

exponent analysis. Present accuracy does not warrant such an attempt as has been tried for $d\rho/dT$.^{5,9,11}

We wish to acknowledge helpful discussions with Dr. D. J. W. Geldart and N. H. Sze, and are grateful to the National Research Council of Canada for a grant in aid to this research.

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¹⁴We are aware that, in general, anomalies due to T_N in nonmagnetic physical properties (such as specific heat, thermal expansion, temperature coefficient of resistivity, etc.) will not be located exactly at T_N because of the effect of a tail in the spontaneous magnetization curve persisting for $T > T_N$. This is especially true of strained or alloyed specimens {K. P. Belov and Ya. Paches, Fiz. Metal. i Metalloved. **4**, 48 (1957) [translation: Phys. Metals Metallog. (USSR) **1**, 35 (1957)]; A. V. Voronel, S. R. Garber, A. P. Simkina, and I. A. Charkina, Zh. Eksperim. i Teor. Fiz. **49**, 429 (1965) [translation: Soviet Phys.—JETP **22**, 301 (1966)]}. However such effects are quite small in annealed pure-metal samples and are likely to be small in the present case as the near coincidence of the susceptibility and $d\rho/dT$ anomalies shows.

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TEMPERATURE DEPENDENCE OF THE WIDTH AND g FACTOR OF A PURELY ELECTRONIC OPTICAL TRANSITION IN MnF_2 †

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(Received 4 June 1969)

We report thermal broadening of the 18418-cm^{-1} purely electronic transition in MnF_3 split by an external magnetic field of 25 kOe. A differential broadening of the split line is observed, demonstrating the important role of Raman scattering of magnons as a mechanism for broadening this optical line at low temperatures. A temperature-dependent reduction of the effective g factor is also observed. Calculations based on a simple model give satisfactory agreement with the observations.

Previous work^{1,2} in zero external field has shown Raman scattering of magnons to be an important factor in the shift and broadening of optical lines in antiferromagnetic crystals at low temperatures. We report here results for the 18418-cm^{-1} [$A_1 \rightarrow {}^4T_1(A_1G)$] purely electronic transition in MnF_2 split by an external magnetic field of 25 kOe.

The temperature-dependent renormalization of magnon energies³ and magnon g factors⁴ in antiferromagnets has been the subject of several recent studies. The renormalization of the g factor in antiferromagnetic resonance has been well established for some time.^{5,6} To our knowledge this Letter reports the first observation of a temperature-dependent reduction of the effective g factor

for the external-magnetic-field splitting of purely electronic optical transitions in antiferromagnetic insulators.

The spectra were photoelectrically recorded using a 1-m Czerny-Turner scanning spectrometer. The temperature was measured by monitoring the resistance of a carbon resistor calibrated against the vapor pressures of neon, hydrogen, and helium which span the temperature range of the experiment. At temperatures where thermal broadening caused considerable overlap of the halves of the split line, the separation and other parameters of the lines were obtained by fitting the absorption curves to Lorentzian line shapes using a nonlinear least-squares-fitting routine on a computer.

An external magnetic field aligned along the c axis of MnF_2 causes ions on opposite sublattices to experience opposite Zeeman energy shifts lifting the sublattice degeneracy of the purely electronic optical transitions. The low-temperature splitting of the transition studied for two crystals used in this work was found to be in good agreement with that previously reported.⁷ An external field of 25 kOe also introduces a gap of 6.67°K between the magnon branches which are degenerate in the absence of the field. Since short-wavelength magnons are confined principally to one sublattice,⁸ we might expect the magnon populations to be somewhat different for the two sublattices in the 15 to 30°K range.

The thermally induced full widths at half-maximum absorbance of the two halves of the split line are given in Fig. 1 as a function of temperature. The width of the zero-field line for our crystals was found to agree closely with that previously reported.¹ Ions with a positive Zeeman energy, whose absorption is observed as the higher energy peak of the split line, sense mainly the larger magnon population of the opposite sublattice which has a negative Zeeman energy. It can be seen in Fig. 1 that the higher energy peak

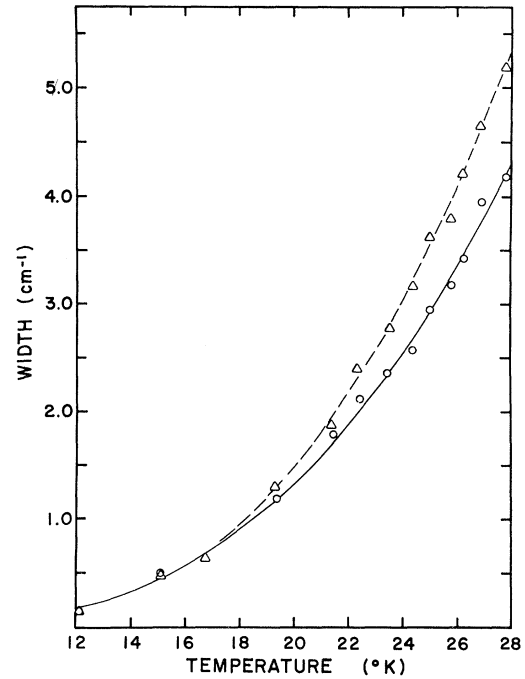


FIG. 1. Full width at half-maximum absorbance versus temperature of the higher (open triangles) and lower (open circles) energy peaks of the 18418-cm⁻¹ line of MnF_2 at 25-kG external magnetic field.

experiences the more severe broadening, as would be expected. This difference in broadening for the absorption of ions on the two sublattices clearly demonstrates the important role of Raman scattering of magnons in the thermal broadening of this optical transition at low temperatures.

The broadening caused by Raman scattering of magnons may be calculated by considering the optically excited ion essentially as an impurity interacting with its nearest neighbors on the opposite sublattice via the Heisenberg exchange Hamiltonian. Upon expanding the spin operators of the neighbor ions in terms of magnon operators, the first-order contribution to the broadening in zero external field is found to be

$$\Gamma(T) = A^2 G(T) = A^2 8 \pi J^2 Z^2 \sum_{k, k'} \frac{\gamma(k-k') (U_k^2 U_{k'}^2 + V_k^2 V_{k'}^2) \exp(E_k/k_B T) \delta(E_k - E_{k'})}{[\exp(E_k/k_B T) - 1.0]^2}, \quad (1)$$

where Z is the number of nearest neighbors on the other sublattice, J is the ground-state exchange integral, U_k and V_k are the coupling coefficients of the sublattice magnons, and A is equal to $S_f - (J_f/J_i)S_f$, approximating the excited state as a pure spin state. The exchange integral when one ion is in the optically excited state is design-

ated as J_f . We have used the usual definition of $\gamma(k)$ which for MnF_2 is equal to

$$\gamma(k) = \cos \frac{1}{2} k_x a \cos \frac{1}{2} k_y a \cos \frac{1}{2} k_z c, \quad (2)$$

where a and c represent the width and height of the unit cell, respectively.

The quantity $\gamma(k-k')$ is near unity for small values of the argument and for energy-conserving scattering processes at all points of high symmetry on the surface of the Brillouin zone. Since these points make the major contributions to the available scattering states we may take $\gamma(k-k')$ as unity and convert the sums of Eq. (1) to an integral over energy, making use of the available magnon density of states for MnF_2 .⁹

Calculations carried out in this manner show the broadening to be heavily dominated by zone-edge magnons supporting our approximation of $\gamma(k-k')$ as unity. The transverse part of the Hamiltonian contributes to the broadening in second order in this model as a product with $\gamma(k)\gamma(k')$ which is zero on the zone surface, and hence these terms may be neglected in MnF_2 .

A result of the calculations is shown in Fig. 2 in which the experimental width in zero external field corrected for intrinsic width is plotted against the computed $G(T)$. The agreement is seen to be good with the slope corresponding to J_f/J_i equal to 1.3 in agreement with the previous determination.¹

Similar calculations including an external magnetic field predict a difference in broadening for ions on opposite sublattices slightly larger than our observations, indicating widths of 5.7 and 4.3 cm^{-1} at 28°K compared with observed values of 5.35 and 4.3 cm^{-1} . The satisfactory agreement of our calculations and observations leads us to conclude that the broadening of this line is dominated by magnon-scattering effects at low temperatures.

The splitting of this line in an external magnetic field is observed to decrease as the crystal is

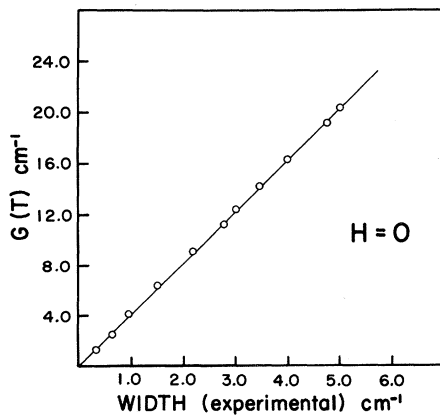


FIG. 2. Calculated versus experimental width of the 18418- cm^{-1} line of MnF_2 in zero external field. Experimental values are corrected for intrinsic width equal to that measured at 1.5°K.

warmed from liquid-helium temperatures. The physical origin of this effect may be seen by considering the optically active ion in a simple two-sublattice antiferromagnet in interaction with the external magnetic field and the exchange field of its nearest neighbors on the opposite sublattice. At a nonzero temperature the external field increases the magnetization of one sublattice and decreases that of the other as well as lifting the sublattice degeneracy of the pure electronic transitions. Since ions on the sublattice with positive Zeeman energy experience the decreased exchange field of the other sublattice, the net effect is a reduction in the splitting of the line. This reduction in the effective g factor can be directly related to the parallel susceptibility of the antiferromagnet by applying an approach similar to that of Ref. 5 to the case of an ion on one sublattice in an optically excited state.

Using the simple model used above we consider a $\Delta S = 1$ spin-forbidden optical transition, and assuming a single-ion exchange interaction with nearest neighbors, we obtain for the temperature-dependent change in the splitting

$$\Delta(T) = \delta(0) - \delta(T) = \frac{4ZVH_0}{Ng\beta} [J_i S - J_f(S-1)] \times \chi_{\parallel}(T), \quad (3)$$

where δ is the splitting of the optical line in an external magnetic field H_0 , Z is the number of nearest neighbors on the opposite sublattice, S is the ground-state spin, and J_f is the single-ion

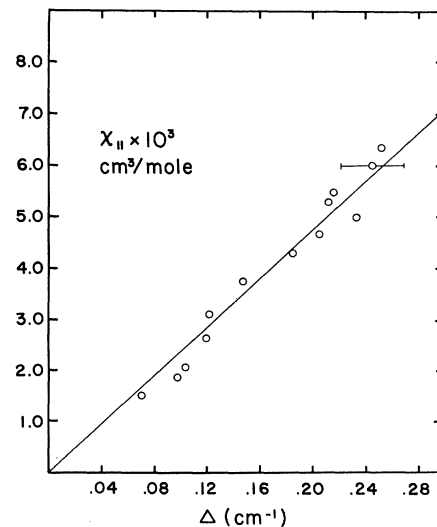


FIG. 3. Experimental parallel susceptibility versus change in splitting for the 18418- cm^{-1} line of MnF_2 at 25-kG external magnetic field.

exchange integral with the nearest-neighbor ions with the ion of interest in an excited state. N/V is the number of spins per unit volume, χ_{\parallel} the parallel susceptibility, β the Bohr magneton, and g the splitting factor of the ground state.

The results are shown in Fig. 3 where the temperature-dependent change in the splitting is plotted against the experimental susceptibility data of Trapp and Stout.¹⁰ The agreement is again seen to be good, and again the slope corresponds to J_f/J_i equal to 1.3.

A careful examination of the thermal behavior of a magnon sideband to the transition studied above (δ_1 in Ref. 7) was made in an attempt to detect the g factor renormalization of nonzero k magnons suggested by Saslow.⁴ The effect could not be detected for this transition in MnF_2 .

We wish to acknowledge illuminating communications from Dr. Wayne Saslow and Professor R. M. White, and the loan of a MnF_2 crystal from J. Holzrichter.

†Work supported by the National Science Foundation under Grant No. G.P. 7900.

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COHESIVE ENERGIES OF TETRAHEDRALLY COORDINATED CRYSTALS*

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(Received 12 May 1969‡)

It is pointed out that the statement made by Phillips that large discrepancies exist between the observed cohesive energy of certain crystals and the values calculated by the electronegativity-difference equation is false. The purported discrepancies occurred because of errors in Phillips's calculations.

The first two sentences of the abstract of a recent Letter by Phillips¹ are, "Pauling resonating-bond theory is reformulated in terms of an itinerant dielectric model. In extreme cases discrepancies of more than 200 kcal/mole between the observed cohesive energy and Pauling's value are reduced to 1 kcal/mole." These discrepancies do not, in fact, exist. The discrepancies reported by Phillips are the result of mistakes made by him in calculating the values.

The substance discussed in detail by Phillips is $\text{BeO}(c)$. He states that the experimental value of the free energy of formation of $\text{BeO}(c)$ from $\text{Be}(g)$ and $\text{O}(g)$ is -243 kcal mole⁻¹, and that the value given by my electronegativity-difference equation² is -468 kcal mole⁻¹. Phillips made three errors in calculating the latter value: First, an erroneous factor 2 in the term in $(X_{\text{Be}}-X_{\text{O}})^2$ led to an error of -184 kcal mole⁻¹; second, the omission of the multiple-bond correction term for O_2 led to an error of 26 kcal mole⁻¹; third, an error of -37 kcal mole⁻¹ seems to have been intro-

duced in some way that is not obvious.

The electronegativity-difference equation for the enthalpy of formation of a normal-valence compound (with no multiple bonds) from the elements in their standard states² in kcal mole⁻¹ is

$$\Delta H_f^0 = -23\sum(X_i - X_j)^2 + 55.4n_N + 26.0n_O, \quad (1)$$

in which the summation is over the single bonds between the unlike atoms i and j with electronegativity values X_i and X_j , and n_N and n_O are the numbers of nitrogen atoms and oxygen atoms in the compound. The terms in n_N and n_O are correction terms for the difference in enthalpy of the multiple bonds in the standard states N_2 and O_2 and single bonds N-N and O-O. For $\text{BeO}(c)$, with two Be-O single bonds (resonating among four positions), and with $X_{\text{Be}}-X_{\text{O}} = 2$, the corresponding expression is

$$\begin{aligned} \Delta H_f^0(\text{BeO}) &= -2 \times 23 \times 4 + 26 = -184 + 26 \\ &= -158 \text{ kcal mole}^{-1}. \end{aligned} \quad (2)$$