EFFECT OF MAGNETIC ORDERING ON THE FLUORESCENCE OF MnF_2†

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In a previous communication,[1] observations were reported of large changes in the fluorescence of MnF_2 and $KMnF_3$ at temperatures well below their Néel points. These changes were not directly related to changes in other measured physical properties such as antiferromagnetic ordering or lattice structure variations below the Néel temperature. In this Letter, observations are reported of smaller alterations in the fluorescence of MnF_2 which occur at the Néel temperature and which, therefore, appear to be related to the magnetic ordering of the lattice. Although effects have been previously found in absorption spectra at this temperature,[2,3] to our knowledge this is the first report of the direct influence of magnetic ordering on the fluorescence properties. We have also observed similar effects in some of the fluorescence properties of $RbMnF_3$, $NaMnF_3$, and $CsMnF_3$.[4]

Measurements of the wavelength maxima and the relative intensity of the fluorescence profiles were taken as a function of temperature using the experimental arrangement and procedure described previously.[1] The excitation was provided by a commercial uv lamp using the 3660A line of Hg. For the observations of the fluorescence lifetime, as a function of temperature, the crystal was flash-excited by a General Radio Strobotac (type 1531-A), and the lifetime was determined from an oscillogram of the output of the photomultiplier monitoring the fluorescence decay. The error in the liftetime measurements was judged to be 10%. The maximum error in the temperature measurements was estimated to be 4°K and the accuracy of determining the wavelength maxima was judged to be ±20 Å.

The temperature dependence of the wavelength of the fluorescence maxima of MnF_2 is shown in Fig. 1. The bracket indicates the region of change in the fluorescence spectrum which is attributed to the magnetic ordering. The observed change near the Néel temperature is approximately 45 Å (~150 cm^{-1}). The shape of the fluorescence profile is independent of temperature. In addition to the changes in the wavelength of the fluorescence, changes are observed in the vicinity of the Néel temperature, in both fluorescent intensity (Fig. 2) and lifetime (Fig. 3). It is found, as expected, that changes in lifetime result in roughly proportional changes in intensity. The figures also show the larger low-temperature effects in the 30-40°K region which have been previously described.[1,4]

The general temperature dependence of the alterations in the fluorescence properties in the vicinity of the Néel temperature is reminiscent of the temperature behavior of the magnetic ordering in MnF_2.[7] The alterations in the fluorescence properties are continuous, beginning (with decreasing temperature) at the Néel temperature, and the major portion of the variation is completed with a few degrees below the Néel temper-

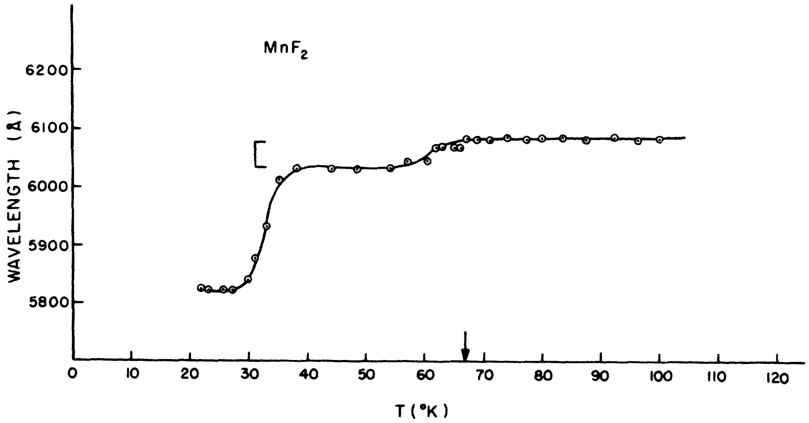

FIG. 1. The temperature dependence of the MnF_2 fluorescence profile maxima. The change in the fluorescence attributed to the magnetic ordering, T(Néel) = 67°K, is indicated by brackets. The large change in the temperature region from 30°K to 40°K is discussed elsewhere.[1,4]

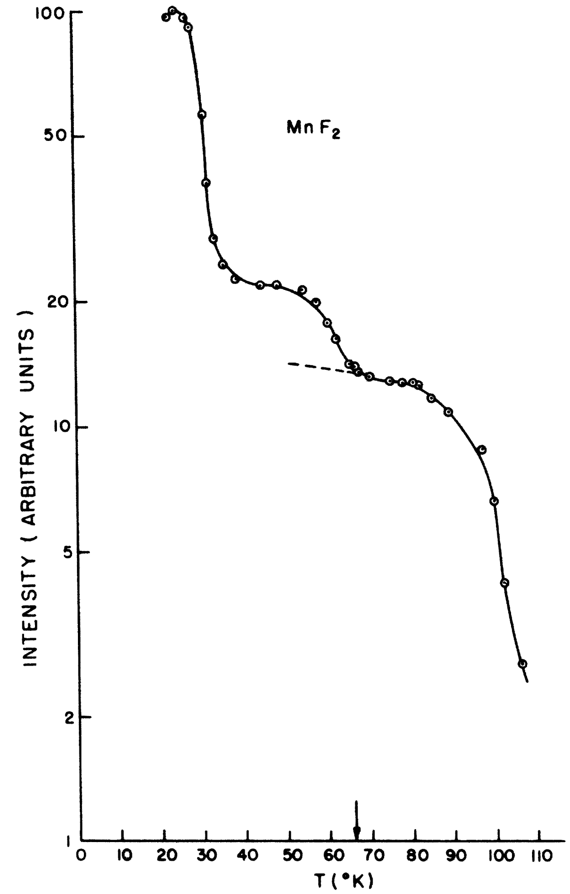

FIG. 2. The temperature dependence of the relative intensity of the fluorescence of MnF_2. The alteration attributed to the magnetic ordering, T(Néel) = 67°K, is emphasized by the dashed line indicating "normal" fluorescence behavior. The large change in the temperature region from 30°K to 40°K is discussed elsewhere.[1,4]

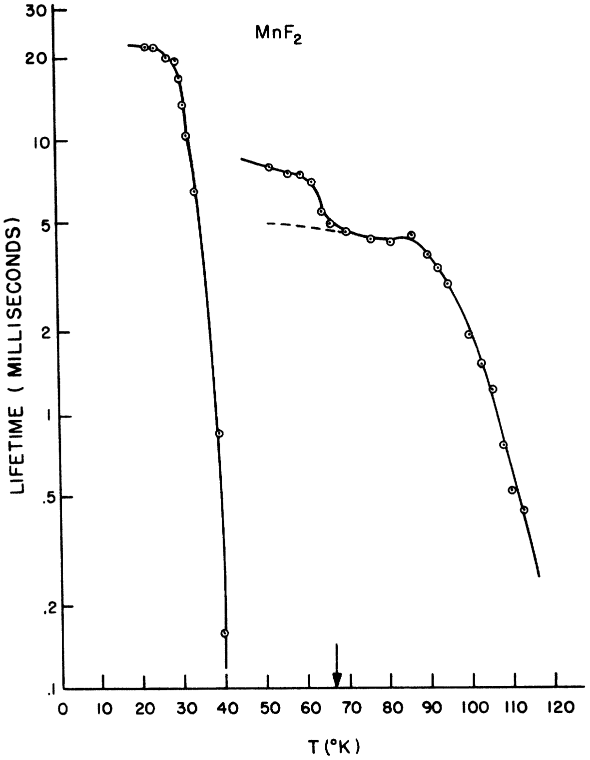

FIG. 3. The temperature dependence of the fluorescence lifetime of MnF_2. The change in the fluorescence lifetime attributed to the magnetic ordering, T(Néel) = 67°K, is emphasized by the dashed line indicating "normal" behavior. The large, apparently discontinuous, change in the temperature region from 30°K to 40°K is described elsewhere.[4]

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The fluorescence of the Mn^{2+} ion in a dilute system has been described[5] as a transition from the $^4G(^4T_{1g})$ level to a $^6S(^6A_{1g})$ level in a distorted lattice site. The configuration diagram model,[6] which accounts for the Stokes shift of the fluorescence, can be adapted to the phenomena observed here if it is assumed that magnetic ordering of the lattice has an effect on the configuration diagram. For example, the mean distances between an excited manganese ion and its nearest-neighbor fluorides will depend upon whether the unexcited manganese ions are magnetically ordered. This effect results from the difference between the interaction energy of a randomly oriented, excited-state spin with, on the one hand, randomly oriented spins of neighbors above the magnetic ordering temperature and, on the other hand, with ordered spins below the magnetic ordering temperature. The observed effects are consistently described by assuming that there is an average lattice dilation in the excited-state configuration which is reduced at temperature below the Néel point.

The alteration of the decay-time constant and quantum yield may also be understood in terms of the relative lateral displacement of the configuration diagrams of the ground and excited states, i.e., by a lattice distortion in the excited state. Nonradiative decay of the fluorescent site may occur either by tunneling from the excited electronic state to the ground state (cf. Chapter VII of reference 6) or by thermal activation to a crossover point of the configuration diagrams. The effect of a decreased lattice change between the ground and excited-state configurations would decrease the probability of nonradiative decay processes. For the case of tunneling decay, this results from a reduced overlap of the ground and excited-state vibrational wave functions. For the thermal activated decay, the reduced lateral displacement would increase the effective barrier height. The decrease in the nonradiative de-excitation processes results in an increased fluorescence lifetime and quantum yield. The expected correlation of reduced Stokes shift and increased fluorescence lifetime are found in the observed data. The present observation of fluorescence changes near the Néel temperature supports the earlier hypotheses that the origin of the lower temperature fluorescent anomalies in MnF_2 and $KMnF_3$ was due to magnetic ordering of the excited state Mn^{2+} spins. A more complete report of other examples of correlation of magnetic and fluorescence effects in manganese salts will be published in the near future.

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[1] W. W. Holloway, Jr., M. Kestigian, R. Newman, and E. W. Prohofsky, Phys. Rev. Letters 11, 82 (1963).

[2] J. W. Stout, J. Chem. Phys. 31, 709 (1959)

[3] A. I. Belyaeua and V. V. Eremenko, Zh. Eksperim. i Teor. Fiz. 44, 469 (1963) [translation: Soviet Phys. – JETP 17, 319 (1963)].

[4] W. W. Holloway, Jr., and M. Kestigian, to be published.

[5] L. E. Orgel, J. Chem. Phys. 23, 1958 (1955).

[6] D. Curie, Luminescence in Crystals (John Wiley & Sons, Inc., New York, 1963).

[7] F. M. Johnson and A. H. Nethercot, Jr., Phys. Rev. 114, 705 (1958).

ANISOTROPIC SPIN-WAVE THERMAL CONDUCTIVITY IN FERROMAGNETS

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Sato[1] has suggested that transport of energy by magnons might be detected at sufficiently low temperatures. Early observations of thermal conductivity in magnetic insulators[2,3] were interpreted in terms of phonon transport limited by phonon-magnon interactions. Magnon transport has been detected in yttrium iron garnet[4-6] and in EuS.[7,8] In principle, if the mean free path is determined by boundary scattering, then magnon transport should be identified by its characteristic temperature dependence, i. e., T^2 in zero internal field. It has been observed[3] that the field dependence is a more reliable indicator: The thermal conductivity decreases with increasing field for magnon transport; it increases with increasing field for phonon transport influenced by phonon-magnon scattering. In this note the theory of magnon thermal conduction of Douthett and Friedberg[3] is modified to include the effects of the ubiquitous long-range magnetic dipolar coupling. The major effect is seen to be a change in the magnon group velocities, which results in a dependence of the magnon conductivity upon the direction of measurement relative to the magnetization direction. The ferromagnetic europium chalcogenides[9] are favorable materials in which to look for the phenomenon because of their large magnetization (measure of the strength of the dipolar coupling) and low Curie point relative to the Debye temperature (indicating a large magnon population relative to that of the phonons).[10]

The flow of heat in the direction $\vec{m}$ ($\vec{m}$ is a unit vector) is related to the thermal gradient in the same direction by the thermal conductivity[11]

$$K_m = \frac{1}{\Omega} \sum_{\text{modes}} (\vec{v}\cdot\vec{m})^2 \tau S. \tag{1}$$

Here Ω is the sample volume and for each mode, $\vec{v}$ is the group velocity, τ the relaxation time, and S the specific heat capacity. For simplicity we assume the scattering to be due to boundaries and define one effective mean free path l for all modes. Then $\tau = l/|\vec{v}|$. The spin-wave energies are given by[12]

$$e_{\vec{k}} = (\epsilon_{\vec{k}} + g\beta H)\{1 + \varphi_{\vec{k}} \sin^2\theta_{\vec{k}}\}^{1/2}, \tag{2}$$

where $\epsilon_{\vec{k}}$ is the exchange energy, $\theta_{\vec{k}}$ is the angle