

Specific heat and magnetic susceptibility of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  at low temperatureC. D. Amarasekara, R. R. Galazka,\* Y. Q. Yang,<sup>†</sup> and P. H. Keesom*Department of Physics, Purdue University, West Lafayette, Indiana 47907*

(Received 1 November 1982)

For the insulating  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  single crystals with composition  $x$  between 0.005 and 0.5, the specific heat was measured between 0.5 and 50 K, and the low-field susceptibility between 4 and 50 K. The samples with  $x \geq 0.2$  show a spin-glass transition at low temperature. The phase diagram for the boundary of the paramagnetic and spin-glass region is presented. The excess specific heat in zero magnetic field of all the paramagnetic samples shows a pronounced maximum at  $\sim 0.3$  K and a broad shoulder at  $\sim 0.9$  K. This sharp maximum is the consequence of single Mn ions for which the crystal field has removed part of the sixfold degeneracy of the lowest  $^6S_{5/2}$  state. To produce a maximum in the specific heat at 0.3 K, the energy-level splitting needed is about 50 times larger than the splitting found by EPR measurements for samples with much lower Mn concentration. It is speculated that this splitting is a consequence of stresses in the crystal lattice caused by substitution of smaller Mn ions for larger Cd. The broad shoulder is a consequence of ions which are paired and have a Heisenberg exchange energy  $J = -1.75$  K.

## I. INTRODUCTION

$\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  is a member of the family of "semi-magnetic semiconductors." This family of ternary mixed crystals became interesting to us as they showed spin-glass properties<sup>1,2</sup> at low temperature. The study of the magnetic and thermal properties of  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ,<sup>1</sup>  $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ ,<sup>2</sup> and  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$  (Ref. 3) provided valuable information about this family. This work on  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  completes the thermodynamic study of these semimagnetic semiconductors and provides some additional information. The compound forms a single crystallographic phase with wurtzite structure for the composition range<sup>4</sup>  $0 \leq x \leq 0.5$ . In  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  the Cd and Mn ions are distributed randomly over an hcp sublattice, while for the other crystals of this family the distribution of the Mn and the metal ions are over an fcc sublattice.

We measured specific heat and low dc field magnetic susceptibility of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  single crystals for  $x$  from 0.005 to 0.4. The specific-heat measurements were carried out over the temperature range of 0.3 to 50 K and that of the susceptibility between 4 and 50 K. The samples with  $x < 0.2$  are paramagnetic at all temperatures. The rest of the samples,  $0.2 < x \leq 0.5$ , show spin-glass transitions at low temperature. In agreement with other members<sup>1-3</sup> of this family, all the paramagnetic samples have a magnetic field-dependent excess specific heat above the lattice contribution. The zero-field excess specific heat of the paramagnetic samples of Cd-Mn-Se show a sharp peak around 0.3 K and a broad shoulder near 0.9 K. The excess specific heat of

CdMnSe and CdMnTe for samples with the same Mn concentration are identical and are somewhat similar to that of the Hg compounds. This zero-field excess specific heat has been a puzzle, as contributions by single Mn ions were excluded, based on EPR measurements, and contribution by Mn pairs do not have a temperature dependence which is

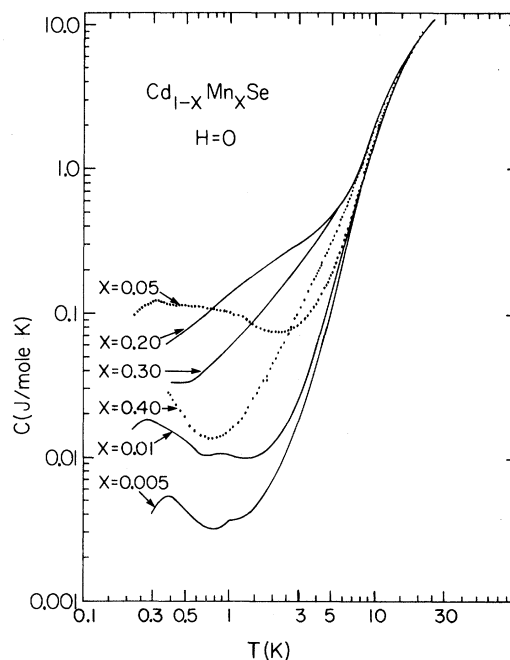


FIG. 1. Specific heat of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  crystals in zero magnetic field is shown as plots of  $\log C$  vs  $\log T$  for several values of  $x$ .

similar to that of the observed specific heat. In this paper we have analyzed the zero-field results by considering single Mn ions in which the ground state is split and therefore are contributing to the specific heat in addition to that by Mn pairs.

## II. EXPERIMENTAL PROCEDURE

Single crystals of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  were prepared by using the Bridgman method<sup>5</sup> at the Institute of Physics of the Polish Academy of Sciences, Warsaw, Poland. Heat-capacity measurements were made using the standard heat-pulse technique in a conventional  $^3\text{He}$  cryostat.<sup>6</sup> The addenda correction was known from previous measurements and was 2–3 % of the total heat capacity of the samples with weights between 1 and 2 g. The specific heat was measured in magnetic fields from 0 up to 2.8 tesla. The susceptibility was measured in fields of 15 G with the use of a superconducting quantum interference device<sup>7</sup> (rf-SQUID).

## III. RESULTS AND DISCUSSION

Figure 1 summarizes the specific heat of all the samples of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  measured in zero field as  $\log C$  vs  $\log T$ . The behavior of the specific heat is

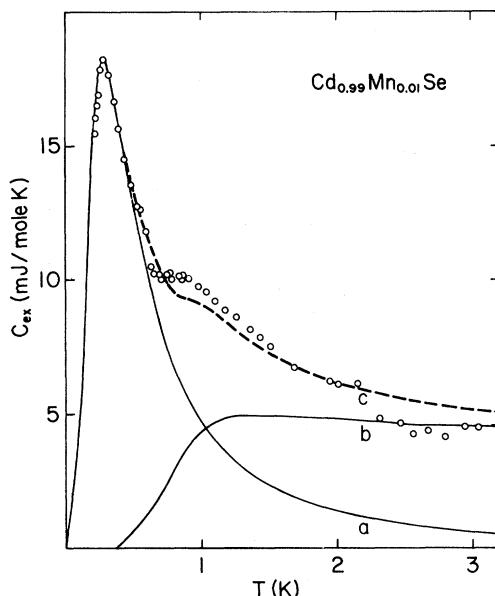


FIG. 2.  $C_{\text{ex}}$  vs  $T$  for sample  $\text{Cd}_{0.99}\text{Mn}_{0.01}\text{Se}$  in zero field. The line  $a$  represents a Schottky contribution to the specific heat using an energy scheme discussed in the text with  $\Delta=0.6$  K and the number of moles of Mn ions contributing is  $9.2 \times 10^{-3}$ . The line  $b$  is the contribution by  $\text{Mn}^{2+}$ - $\text{Mn}^{2+}$  pairs with exchange constant  $J=-1.75$  K. The calculated total excess specific heat is given by the dashed line  $c$ .

quite similar to that observed for  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ , and resembles the result of  $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$  and  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ .

As CdSe is an insulator at very low temperature the specific heat  $C_L$  is proportional to  $T^3$ . Adding magnetic Mn ions to CdSe leads to an excess specific heat  $C_{\text{ex}}$  above the lattice contribution. We define  $C_{\text{ex}}=C-C_L$ , and will assume that  $C_L$  is cubic, at least below 4 K.

The samples of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  with  $x=0.05, 0.01, 0.005$ , which are paramagnetic, show an excess specific heat which is markedly magnetic field dependent in contrast to that of samples having  $x \geq 0.2$ . A similar behavior was observed previously for the other semimagnetic semiconductors<sup>1–3</sup> of the same family. Figure 2 shows the excess specific heat in zero magnetic field for the sample with  $x=0.01$ . This result is nearly identical to that of  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  (Ref. 1) with the same concentration. Both show a pronounced peak around 0.3 K. At that time we accepted the EPR results<sup>8</sup> which observed for Mn concentrations less than 0.0005, a negligibly small zero-field splitting. Therefore, we expected no contribution from single Mn ions to the specific heat in zero field at the temperatures we measured. However, it was impossible to use the contributions by pairs of Mn ions, for which the six-fold degeneracy is removed by the Heisenberg exchange interaction, as the temperature dependence of  $C_{\text{ex}}$  is quite different from that of pair contribution.

As shown in Fig. 2, the excess specific heat for  $\text{Cd}_{0.99}\text{Mn}_{0.01}\text{Se}$  shows a pronounced peak at 0.28 K, which has the characteristics of a Schottky anomaly. We will then assume, notwithstanding the EPR results, that the independent Mn ions are responsible for this peak and that the Mn and Cd ions are randomly distributed over their sublattice. In addition, we assume that the  $^6S_{5/2}$  ground state of  $\text{Mn}^{2+}$  is split in a quartet and a doublet, the latter 0.6 K above the former. With the use of  $x=0.0104$ , curve  $a$  in Fig. 2 was calculated, and this curve fits the experimental data around 0.28 K surprisingly well. The shoulder near 0.8 K is then the contribution of paired Mn ions, about 10% of the total Mn ions. Curve  $b$  represents the calculated pair contribution using the energy-level scheme given by Nagata *et al.*,<sup>2</sup> with the value of  $J=-1.75$  K. The sum of the two contributions, curve  $c$ , is close to the experimental data and, possibly, incorporating the zero-field splitting into the pair calculation could have removed the 10% difference around 0.8 K.

This model must be an oversimplification, as it does not lead to the specific heat in an applied magnetic field. Kronig and Bouwkamp<sup>9</sup> derived the level diagram for an  $^6S_{5/2}$  state in cubic surrounding

and for applied magnetic fields. The level spacing depends on the direction of the applied field with respect to the cubic crystal and this leads to different Schottky contributions. For a zero-field splitting of 0.6 K and an applied field of 1 tesla, the smallest value of the maximum of the different Schottky curves is  $0.79k_B$  per  $Mn^{2+}$  ion, while experimentally we observe a still lower value,  $0.71k_B$  per ion;  $k_B$  is the Boltzmann constant.

The excess specific heat for the other samples in the paramagnetic range gives additional troubles with this simple model. The sample  $Cd_{0.998}Mn_{0.002}Te$  (Ref. 1) could not be measured

below 0.8 K as its specific heat was too small. Probably the zero-field splitting of the  $Mn^{2+}$  is so small that the Schottky anomaly is well below 0.3 K. An excess specific heat could be measured for  $Cd_{0.995}Mn_{0.005}Se$ , but for this sample the assumption that all the Mn ions contribute to  $C_{ex}$  is untenable. The contribution at  $T_{max}$  per Mn ion would then be so low that not even a zero-field splitting into a five-fold lower state and one state above it, actually forbidden by Kramers theorem, cannot give such a low value. Finally, for  $Cd_{0.95}Mn_{0.05}Se$  we can only fit the zero-field result if we assume that the ground state is split into a set of three doublets, located at 0,

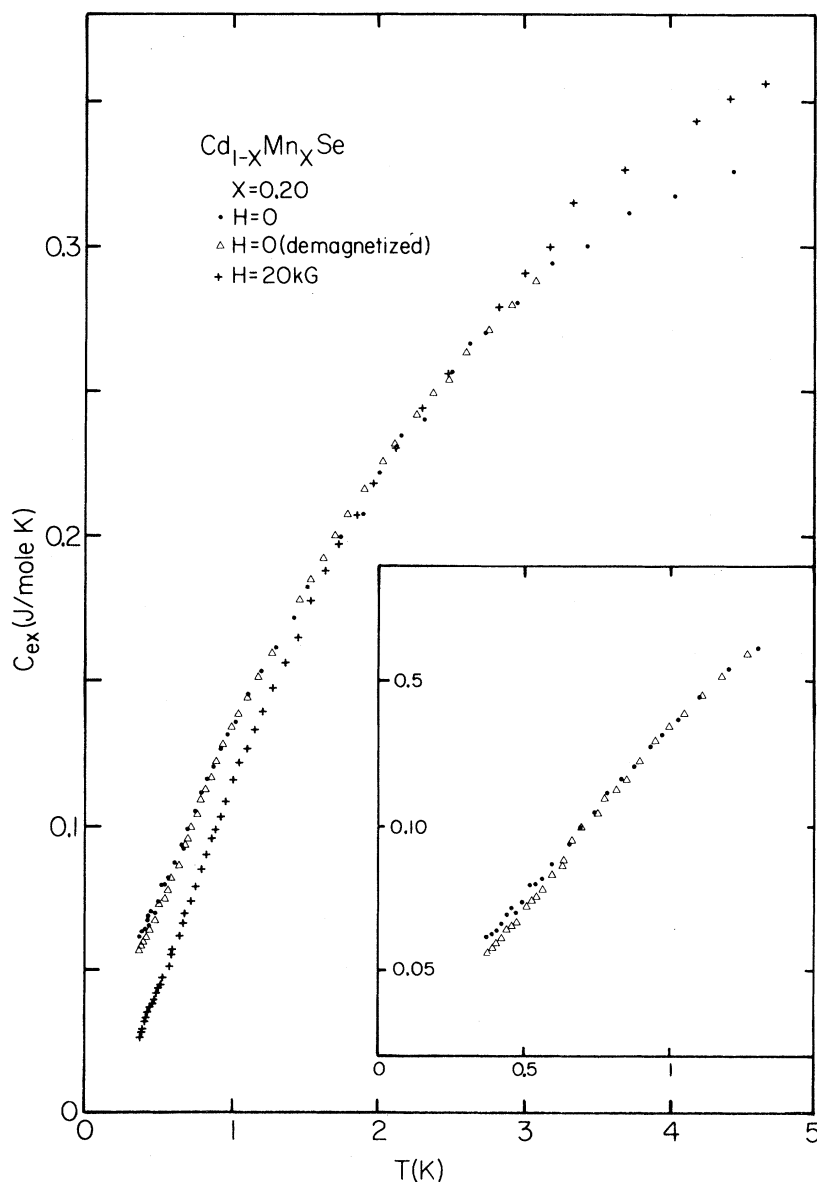


FIG. 3.  $C_{ex}$  vs  $T$  for  $Cd_{1-x}Mn_xSe$  with  $x=0.2$  in 0 and 2.0 tesla. Also shown are measurements in zero field after demagnetization from 2 tesla. Inset shows the zero-field data at low temperature.

0.4, and 1.1 K in energy, and add to this the pair contribution with  $J = -1.75$  K.

From all the measured Cd-Mn-Se or Cd-Mn-Te samples, in the paramagnetic region, the following picture emerges. Substitution of Mn ions which have ionic radii of 0.80 Å for Cd, with radii of 0.97 Å, or for Hg, with radii of 1.10 Å, induces stresses in the crystal lattice. For low concentration, when  $x < 0.005$  the symmetry and the zero-field splitting of  $\text{Mn}^{2+}$  are not affected, so that EPR shows a very small zero-field splitting, and consequently  $C_{\text{ex}}$  cannot be measured. When  $x$  reaches 0.05, some of the Mn ions are being influenced by stresses. These stresses change the local surroundings and increases the zero-field splitting by a factor of 50. The EPR measurements apparently cannot tell anything about the samples with these high concentration and the specific heat can only tell that something is occurring, but is not able to pin down exactly what the new level scheme is.

The plot of  $C_{\text{ex}}$  vs  $T$  for sample  $x = 0.2$  is shown in Fig. 3. Below 1 K,  $C_{\text{ex}}$  is nearly linear with temperature, characteristic of spin-glasses or at least of random magnetic systems. A slight decrease of the specific heat below 2 K is observed in a magnetic field of 2.8 tesla and this can be understood qualitatively by assuming the presence of loosely bound spins in addition to clusters of Mn ions. When the thermal energy becomes comparable to the binding energy of the loosely bound spins, these spins will start to contribute to the specific heat. However, in an external magnetic field these spins may bind stronger to clusters, and hence do not contribute to the specific heat. At higher temperature these spins break away from clusters and will increase  $C_{\text{ex}}$  above the value in zero field; this increase is observed above 3 K. Of course from entropy consideration it would also follow that if a magnetic field lowers  $C_{\text{ex}}$  at low temperature, it will increase  $C_{\text{ex}}$  at higher temperatures. This magnetic field dependence of  $C_{\text{ex}}$  is also observed in  $x = 0.3$ , but is substantially smaller. This is to be expected as the sample with  $x = 0.2$  is just above the percolation limit and has more loosely bound spins than the samples with higher concentrations of Mn ions.

At the lowest temperature we observed for the sample with  $x = 0.20$  that  $C_{\text{ex}}$  is slightly history dependent. The value of  $C_{\text{ex}}$  measured in zero magnetic field depends on how the sample is cooled: either in zero field, or first cooled in magnetic field and then demagnetized at the lowest temperature. The inset of Fig. 3 shows the two sets of results. The difference in specific heat is small, about 10%, but is real, and is probably also a consequence of loose spins which are bound to large clusters by a magnetic field and then remain frozen after demag-

netization. The same effect is also observed in the sample with  $x = 0.30$ , but is very much smaller. For the  $x = 0.4$  sample the effect is not observed at all, agreeing with almost complete absence of loosely bound spins. The specific heat below 1 K for this sample shows an upward swing indicating an additional contribution. It can be represented below 3 K by

$$C = 3.9T^{-2} + 12T + 2.5T^3$$

in units of mJ/mole K. The contribution proportional to  $T^{-2}$  is almost magnetic field independent and leads us to ascribe it to the presence of a nuclear specific heat at the lowest temperature. The hyperfine level splitting of  $\text{Mn}^{2+}$  nuclei is produced by the interaction of nuclear magnetic moments with that of electrons. The nuclear Schottky specific heat is given by

$$C_N = N(\mu_N H)^2 I(I+1) / 3k_B T^2 = A_N T^{-2},$$

where  $N$  and  $I$  are the number of magnetic nuclei and the nuclear spin ( $I = \frac{5}{2}$  for Mn nuclei), respectively. The nuclear magnetic moment  $\mu_N$  is  $6.98 \times 10^{-27} \text{JT}^{-1}$  for Mn from NMR experiments. Then it follows that for a mole of Mn ions

$$A_N = 6.38 \times 10^{-3} H^2,$$

in units of mJK/mole of Mn, where  $H$  is in tesla. From a graph of  $CT^2$  vs  $T^3$  for this samples with  $x = 0.4$  we found for  $A_N$ , 9.75 mJ K/mole of Mn which corresponds to a nuclear hyperfine field of 39.1 tesla. This value of hyperfine field is the same as found for CdMnTe.

The variation of the dc susceptibility ( $\chi = M/H$ ) with temperature was investigated using a SQUID

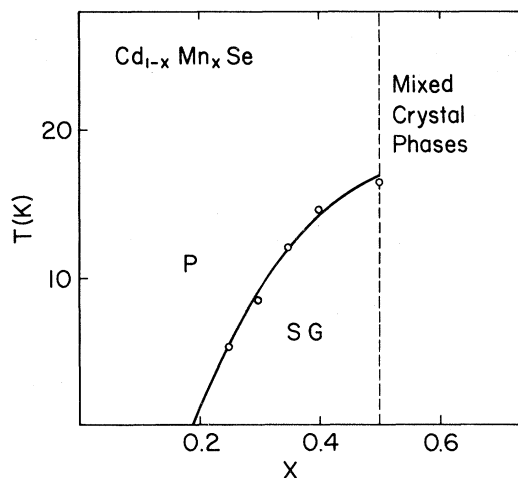


FIG. 4. Phase diagram of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  for temperature  $T$  vs Mn concentration  $x$ . Paramagnetic and spin-glass regions are indicated by  $P$  and  $SG$ , respectively.

magnetometer. Our susceptibility results on  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  are in good agreement with prior measurements<sup>10</sup> and so we do not repeat the details. All the samples with  $0.2 \leq x \leq 0.5$  show a cusplike peak in the susceptibility at the spin-glass transition temperature  $T_s$ , when cooled in zero field and then measured in a constant field of 15 G. A similar behavior for other compounds<sup>1-3</sup> in this family was observed earlier.

In Fig. 4 is shown the spin-glass transition temperature  $T_s$  as a function of concentration  $x$ . This phase diagram agrees qualitatively with the theory,<sup>11</sup> which predicted the presence of spin-glass phase as a consequence of frustration in an fcc lattice when the magnetic ions interact antiferromagnetically. This theory discusses an fcc lattice, but is also applicable to the wurtzite crystal structure of  $\text{CdMnSe}$ , as up to the next-nearest neighbors, the two crystal structures are essentially identical.

In conclusion, the specific heat and magnetic sus-

ceptibility of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  are quite similar to that of other members of this family of semimagnetic semiconductors. We have presented a probable explanation for the observed excess specific heat of paramagnetic samples of  $\text{CdMnSe}$  in zero field. We assumed contributions to the specific heat from single Mn ions, whose ground states are split, and added to this the contribution by pairs of Mn ions. It is likely that the zero-field splitting of the Mn ions is a consequence of the crystalline field and originates in small distortions in the crystal lattice when the smaller Mn ions substitute for the group-II ions like Cd or Hg.

#### ACKNOWLEDGMENT

This work was supported by the National Science Foundation—Materials Research Laboratory Program No. DMR80-20249.

\*Present address: Institute of Physics, Polish Academy of Sciences, Warsaw, Poland.

†Permanent address: Department of Physics, University of Science and Technology of China, Hefei, Anhui, China.

<sup>1</sup>R. R. Galazka, S. Nagata, and P. H. Keesom, *Phys. Rev. B* **22**, 3344 (1980).

<sup>2</sup>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).

<sup>3</sup>G. D. Khattak, C. D. Amarasekara, S. Nagata, R. R. Galazka, and P. H. Keesom, *Phys. Rev. B* **23**, 3553 (1981).

<sup>4</sup>R. R. Galazka, *Proceedings of the 14th International*

*Conference on the Physics of Semiconductors, Edinburgh, 1978*, edited by B. L. H. Wilson (The Institute of Physics, Bristol, 1978), p. 133.

<sup>5</sup>D. P. Mullin, Ph.D. thesis, Purdue University, 1980 (unpublished).

<sup>6</sup>G. D. Khattak, P. H. Keesom, and S. P. Faile, *Solid State Commun.* **26**, 441 (1978).

<sup>7</sup>S. Nagata, P. H. Keesom, and H. R. Harrison, *Phys. Rev. B* **19**, 1633 (1979).

<sup>8</sup>J. Lambe and C. Kikuchi, *Phys. Rev.* **119**, 1256 (1960).

<sup>9</sup>R. de L. Kronig and C. J. Bouwkamp, *Physica* **6**, 290 (1939).

<sup>10</sup>S. B. Oseroff, *Phys. Rev. B* **25**, 6584 (1982).

<sup>11</sup>L. De Seze, *J. Phys. C* **10**, L353 (1977).