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Paramagnetic Susceptibilities of Solid Solutions of MnF_2 and ZnF_2*

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The paramagnetic susceptibilities of solid solutions of MnF_2 and ZnF_2 have been measured as a function of temperature. The Curie-Weiss law $X=C/T+\Delta$ is obeyed by all the solutions examined over the temperature range 76°–295°K. The constant Δ was found to be a linear function of the mole fraction of MnF_2. This behavior is consistent with the assumption that the magnetic interaction energy associated with a given ion is proportional to the number of its paramagnetic neighbors.

THE existence of exchange forces in paramagnetic salts has been inferred from the fact that a large number of substances have magnetic susceptibilities which follow the Curie-Weiss law

$$X=C/(T+\Delta).$$

An attempt has been made to study the magnetic behavior of a paramagnetic salt as it is diluted with an isomorphous diamagnetic salt, since the interaction effects presumably responsible for the Δ term should disappear on sufficient dilution.[1]

The system chosen was manganous fluoride, MnF_2, and zinc fluoride, ZnF_2. The manganous ion, Mn^{++}, which is responsible for the paramagnetism, is in a ${}^6S_{5/2}$ ground state, and to a first approximation the susceptibility of its salts should not show a crystalline field effect.[2] It is also to be noted that the electrical environment of the Mn^{++} ion is substantially unchanged when MnF_2 is diluted with ZnF_2. These two compounds have the rutile structure. Each metal ion is surrounded octahedrally by fluoride ions in the first coordination zone and by ten other metal ions in the second zone. The lattice dimensions of the two salts differ by only three percent.

The magnetic susceptibility of manganous fluoride has been reported by Bizette and Tsai[3] to follow a Curie-Weiss law. It has also been measured by De Haas, Schultz, and Koolhaas[4] who found some deviation from this law. The results reported here are based on measurements made with C.P. materials which were analyzed chemically and spectroscopically, particularly for paramagnetic impurities; none of which were found in significant concentration. The magnetic susceptibilities agree with those obtained with a sample of manganous fluoride kindly given by Dr. Stout and Dr. Griffel at the Institute of Metals, the University of Chicago. The results of the various investigations are shown in Fig. 1.

Samples of C.P. MnF_2 and C.P. ZnF_2 were weighed out, intimately mixed, and fused in a closed platinum crucible inside a nickel reaction vessel. An atmosphere of anhydrous HF was maintained in the container. The fused mixtures were ground to fine powders for the magnetic measurements, which were made by the Gouy method. X-ray powder photographs were taken, and the fused samples were determined to be homogeneous in composition and to have lattice spacings which obeyed Vegard's rule.

Magnetic susceptibilities were measured at liquid nitrogen, dry ice, and room temperatures. Three or more samples of each composition were used and the data averaged with an average deviation of ± 1 percent. The results are shown in Fig. 2. The dotted line passing through the origin in the graph is calculated for the free ion, and represents the situation approached by manganous fluoride on dilution with zinc fluoride.

From the susceptibility data were calculated values of the Curie constant C, the magnetic moment μ, and

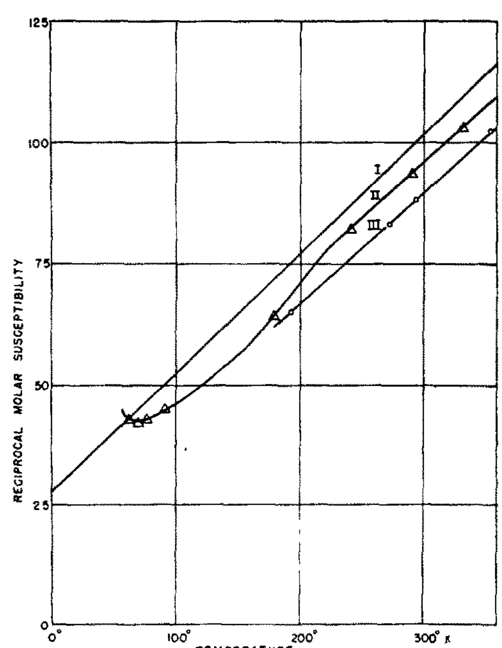

FIG. 1. Magnetic susceptibility of MnF_2 as a function of temperature. I. Bizette and Tsai (empirical formula); II. De Haas, Schultz and Koolhaas; III. Corliss, Delabarre and Elliott.

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[1] For other experiments see P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York), pp. 89, 110; and Michel and Pouillard, Comptes Rendus **227**, 194 (1948).

[2] For a discussion of the effect of crystal fields on magnetic behavior see J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, London, 1932), p. 286. Application of the theory to magnetically dilute manganous salts is given by J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

[3] H. Bizette and B. Tsai, Comptes Rendus **209**, 205 (1939).

[4] De Haas, Schultz, and Koolhaas, Physica **VII**, No. 1, 57 (1940).

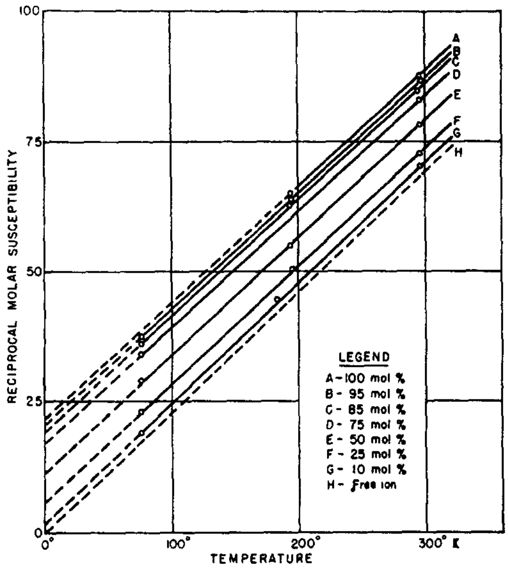

FIG. 2. Magnetic susceptibility of MnF_2 as a function of temperature and concentration (Mole percent MnF_2).

the paramagnetic Curie temperature Δ. These are given in Table I.

The magnetic moments found are in good agreement with the calculated value, 5.92 Bohr magnetons for the $^6S_{\frac{5}{2}}$ state.

In Fig. 3 the paramagnetic Curie temperatures are plotted against the mole percent of MnF_2 in the samples. Except for a small deviation in the neighborhood of pure MnF_2, the experimental curve is linear and passes through the origin. These results suggest a simple and admittedly naive interpretation. Let us assume that the exchange interaction energy for any one Mn^{++} ion is proportional to the number of nearest neighbors. This is analogous to Stoner's approximation in the theory of ferromagnetism.[5] We can then divide the Mn^{++} ions into groups having 0, 1, $\cdots z$ nearest neighbors ($z=10$ in this case). The average value of Δ will then be given by

$$\bar{\Delta}=\sum_{k=0}^{k=z} f_k k\delta,$$

where f_k is the fraction of the Mn^{++} ions having k Mn^{++} nearest neighbors and δ represents the contribution to the total Δ of one of the equivalent nearest neighbors. The fraction f_k is the probability that a given Mn^{++} ion will have k nearest neighbor positions occupied by Mn^{++} ions and $z-k$ positions occupied by Zn^{++} ions. Thus,

$$f_k=\frac{z!}{k!(z-k)!}x^k(1-x)^{z-k},$$

where x is the mole fraction of MnF_2. From this in turn it follows by direct summation that

$$\bar{\Delta}=xz\delta=x\Delta_{\text{pure MnF}_2}$$

which is the desired relationship.

We wish to thank Dr. Bigeleisen, Dr. Freed, Mr. Slavin, and Dr. Stoenner for their help during the course of this experiment.

[5] Edmund C. Stoner, *Magnetism and Matter* (Methuen and Co. Ltd., London), p. 358

TABLE I

Mole % MnF_2	C	Δ	μ (Bohr Magnetons)
5%	4.33	5.5°K	5.90
10%	4.33	9.5°	5.90
25%	4.40	25.5	5.95
50%	4 40	49.5	5.95
75%	4.47	76.5	5.98
85%	4.47	85.0	5.98
95%	4.47	93.0	5.98
100%	4.47	97.0	5.98

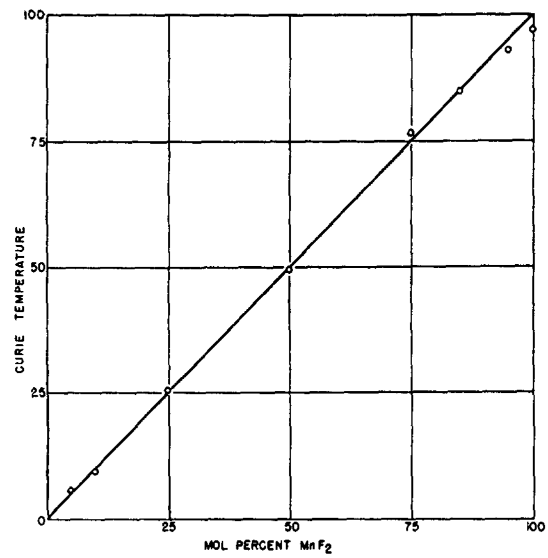

FIG. 3. Paramagnetic Curie temperature as a function of molar concentration of MnF_2.