe$,[6] $Cd_{1-x}Mn_xSe$,[7] $Cd_{1-x}Mn_xS$,[8,9] $Zn_{1-x}Mn_xSe$,[10] and $Zn_{1-x}Mn_xS$.[11] All these experimental results are fairly close to the universal theoretical curve. The reasonably good agreement for x as large as 0.1 may seem surprising because Eq. (7) does not include the contribution of NN clusters of four spins or more. The fraction of these "missing" spins grows from 11% for $x = 0.05$ to 41% for $x = 0.1$. However, a qualitative argument by Kreitman, Milford, Kenan, and Daunt[3] suggests that the contribution of the missing spins is relatively small because many of them are in NN quadruplets with small S_T. According to Kreitman *et al.* an upper bound for the contribution of the missing spins can be estimated by assuming that all missing spins are in NN quintets, with $S_T = \frac{5}{2}$ for each quintet. If one accepts this suggestion then the estimated upper bound for $\bar{x}/x$ is

$$\bar{x}/x = [P_1 + (P_3/3) + (P_4/15)] + [(1 - P_1 - P_2 - P_3 - P_4)/5] \ . \tag{8}$$

Equation (8) is shown in Fig. 1 as a dashed curve. The results for $x = 0.1$ are close to this curve.

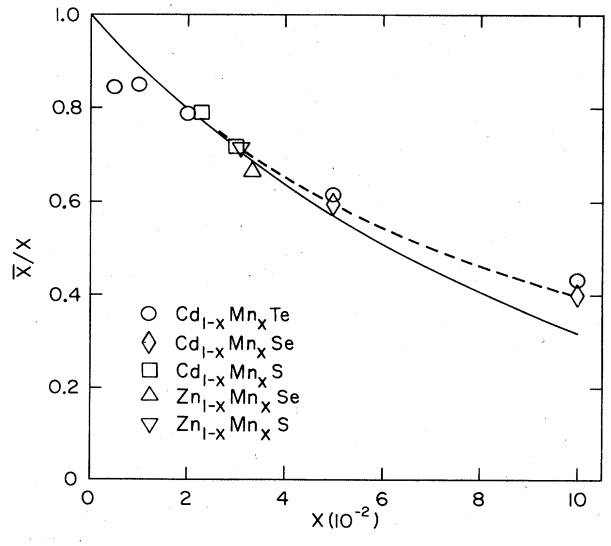

FIG. 1. Comparison between experimental results for $\bar{x}/x$ in various materials (Refs. 6–11) and theoretical predictions. The solid line represents Eq. (7), which ignores clusters larger than triangles. The dashed line represents Eq. (8), which includes a suggested estimate (Ref. 3) for the maximum contribution of these larger clusters.

We now discuss the magnetization for $H > 100$ kOe. From Eq. (5) it can be shown that the magnetization of a pair at $T = 0$ exhibits a series of positive steps at reduced fields $h \equiv g\mu_B H/|J| = 2, 4, 6, 8, 10$. The step at $h = 2$, for example, occurs because the energy for $S_T = m = 1$ becomes lower than that for $S_T = m = 0$. The magnitude of each of the five magnetization steps is $\delta M/M_0 = P_2/5$, or $\delta M/M_s = (P_2/5)(x/\bar{x})$. These steps will be broadened at finite temperatures, but should remain observable if $kT \ll 2|J|$. The magnetic fields at which the steps occur give J directly. The size δM of each step provides a test of the assumption of a random distribution of the Mn ions.

The open and closed triangles also lead to magnetization steps, but these are more difficult to observe. The steps for the OT's should occur at $h = 7, 9, 11, 13, 15$. Thus, for $J/k = -10$ K the first step is at $H = 521$ kOe, which can be reached only with pulsed fields. For the CT's the steps are at $h = 3, 5, \ldots, 15$, but δM for each step is quite small because the probability P_4 never exceeds 2.5% for any x. In contrast, the probability P_2 that an ion is in a pair reaches a maximum of 24% near $x = 0.05$.

The first magnetization step due to the pairs, at $g\mu_B H = 2|J|$, was observed in single crystals of $Cd_{1-x}Mn_xSe$ with $x = 0.049$ and $Zn_{1-x}Mn_xSe$ with $x = 0.033$. The CdMnSe sample was grown at Brown University by the Bridgman method. The ZnMnSe sample was obtained from Eagle-Picher Industries. The Mn concentrations were determined by atomic absorption. Magnetization data were taken at 1.5 K in dc fields up to 230 kOe. The magnetometer is described in Ref. 12. For $Cd_{1-x}Mn_xSe$ (Fig. 2) the magnetization step is centered at 124 ± 10 kOe, corresponding to $J/k = -8.3 \pm 0.7$ K. The next magnetization step due to the pairs should occur near 248 kOe. This second step, as well as the first step, were recently observed in a pulsed-field experiment.[13] For $Zn_{1-x}Mn_xSe$ (Fig. 3) the first magnetization step is near 190 kOe, corresponding to $J/K \cong -13$ K. Note that in both materials J/k is of order -10 K, as assumed in the model. There is also evidence that $-J/k \sim 10$ K in $Cd_{1-x}Mn_xTe$[2] and in $Zn_{1-x}Mn_xS$,[14] and that $-J/k > 4$ K in CdMnS.[3]

The theoretically predicted magnitude of δM is also shown in Figs. 2 and 3. The good agreement with experiment indicates that the actual probability P_2 is close to that obtained from a random Mn distribution. The results in Fig. 1 also support a random distribution, because such a distribution was used to obtain the theoretical curves.

Further support for the model was obtained from low-field susceptibility measurements on the same CdMnSe and ZnMnSe samples for $150 < T < 300$ K. Corrections for the diamagnetic susceptibility of the lattice were made.[10,11] The Curie constants for both samples were within 3% of the values calculated from the model's assumptions $S = \frac{5}{2}$ and $g = 2$. The Curie-Weiss temperature Θ was used to estimate

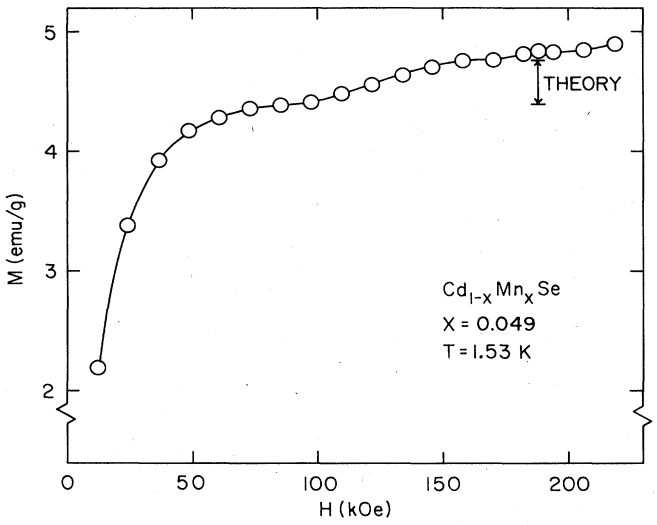

FIG. 2. Magnetization M of $Cd_{1-x}Mn_xSe$ as a function of magnetic field H. Note the broad step near 124 kOe. The theoretical prediction for the size δM of the step, assuming a random distribution of Mn ions, is shown.

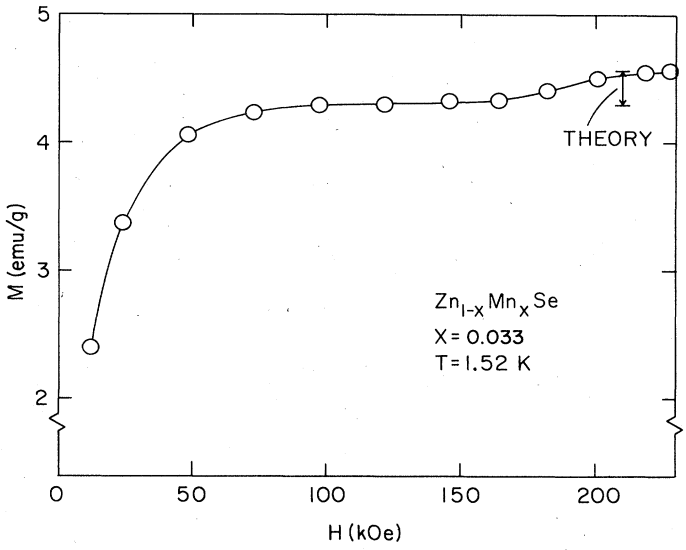

FIG. 3. Magnetization curve for $Zn_{1-x}Mn_xSe$ with $x = 0.033$. The theoretically predicted size of the magnetization step is indicated.

J.[15] Here, we made a correction for the difference between the effective Θ in the range 150–300 K and the true (high-T) Θ.[16] This gave $J/k \cong -9$ K for $Cd_{1-x}Mn_xSe$ and $J/k \cong -18$ K for $Zn_{1-x}Mn_xSe$. We regard the values of J obtained from the magnetization steps in Figs. 2 and 3 as more accurate. However, the rough agreement between the values of J obtained from the two methods supports the interpretation of the magnetization steps.

Finally we comment on the value $J/k = -0.55$ K which was reported for $Cd_{1-x}Mn_xTe$.[2,4] For such a low value of J, all pairs and triangles at 1.5 K should be magnetically saturated at 155 kOe. However, the experimental data for low x strongly suggest that this is not the case.[6] We, therefore, believe that the value -0.55 K relates not to the NN interaction but rather to an interaction between more distant spins, e.g., NNN's. The NNN exchange constant is expected to be much smaller than J,[14] and is probably of order 0.1 K.[3] Such a NNN interaction is still important in determining the magnetic properties in the low-field and low-temperature range where much of the data of Galazka and co-workers[4] were taken.

This work was supported in part by U.S. Office of Naval Research Contract No. N00014-81-K-0654. The National Magnet Laboratory is supported by National Science Foundation. Crystal growth facilities were provided by Brown University's Materials Research Laboratory, supported by the National Science Foundation. We are grateful to J. Warnock for numerical calculations and to R. L. Aggarwal for useful discussions.

[1]J. K. Furdyna, J. Appl. Phys. **53**, 7637 (1982).
[2]R. R. Galazka, in *Physics of Narrow Gap Semiconductors,* proceedings of the International Conference on Narrow Gap Semiconductors, Linz, 1981, Lecture Notes in Physics, Vol. 152, edited by E. Gornik, H. Heinrich, and L. Palmetshofer (Springer, Berlin, 1982), p. 294.
[3]M. M. Kreitman, F. J. Milford, R. P. Kenan, and J. G. Daunt, Phys. Rev. **144**, 367 (1966).
[4]S. Nagata, R. R. Galazka, D. P. Mullin, H. Akbarzadeh, G. D. Khattak, J. K. Furdyna, and P. H. Keesom, Phys. Rev. B **22**, 3331 (1980); R. R. Galazka, S. Nagata, and P. H. Keesom, *ibid.* **22**, 3344 (1980).
[5]R. E. Behringer, J. Chem. Phys. **29**, 537 (1958).
[6]J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. **29**, 435 (1979).
[7]D. Heiman, Y. Shapira, S. Foner, B. Khazai, R. Kershaw, K. Dwight, and A. Wold, Phys. Rev. B **29**, 5634 (1984).
[8]D. Heiman, Y. Shapira, and S. Foner, Solid State Commun. **45**, 899 (1983).
[9]M. Nawrocki, R. Planel, F. Mollot, and M. J. Kozielski, Phys. Status Solidi B **123**, 99 (1984).
[10]D. Heiman, Y. Shapira, and S. Foner (unpublished).
[11]Y. Shapira and S. Foner (unpublished).
[12]S. Foner and E. J. McNiff, Jr., Rev. Sci. Instrum. **39**, 171 (1968).
[13]R. L. Aggarwal, S. N. Jasperson, Y. Shapira, S. Foner, T. Skakibara, T. Goto, N. Miura, K. Dwight, and A. Wold (unpublished). The first indications that the magnetization of $Cd_{1-x}Mn_xSe$ rises above M_s came from magnetoreflectance data up to 150 kOe [R. L. Aggarwal, S. N. Jasperson, J. Stankiewicz, Y. Shapira, S. Foner, B. Khazai, and A. Wold, Phys. Rev. B **28**, 6907 (1983)] and from magnetization data up to 110 kOe [Y. Shapira and S. Foner (unpublished)].
[14]W. H. Brumage, C. R. Yager, and C. C. Lin, Phys. Rev. **133**, A765 (1964).
[15]J. Spalek, A. Lewicki, Z. Tarnawski, Z. Obuszko, and R. R. Galazka (unpublished).
[16]The correction for Θ was based on numerical results provided by J. Warnock. The corresponding correction for the Curie constant was insignificant.