

## Effect of the Exchange Coupling of $Mn^{++}$ Ions on the Magnetic Susceptibilities of $ZnS:MnS$ Crystals\*

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The magnetic susceptibilities have been measured over the temperature range of 20–500°K for five ZnS single crystals doped with  $Mn^{++}$  in varying concentrations from 0.5 to 7.5%. The susceptibilities are essentially linear in  $1/T$  for  $T < 77^\circ K$ , but above this temperature the graphs of  $\chi$  show appreciable curvatures which increase with the  $Mn^{++}$  concentration. The departure from the Curie behavior can be explained by the antiferromagnetic coupling between the  $Mn^{++}$  ions situated at the nearest-neighbor sites in the ZnS lattice. By assuming that the numbers of clusters of various types are determined by statistics, the total magnetic susceptibilities of the single ions, pairs, and triples of  $Mn^{++}$  in the ZnS crystals have been calculated. The observed susceptibilities can be fitted to the theoretical values if the exchange coupling is taken as the form  $-2J(\mathbf{s}_1 \cdot \mathbf{s}_2)$  with  $J$  equal to  $-9 \pm 1 \text{ cm}^{-1}$ .

### INTRODUCTION

THE exchange coupling of pairs of paramagnetic ions in dilute crystals have been studied by electron spin resonance<sup>1-3</sup> and by optical spectroscopy<sup>4,5</sup> at various laboratories. The exchange integrals have been determined from these experiments and correlated to the exchange couplings of the same kind of cations in pure crystals.<sup>6</sup> McClure<sup>5</sup> has recently studied the optical spectrum of  $Mn^{++}:ZnS$  crystals and found certain bands which arise from the exchange coupling between two neighboring  $Mn^{++}$  ions in the ZnS crystal. By assuming an isotropic exchange Hamiltonian of the form  $-2J(\mathbf{s}_1 \cdot \mathbf{s}_2)$ , McClure<sup>5</sup> determined, from the optical data, the exchange integral as  $J = -9 \text{ cm}^{-1}$  which is very close to the value of  $-8.7 \text{ cm}^{-1}$  found for  $\beta$ -cubic MnS by Danielian and Stevens.<sup>7</sup> In this paper we shall report some measurements of the paramagnetic susceptibilities of  $Mn^{++}:ZnS$  crystals with concentration ranging from 0.5 to 7.5%. It is found that the experimental data can also be explained by assuming an isotropic exchange coupling between two nearest-neighbor  $Mn^{++}$  ions.

### EXPERIMENT

The  $Mn^{++}:ZnS$  crystals of different concentrations were furnished by McClure.<sup>5</sup> The concentrations of the  $Mn^{++}$  ions, as determined from the analysis of the magnetic data, are 0.5, 3.1, 3.6, 5.7, and 7.5%. The measurements of the magnetic susceptibilities were made over the temperature region of 20–500°K by means of the apparatus used in our previous work.<sup>8</sup> The results are

shown in Figs. 1 and 2 (circles). All these crystals are found to be magnetically isotropic.

### ANALYSIS

The ZnS (zincblende arrangement) crystals are known to have almost perfectly cubic structure.<sup>9</sup> For ZnS crystals doped with  $Co^{++}$ ,  $Ni^{++}$ , and  $Mn^{++}$ , the optical spectra of the transition elements ions show high degree of isotropy<sup>10,11</sup> which is indicative of the essentially cubic (tetrahedral) environment of the impurity sites. Furthermore, for a  $Mn^{++}$  in ZnS, only the ground state  ${}^6A_1(S)$  is important as far as magnetic properties are concerned and this state is not affected to the first order by the crystal field of lower symmetry. The splitting of the spin sextet of the  ${}^6A_1(S)$  state due to the lower fields are far too small to produce any effect on the magnetic susceptibilities in the temperature range of our interest.<sup>12</sup> Thus, for the susceptibility work, the crystal field will be taken as being completely cubic.

The susceptibilities of the  $Mn^{++}:ZnS$  crystals show considerable deviations from Curie's Law as is evident from Fig. 1. Since the curvatures of the graphs increase with the concentration of the  $Mn^{++}$  ions, it is suggested that the exchange coupling between the neighboring  $Mn^{++}$  ions could be responsible for the nonlinear dependence of  $\chi$  on  $1/T$ . In fact, the qualitative features of Fig. 1 can be explained readily in terms of the exchange coupling. At very high temperature the exchange effect is completely overpowered by the thermal energy; all the  $Mn^{++}$  ions contribute to the total magnetic moment of the sample. When the temperature becomes sufficiently low, the antiferromagnetic coupling of the two neighboring  $Mn^{++}$  ions produces essentially a net zero magnetic moment for the ion pair with the result of a decrease of the total susceptibility. Upon plotting  $\chi$  against  $1/T$ , we may expect to start with a straight line with a slope corresponding to the magnetic moment at

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<sup>1</sup> J. Owen, *J. Appl. Phys.* **32**, 213S (1961); **33**, 355 (1962).

<sup>2</sup> B. S. Coles, J. W. Orton, and J. Owen, *Phys. Rev. Letters* **4**, 116 (1960).

<sup>3</sup> J. H. E. Griffiths, J. Owen, J. G. Park, and M. F. Partridge, *Proc. Roy. Soc. (London)* **A250**, 84 (1959).

<sup>4</sup> A. L. Schawlow, *J. Appl. Phys.* **33**, 395 (1962).

<sup>5</sup> D. S. McClure, *J. Chem. Phys.* **39**, 2850 (1963).

<sup>6</sup> A. H. Cooke, R. Lazenby, F. R. McKim, J. Owen, and W. P. Wolf, *Proc. Roy. Soc. (London)* **A250**, 97 (1959).

<sup>7</sup> A. Danielian and K. W. H. Stevens, *Proc. Phys. Soc. (London)* **A77**, 124 (1961).

<sup>8</sup> W. H. Brumage, C. R. Quade, and C. C. Lin, *Phys. Rev.* **131**, 949 (1963); W. H. Brumage, C. C. Lin, and J. H. Van Vleck, *Phys. Rev.* **132**, 608 (1963).

<sup>9</sup> R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Vol. 1, Table III, 10.

<sup>10</sup> H. A. Weakliem, *J. Chem. Phys.* **36**, 2117 (1962).

<sup>11</sup> D. S. McClure (private communication).

<sup>12</sup> W. Low, *Paramagnetic Resonance in Solids, Solid State Physics Suppl.* **2** (Academic Press Inc., New York, 1960), p. 118.

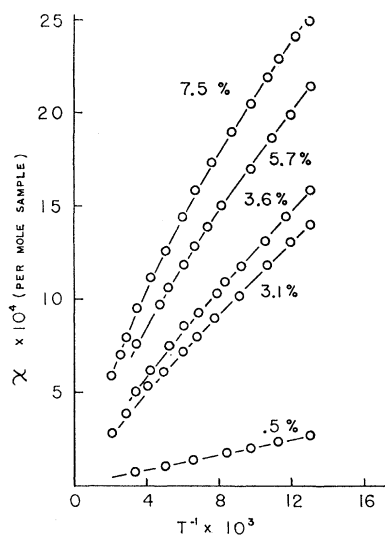


FIG. 1. Magnetic susceptibility versus  $1/T$  from 77–500°K. The circles denote the experimental points and the solid curves give the theoretical values.

high temperature. The slope then gradually decreases until it reaches the limiting low-temperature value.

To put this idea on a more quantitative basis, we shall first assume that the numbers of clusters of various types are determined statistically by assuming a random distribution. In Fig. 3 is shown the percentage distributions of the single ions, pairs, and triples as functions of the total  $Mn^{++}$  concentration in the ZnS crystal. The coupling between two  $Mn^{++}$  in the nearest-neighbor cation positions is taken to be of the usual form

$$-2J(\mathbf{s}_1 \cdot \mathbf{s}_2), \quad (1)$$

where  $\mathbf{s}_1$  and  $\mathbf{s}_2$  are the spins of the two ions. The anisotropic exchange term is presumably much smaller<sup>1-3</sup> and will be neglected, because the small splittings associated with the anisotropic interactions do not affect the susceptibilities significantly. The same isotropic exchange Hamiltonian was also used by McClure to explain the special features of the optical spectra of these crystals.<sup>5</sup> We have further assumed that the exchange coupling constant for the next-nearest-neighbor cations ( $J_{nnn}$ ) is zero. Thus, for the triples where all three cations are

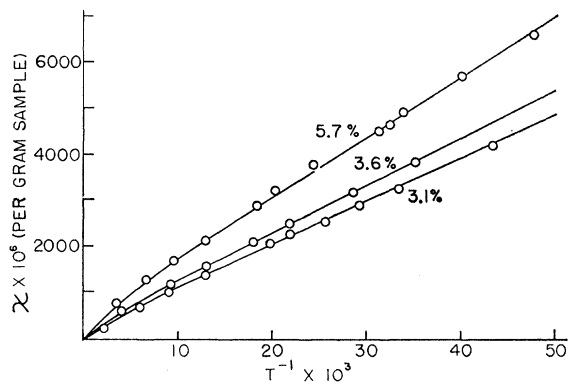


FIG. 2. Magnetic susceptibility versus  $1/T$  from 20 to 500°K. The circles denote the experimental points and the solid curves give the theoretical values.

equivalent, the exchange Hamiltonian is

$$-2J(\mathbf{s}_1 \cdot \mathbf{s}_2 + \mathbf{s}_2 \cdot \mathbf{s}_3 + \mathbf{s}_3 \cdot \mathbf{s}_1), \quad (2)$$

while the exchange term for a cluster of three non-equivalent neighbor ions has the form

$$-2J(\mathbf{s}_1 \cdot \mathbf{s}_2 + \mathbf{s}_2 \cdot \mathbf{s}_3). \quad (3)$$

The question of the magnitude of the next-nearest-neighbor interaction is an interesting one. For  $Mn^{++}$ :MgO it was found that  $J_{nnn}$  is of the same order of magnitude as  $J_{nn}$ .<sup>1</sup> At first thought, one might expect similar results for  $Mn^{++}$ :ZnS. However, the difference between these two cases lies on the structure of the host

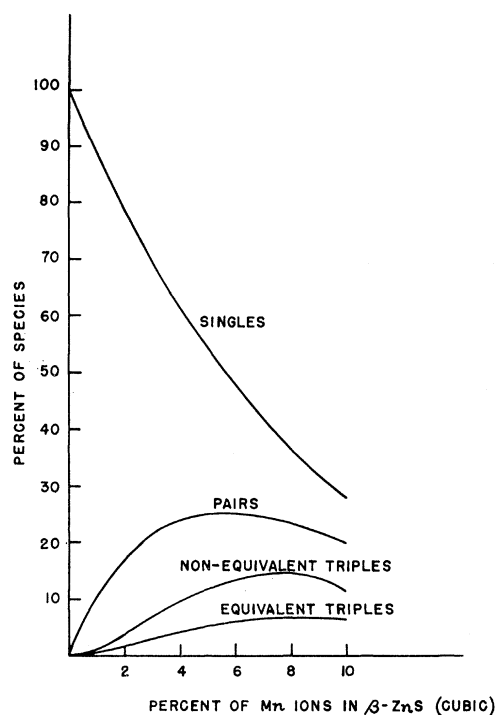
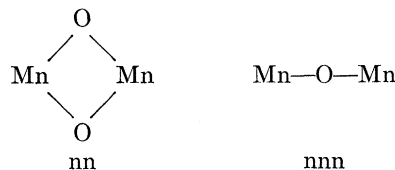
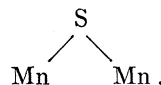


FIG. 3. Percentage distribution of the various species in  $Mn^{++}$ :ZnS crystals.

crystals. In  $Mn^{++}$ :MgO (octahedral) there are two kinds of "pairs" which are designated as "nearest-neighbor" and "next-nearest neighbor" in the following way:



The two nnn ions are separated by only one oxygen ion. For  $Mn^{++}$  in ZnS, the nn configuration is of the form



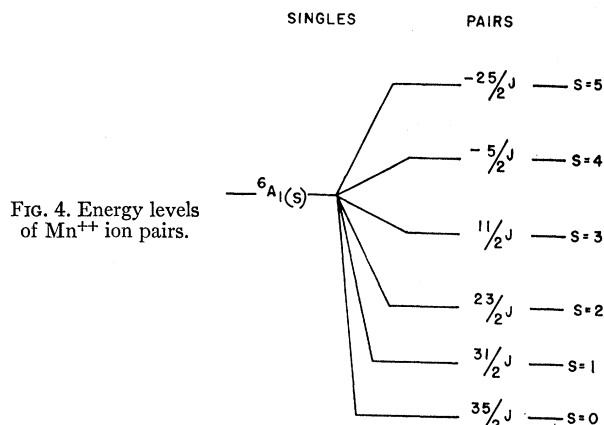


FIG. 4. Energy levels of  $Mn^{++}$  ion pairs.

whereas between two  $Mn^{++}$  ions in the next-nearest-neighbor cation sites, there are two intervening  $S^=$  and one  $Zn^{++}$  ions. One should then expect  $J_{nnn}$  to be much smaller than  $J_{nn}$  in the case of  $Mn^{++}:ZnS$ . The same sort of assumption was used by Danielian and Stevens.<sup>7</sup> They suggested that  $J_{nnn} \ll J_{nn}$  for  $\beta$ -MnS (zincblende structure), but  $J_{nnn} > J_{nn}$  for the  $\alpha$  form (NaCl structure). Furthermore, for crystals with less than 5.7% paramagnetic impurities, the nonequivalent triples give a relatively small contribution to the total susceptibility, thus omission of the next-nearest-neighbor coupling will not lead to a significant errors in the calculation of the susceptibilities.

With this model the magnetic susceptibilities can be calculated readily. The magnetic moment of the single ions is, of course, given by the "spin-only" formula. A  $Mn^{++}$  pair is regarded as two ions, each with  $s = \frac{5}{2}$ , coupled through the exchange operator in (1). For a given  $Mn^{++}$ , only the ground state  ${}^6A_1(S)$  need be considered as far as magnetic properties are concerned. The spins of the two ions in a pair then couple to form the total spin  $S$  which is capable of an integral value between 0 and 5. The energy levels of an ion pair are shown in Fig. 4. The magnetic susceptibilities are now calculated from the standard formula<sup>13</sup> by summing over the manifold of energy levels from  $S=0$  to  $S=5$ . A similar procedure can be used to calculate the susceptibilities of the triples. Here we must distinguish the equivalent triples from the nonequivalent ones since different coupling Hamiltonians must be used for these two types of clusters. For clusters containing four or more  $Mn^{++}$  ions, no detailed calculations have been made; rather, they are assumed to have the same magnetic susceptibility as the pairs (per ion). In view of the extremely low concentration of the quartets and quintets, etc., the errors entailed in this step should be quite small. A

breakdown of the contributions to the total susceptibility from the various types of clusters is shown in Table I.

TABLE I. Magnetic susceptibilities contributed by the various types of clusters for ZnS containing 5.7%  $Mn^{++}$ .

Type of clusters	Magnetic susceptibilities per g-ion of $Mn^{++}$ impurity in units of $10^{-3}$ cgs-emu.					
	20°K	60°K	100°K	200°K	300°K	500°K
Single ions (49.4%)	108.2	36.1	21.6	10.8	7.21	4.33
Pairs (25.2%)	3.76	4.50	4.46	3.55	2.77	1.88
Equivalent triples (5.7%)	0.98	0.93	0.82	0.63	0.51	0.37
Nonequivalent triples (12.7%)	9.20	3.40	2.44	1.69	1.31	0.90
Others (7.0%)	1.04	1.25	1.23	0.98	0.77	0.52

It is possible to fit the experimental data to the theoretical susceptibilities for all the crystals by choosing  $J$  as anywhere from  $-8$  to  $-10$   $cm^{-1}$ , although  $J = -9$   $cm^{-1}$  gives a slightly better fit. This result is in good agreement with that of McClure.<sup>5</sup> The concentrations of the impurity ions ( $Mn^{++}$ ) in the crystals are treated as adjustable parameters in our analysis as was done in the magnetic studies of  $V^{+3}$  in corundum.<sup>8</sup> The calculated susceptibilities are shown as solid curves in Figs. 1 and 2. The agreement between theory and experiment is quite satisfactory, particularly in view of the simple model used in the calculations.

Harris and Owen<sup>14</sup> have recently suggested that there is an appreciable biquadratic contribution of the form  $2j(\mathbf{s}_1 \cdot \mathbf{s}_2)^2$  to the exchange between two  $Mn^{++}$  pairs in  $MgO$ , in addition to the usual bilinear term  $-2J(\mathbf{s}_1 \cdot \mathbf{s}_2)$ . Unfortunately, it is difficult to determine the magnitude of the biquadratic exchange in  $Mn^{++}:ZnS$  from the susceptibility data, since a good agreement between the theory and experiment can be gotten with the bilinear term alone. Upon introducing the biquadratic term, we can slightly improve the data fitting by choosing  $J = -7$  and  $j/J = 0.02$ . However, these results have little quantitative significance since the calculated susceptibilities are not very sensitive to the parameter  $j$ . Our conclusion is that the magnetic measurements of the various  $Mn^{++}:ZnS$  crystals studied in this work can be explained satisfactorily by assuming an exchange term  $-2J(\mathbf{s}_1 \cdot \mathbf{s}_2)$  between two neighboring  $Mn^{++}$  ions with  $J \approx -9$   $cm^{-1}$ .

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<sup>13</sup> J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 182.

<sup>14</sup> E. A. Harris and J. Owen, *Phys. Rev. Letters* **11**, 9 (1963).