MAGNETIC SUSCEPTIBILITY OF MnF_2

Charles Trapp* and J. W. Stout
Department of Chemistry and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois
(Received 3 December 1962)

MnF_2 has been much investigated as an example of a substance exhibiting simple antiferromagnetic behavior.[1] At low temperatures the properties of an antiferromagnet are described in terms of spin-wave theory.[2-10] Measurements of the antiferromagnetic resonance[11,12] of MnF_2 give evidence for the existence of an energy gap in the spin-wave spectrum, and measurements of the fluorine nuclear resonance[13,14] show the temperature variation of the sublattice magnetization. None of the reported measurements of the magnetic susceptibility[15-18] of MnF_2 at low temperatures are sufficient to demonstrate the behavior of the susceptibilities parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to the axis of spin alignment which is predicted by spin-wave theory. Indeed, it has been suggested[19] that interaction with the lattice vibrations may significantly alter the temperature dependence of $\chi_{\parallel}$ and $\chi_{\perp}$.

We have made precise measurements of $\chi_{\parallel}$ and $\chi_{\perp}$ of MnF_2 between 1 and 300°K. The method used is an adaptation of that used by Arrott and Goldman[20] and is described fully elsewhere.[21] The single-crystal specimens were in the form of right circular cylinders, 0.76 cm in diameter and about 0.7 cm long, with the cylinder axis parallel or perpendicular to the tetragonal axis of the crystal. A current in a null coil of No. 40 copper wire wound on the surface of the cylinder serves to cancel at all exterior points the field produced by the magnetization of the sample which is in the uniform magnetic field of a solenoid. The current through the null coil is varied until no signal is observed when the sample and null coil are moved together between two detection coils connected to a photoelectric galvanometer. The method permits exact correction for demagnetization effects. A calculated correction of 0.1% is made for the noncoincidence of the null coil and the surface of the sample arising from the thickness of the copper wire. From the mass of the sample, the magnetic field of the solenoid, the experimentally measured turn area of the null coil, and the current required for the null, the magnetic susceptibility may be calculated. The sensitivity of the method is such that in the temperature range below 73°K the precision of the measurements is 0.05% or 5×10^{-6} cm^3 $mole^{-1}$, whichever is larger. Considerations of the accuracy of calibrations of the solenoid field and turn areas of null coils lead to an estimate of 0.2% or 10^{-5} cm^3 $mole^{-1}$ for the absolute probable error.

At 1°K, $\chi_{\perp}$ is 0.02524 ± 0.00005 cm^3 $mole^{-1}$. The change between 1 and 4.2°K is less than 0.1%; but above 4.2°K, $\chi_{\perp}$ decreases more rapidly, dropping by 1.9% to a minimum near 45°K. $\chi_{\perp}$ then increases, reaching a broad maximum near 69°K, where the susceptibility is 0.3% larger than its value at 1°K, and then decreases monotonically as the temperature rises. The drop in $\chi_{\perp}$, which has not been observed previously, was predicted by Kubo[3] in his "second approximation" spin-wave calculation. Ziman,[4] on the other hand, predicted that $\chi_{\perp}$ should be strictly independent of temperature. In Fig. 1 are shown our measured values of $\chi_{\perp}$ in the temperature range 1-20.4°K. Also shown are curves calculated from Kubo's formula and from a semiempirical method used by Kanamori and Tachiki.[10] These authors

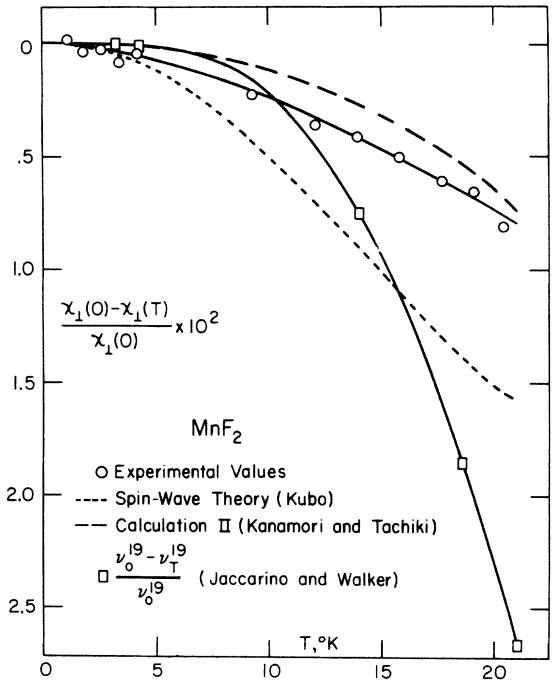

FIG. 1. Temperature variation of the perpendicular magnetic susceptibility (plotted as circles) and the sublattice magnetization (plotted as squares) of MnF_2. The dashed curves are theoretical calculations discussed in the text.

used experimental values of the magnetic heat capacity[22] and sublattice magnetization[14] of MnF_2, together with relations between these quantities and $\chi_\perp$ given by spin-wave theory, to calculate the temperature variation of $\chi_\perp$. The agreement of our measurements with this semiempirical calculation is good. Also shown in Fig. 1 is the temperature variation of the sublattice magnetization as determined experimentally by Jaccarino and Walker.[14] The sublattice magnetization drops much more rapidly with increasing temperature than does $\chi_\perp$.

The Hamiltonian for the exchange interactions is $H = -2\sum J_{ij}\vec{S}_i \cdot \vec{S}_j$. Let J_2 be the interaction between a Mn^{++} atom on one sublattice and its eight neighbors ($z_2 = 8$) on the opposite sublattice, and J_1 be the interaction between an atom and its two neighbors ($z_1 = 2$) on the same sublattice. The perpendicular susceptibility at very low temperatures is given by spin-wave theory (first part of reference 3) as

$$\chi_\perp = Ng^2\beta^2(1 - 0.112S^{-1})(4z_2|J_2| + 2K)^{-1}$$

and the antiferromagnetic resonance frequency, ν, by $(h\nu)^2 = 2Ng^2\beta^2KS^2(\chi_\perp)^{-1}$. Here K is the anisotropy constant; $S = \frac{5}{2}$ and $g = 2.00$ for Mn^{++}; and the other symbols have their usual meaning. By use of our value for $\chi_\perp$ at 1°K and the low-temperature antiferromagnetic resonance frequency, $\nu = 2.146 \times 10^{11}$ sec^{-1}, measured by Johnson and Nethercot,[11] one calculates for MnF_2, $J_2 = -1.76k$ and $K = 0.212k$. Eisele and Keffer[6] have written Kubo's[3] expression for the parallel susceptibility in the convenient form

$$\chi_{\parallel} = \tfrac{1}{6}Ng^2\beta^2(kT)^2(z|J|S)^{-3}\chi(T/T_{AE}).$$

The factor $\chi(T/T_{AE})$, which goes exponentially to zero at low temperatures, arises because the anisotropy introduces an energy gap, kT_{AE}, in the spin-wave spectrum. $\chi_{\parallel}$ then drops below the T^2 dependence which it would have in the absence of anisotropy. At 1.16°K the measured parallel susceptibility of MnF_2 is diamagnetic, $\chi_{\parallel} = -(1.6 \pm 1.0) \times 10^{-5}$ cm^3 mole^{-1}. The estimated diamagnetic contribution to the susceptibility is -3.8×10^{-5} cm^3 mole^{-1}, and there is a negligible contribution, $0.2 \times 10^{-5}\, T^{-1}$ cm^3 mole^{-1}, from the nuclear paramagnetism. The remaining contribution to $\chi_{\parallel}$ at 1.1°K, about 2×10^{-5} cm^3 mole^{-1}, is ascribed to the Van Vleck temperature-independent paramagnetism. In order to correct for the diamagnetism and temperature-independent paramagnetism we have subtracted from the observed parallel susceptibilities the value at 1.16°K. In Fig. 2 are plotted the measured values of $\chi_{\parallel} \times 10^6 + 16$ divided by T^2. The half-height of the vertical lines drawn through the points in the helium temperature range corresponds to the estimated precision of 0.5×10^{-5} cm^3 mole^{-1}. The solid line in Fig. 2 is $\chi_{\parallel}T^{-2}$ calculated from the Eisele and Keffer formula[6] with $8J_2 = -14.1k$, determined from $\chi_\perp$, and $T_{AE} = 12.54$°K. From the Néel temperature of 67°K one calculates, in the molecular field approximation,[1] $zJ = 8J_2 - 2J_1 = -11.5k$. The dashed curve in Fig. 2 is $\chi_{\parallel}T^{-2}$ calculated from the Eisele and Keffer formula with $z|J| = 11.5k$ and $T_{AE} = 12.54$°K. The antiferromagnetic resonance measurements[11,12] show that T_{AE} decreases with rising temperature. If one uses the observed temperature-dependent values of T_{AE} in the Eisele and Keffer formula, the curves in Fig. 2 are raised by one percent at 20°K and 0.5% at 14°K.

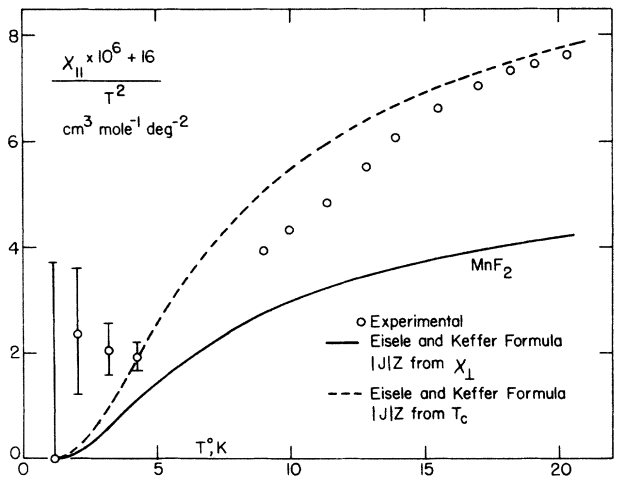

FIG. 2. Comparison of the parallel magnetic susceptibility of MnF_2 with spin-wave calculations (see text).

The observed behavior of $\chi_{\parallel}T^{-2}$ corresponds to that predicted by spin-wave theory and is evidence for the existence of an energy gap in the spin-wave spectrum. In order to obtain quantitative agreement, the value of $z|J|$ determined from $\chi_\perp$ must be decreased by about 20%. Kanamori and Tachiki[10] have found a similar reduction of $z|J|$ is necessary in order to fit the sublattice magnetization measurements[14] to a spin-wave calculation. The necessary reduction in $z|J|$ would be obtained with an antiferromagnetic interaction between neighbors on the same sublattice, $J_1 = -1.3k$. From our susceptibility data extending to room temperature, we estimate that the limiting high-temperature value of the Weiss constant for MnF_2 is $\theta = 82$°K. The

value calculated from molecular field theory with $J_1 = 0$ and $J_2 = -1.76k$ is 82°K, whereas with $J_1 = -1.3k$ and $J_2 = -1.76k$ a θ value of 97°K is obtained. From paramagnetic resonance measurements on dilute solid solutions of MnF_2 in ZnF_2, Owen, Brown, Coles, and Stevenson[23] have concluded that J_1 is ferromagnetic and equal to $(0.2 \pm 0.1)k$ which within experimental error is consistent with our limiting Weiss θ but not with the value of $J_1 = -1.3k$ inferred from the low-temperature values of $\chi_{\|}$. The reason for this discrepancy is not clear.

We thank Professor J. Kanamori of Osaka University and Professor F. Keffer of the University of Pittsburgh for illuminating correspondence and Mr. Stanley Reed for growing the single crystals of MnF_2. This research was supported in part by the National Science Foundation and by the Office of Naval Research.

*National Science Foundation predoctoral Fellow, 1959-62.

[1]See T. Nagamiya, K. Yosida, and R. Kubo, Suppl. Phil. Mag. 4, 1 (1955) for a review of antiferromagnetism.
[2]P. W. Anderson, Phys. Rev. 86, 694 (1952).
[3]R. Kubo, Phys. Rev. 87, 568 (1952); Rev. Modern Phys. 25, 344 (1953).
[4]J. M. Ziman, Proc. Phys. Soc. (London) A65, 540, 548 (1952).
[5]J. R. Tessman, Phys. Rev. 88, 1132 (1952).
[6]J. A. Eisele and F. Keffer, Phys. Rev. 96, 929 (1954).
[7]J. Kanamori and K. Yosida, Progr. Theoret. Phys. (Kyoto) 14, 423 (1955).
[8]T. Oguchi, Phys. Rev. 111, 1063 (1958); 117, 117 (1960).
[9]F. Keffer and R. Loudon, Suppl. J. Appl. Phys. 32, 2S (1961).
[10]J. Kanamori and M. Tachiki, J. Phys. Soc. Japan 17, 1384 (1962).
[11]F. H. Johnson and A. H. Nethercot, Jr., Phys. Rev. 114, 705 (1959).
[12]S. Foner, Phys. Rev. 107, 683 (1957).
[13]V. Jaccarino and R. G. Shulman, Phys. Rev. 107, 1196 (1957).
[14]V. Jaccarino and L. R. Walker, J. Phys. Radium 20, 341 (1959).
[15]H. Bizette and B. Tsai, Compt. Rend. 209, 205 (1939); 238, 1575 (1954).
[16]W. J. de Haas, B. H. Schultz, and J. Koolhaas, Physica 7, 57 (1940).
[17]M. Griffel and J. W. Stout, J. Chem. Phys. 18, 1455 (1950).
[18]S. Foner, J. Phys. Radium 20, 336 (1959).
[19]P. Pincus and J. Winter, Phys. Rev. Letters 7, 269 (1961).
[20]A. Arrott and J. E. Goldman, Rev. Sci. Instr. 28, 99 (1957).
[21]C. L. Brandt, Ph.D. thesis, University of Chicago, 1959 (unpublished).
[22]J. W. Stout and E. Catalano, J. Chem. Phys. 23, 2013 (1955).
[23]J. Owen, M. R. Brown, B. A. Coles, and R. W. H. Stevenson, Suppl. J. Phys. Soc. Japan 17, 428 (1961).

EFFECT OF CORRELATION ON THE FERROMAGNETISM OF TRANSITION METALS

Martin C. Gutzwiller
Research Laboratory Zurich, International Business Machines Corporation, Rüschlikon ZH, Switzerland
(Received 27 September 1962)

The purpose of this Letter is to present a new approach to the problem of ferromagnetism in a metal. A correlated wave function for the electrons in the $3d$ band is proposed as approximation to the ground state. The expectation value of the energy is evaluated by diagram techniques. The simplest example of a face-centered cubic structure (whose density-of-states curve is parabolic at the bottom and has a peak at the top) is discussed. Under these assumptions the arguments show that the ferromagnetic state is lower if the band is nearly full, whereas the nonmagnetic state has the lower energy if the band is nearly empty.

The main attempt so far to explain ferromagnetism in metals is based on the collective electron theory of ferromagnetism,[1] in which both the magnetic and the nonmagnetic ground states are assumed to be antisymmetrized products of Bloch functions. The expectation value of the energy in the nonmagnetic state contains a large term which is due to the repulsion of two electrons of opposite spin at the same lattice site. Slater,[2] in particular, pointed out that this term should be reduced by considering correlated wave functions before the effects of exchange are discussed. The collective electron theory fails especially in the limit of large spacing between the lattice sites, a situation comparable to that of the relatively tight $3d$ levels in the transition metals.

The present model is an attempt to deal with