LOCALIZED MAGNETIC MODE IN MnF_2:Fe^{2+}†

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A magnetic-dipole-active local mode has been observed in MnF_2:Fe^{2+} at 94.8 cm^{-1} by means of far-infrared spectroscopic techniques. For a magnetic field parallel to the c axis of the crystal, the absorption line shows a linear splitting. A g factor of 2.3 is derived from the data.

The introduction of magnetic impurities into a magnetic lattice alters the spin-wave states and can lead to spatially localized states outside the magnon bands.[1] The situation is somewhat similar to the case of nonmagnetic impurities in crystal lattices, where the phonon states are perturbed.[2] The latter problem has been studied in many investigations in the past. Most of the experimental work has been done using far-infrared spectroscopic techniques.

Up to now there is little experimental evidence for magnetic-impurity-induced states. A number of different techniques have been used in these investigations. A resonant-band mode has been reported by Møller, Houmann, and Mackintosh in Tb:Ho by means of the neutron spectroscopic technique.[3] Using the same technique, a localized mode in MnF_2:Co^{2+} has been found at 119 cm^{-1} by Buyers et al.[4] Localized states in MnF_2, $RbMnF_3$, and $KMnF_3$ due to Ni^{2+} impurities have been found in optical experiments as spin-wave sidebands.[5,6] Recently also a localized state in $KMnF_3$:Eu^{3+} was observed in the fluorescence spectrum.[7] In the low-frequency region below the antiferromagnetic resonance frequency of $FeCl_2$ and MnF_2, localized states due to Fe^{3+} and Er^{3+} impurities, respectively, have been studied by means of EPR methods.[8,9] Finally, using far-infrared techniques, Richards has reported a line in FeF_2 at 50.1 cm^{-1}, which might be due to an as yet unidentified magnetic impurity.[10]

We wish to report the first direct spectroscopic evidence using far-infrared techniques for a magnetic-dipole-active localized mode in MnF_2 :Fe^{2+}, which has been observed at 94.8 cm^{-1} at 1.2°K.

The measurements have been carried out with a Strong-type lamellar interferometer[11] together with a liquid-He^3-cooled germanium bolometer.[12] The magnetic field dependence of the line has been investigated by means of a 50-kG superconducting magnet.

The doped and undoped single crystals were obtained from Optovac, Inc. The samples contained 1-mole% FeF_2 in the melt.

The spectral region between 2 cm^{-1} and 130 cm^{-1} has been investigated. Besides the line at 94.8 cm^{-1}, no other impurity-induced lines have been found. However, the antiferromagnetic resonance frequency shows a shift from 8.7 cm^{-1} in the pure crystal to 9.2 cm^{-1}.

The line at 94.8 cm^{-1} has the following features. The half-width is 0.4 cm^{-1} and the absorption strength $\int \alpha d\tilde{\nu} \sim 1$ cm^{-2}, which is comparable with that of the antiferromagnetic resonance. Measurements with polarized radiation show that the line is magnetic dipole active with $\bar{H}$ of the incident radiation perpendicular to the c axes. No line was observed for $\bar{H} \parallel c$. With increasing temperature, the line shifts to lower frequencies and finally disappears at about 25°K. The shift at 21°K is 1.2 cm^{-1}. With a magnetic field applied parallel to the c axis of the sample, the line shows a linear splitting. From the measurements, a g factor of 2.3 is derived.

The experimental results at 1.2°K can be understood satisfactorily both with a simple molecular-field picture and, also, with the help of a simple spin-wave calculation. First we give the molecular-field treatment.

The ground term of Fe^{2+} is $3d^6\,{}^5D$. The fivefold orbital degeneracy is reduced by the cubic field to an upper doublet and a lower triplet. Addition of the terms of only rhombic symmetry lifts all the remaining orbital degeneracy. The first excited orbital level lies an interval of the order 10^3 cm^{-1} above the orbital ground state.[13] Therefore, it is sufficient for the present work to consider the orbital ground state only. In addition, the g factor of 2.3 indicates that the observed line is due to a transition within the spin manifold of the ground orbital level, for the value is very close to the measured g factor in FeF_2 of 2.25.[14]

The fivefold spin degeneracy of the orbital ground state is split by the Fe^{2+}-Mn^{2+} exchange field and the anisotropy field. The latter is essentially given by an expression of the form $-DS_z'^2$, where D is a positive constant. S_z' is the spin component of the impurity in z direction, which is chosen parallel to the c axis of the crystal. The effective spin Hamiltonian for the impurity in the molecular-field approximation is then[15]

$$\mathcal{H}=-g'\mu_B(H_{ex}\pm H_0)S_z'-DS_z'^2. \qquad (1)$$

Here g' is the g factor of the impurity, and μ_B is the Bohr magneton. H_{ex} means the molecular field acting on the impurity spin, and H_0 the external applied magnetic field. The different signs refer to the site of the impurity in the two sublattices.

We correlate the observed line in the molecular-field picture to the transition between the ground and the first excited spin level of the orbital ground state. According to (1) the energy difference between these two states at zero temperature is

$$\hbar\,\Delta\omega=g'\mu_B(H_{ex}\pm H_0)+3D; \qquad H_{ex}=2J'zS/g'\mu_B. \qquad (2)$$

For MnF_2, $z=8$, $S=\frac{5}{2}$. For D we use the value obtained for FeF_2, $D=6.5\ \mathrm{cm}^{-1}$.[5] To take into account the dipolar interaction, we add $0.8\ \mathrm{cm}^{-1}$ to the anisotropy term. In order that (2) fits the observed value for the frequency, we have to choose $J'=1.9\ \mathrm{cm}^{-1}$.

The same value for J' is obtained by a simple spin-wave calculation, which we give now. The calculation is based on a simple two-sublattice model,[16] neglecting the tetragonal distortion of MnF_2. Only nearest-neighbor exchange coupling is again taken into account. The uniaxial anisotropy field is denoted by H_A. γ is the gyromagnetic ratio. The corresponding impurity parameters are denoted by a prime.

The calculation is done semiclassically. Because the observed line lies nearly a factor of 2 above the upper spin-wave zone frequency of MnF_2, we consider next-nearest spins and more distant spins as frozen in place.

For the frequency of the magnetic-dipole-active localized mode, one obtains in this approximation

$$\frac{\omega_L}{\omega_E}=\frac{1}{2}\left(C_1\pm\frac{\omega_0+\omega_0'}{\omega_E}\right)+\left[\frac{1}{4}C_1^2+C_2\pm C_3\frac{\omega_0'-\omega_0}{\omega_E}+\frac{1}{4}\frac{(\omega_0'-\omega_0)^2}{\omega_E^2}\right]^{1/2}, \qquad (3)$$

where

$$C_1=-\frac{7}{8}+\frac{J'}{J}-\frac{1}{8}\frac{J'}{J}\frac{S'}{S}+\frac{\omega_A'-\omega_A}{\omega_E}, \qquad C_2=\left(\frac{7}{8}+\frac{\omega_A}{\omega_E}\right)\left(\frac{J'}{J}+\frac{\omega_A'}{\omega_E}\right)+\frac{1}{8}\frac{J'}{J}\frac{S'}{S}\frac{\omega_A'}{\omega_E},$$

$$C_3=\frac{1}{2}\left(\frac{7}{8}+\frac{J'}{J}+\frac{1}{8}\frac{J'}{J}\frac{S'}{S}+\frac{\omega_A'-\omega_A}{\omega_E}\right),$$

and ω_E is the upper spin-wave band frequency in MnF_2, given by $\omega_E=16SJ/\hbar$. Furthermore, in Eq. (3),

$$\omega_A=\gamma H_A;\quad \omega_A'=\gamma' H_A';\quad \omega_0=\gamma H_0;\quad \omega_0'=\gamma' H_0;\quad \gamma=g\mu_B/\hbar;\quad \gamma'=g'\mu_B/\hbar.$$

First let us consider the case without applied magnetic field. Using for J the value $J=1.22\ \mathrm{cm}^{-1}$,[17] and the same values for the other parameters as in the molecular-field picture, the Fe^{2+}-Mn^{2+} exchange coupling constant turns out to be $J'=1.9\ \mathrm{cm}^{-1}$.

The value for J', obtained by fitting the frequency in the molecular-field formula (2) and the spin-wave formula (3), respectively, to the observed frequency is in fair agreement with the value $J'=1.5\ \mathrm{cm}^{-1}$ obtained by Wertheim, Guggenheim, and Buchanan,[18] although our value is somewhat larger.

When an applied magnetic field is taken into account, Eq. (3) yields the expected splitting of the localized state. In general the frequency shifts of the two modes are not linear with field.

This is because the magnetic field affects the impurity spin and the rest of the spins differently, according to their g factors. Therefore, the frequency distance between highest band frequency and localized-mode frequency is changed by the external field. As a consequence, the spatial localization of the localized mode is altered, which in turn influences the localized-mode frequency. Such a nonlinear frequency shift is, however, to be expected only for large differences in the g factors. In the present case, the measurements indicate that the difference in the g factors of Fe^{2+} and MnF_2 is too small to observe the nonlinear frequency shift. We can, therefore, neglect the quadratic magnetic field term and expand the root in terms of $\omega_0'-\omega_0$, yielding the observed linear frequency shifts in a good approximation. The g factor of the localized mode turns out to be approximately the g factor of the Fe^{2+} impurity alone. From the expanded form of (3) one obtains $g'=2.3$.

The large value of the oscillator strength of the localized mode is readily understood with a semiclassical picture. For the $q=0$ magnon mode, the strength is proportional to the square of the difference in the precession amplitude of the spins in the two sublattices, whereas for the localized mode it is approximately proportional to the square of the precession amplitude of the impurity spin alone. The resulting strength per spin is about 100 times larger for the localized mode as compared with the antiferromagnetic resonance in MnF_2.

Finally, we come to the temperature dependence of the localized mode. The frequency shift of the line with increasing temperature is smaller than the shift of the antiferromagnetic resonance frequency. The result is predicted by the theory for a localized mode above the band.[19] The relatively large half-width of the line and the large broadening indicate a coupling of the localized mode to other excitations. Work is in progress to investigate this behavior.

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[1] S. W. Lovesey, J. Phys. C: Phys. Soc. (London) Proc. 1, 102, 118 (1968); for further references see therein.

[2] See, for example, A. A. Maradudin, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1966), Vol. 19, p. 1.

[3] H. B. Møller, J. C. G. Houmann, and A. R. Mackintosh, Phys. Rev. Letters 19, 312 (1967).

[4] W. J. L. Buyers, R. A. Cowley, P. M. Holden, and R. W. H. Stevenson, J. Appl. Phys. 39, 1118 (1968).

[5] L. F. Johnson, R. E. Dietz, and H. J. Guggenheim, Phys. Rev. Letters 17, 13 (1966).

[6] A. Misetich and R. E. Dietz, Phys. Rev. Letters 17, 392 (1966).

[7] S. Shionoya and M. Hirano, Phys. Letters 26A, 533 (1968).

[8] M. Motokawa and M. Date, J. Phys. Soc. Japan 23, 1216 (1967).

[9] L. L. Chase and H. J. Guggenheim, Bull. Am. Phys. Soc. 13, 390 (1968).

[10] P. L. Richards, J. Appl. Phys. 38, 1500 (1967).

[11] I. G. Nolt, thesis, Cornell University (1967), Cornell University Materials Science Center Report No. 765 (unpublished).

[12] H. D. Drew, thesis, Cornell University (1968), Cornell University Materials Science Center Report No. 939 (unpublished).

[13] M. Tinkham, Proc. Phys. Soc. (London) A68, 258 (1955).

[14] R. C. Ohlmann and M. Tinkham, Phys. Rev. 123, 425 (1961).

[15] J. Kanamori and H. Minatono, Phys. Soc. Japan 17, 1759 (1962).

[16] R. Weber, to be published.

[17] G. G. Low, A. Okazaki, R. W. H. Stevenson, and K. C. Turberfield, J. Appl. Phys. 35, 998 (1964).

[18] G. K. Wertheim, H. J. Guggenheim, and D. N. E. Buchanan, Phys. Rev. Letters 20, 1158 (1968).

[19] D. Hone, H. Callen, and R. L. Walker, Phys. Rev. 144, 283 (1966).