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IN $\text{MnF}_2:\text{Fe}^{2+}$

K. C. Johnson and A. J. Sievers

Laboratory of Atomic and Solid State Physics
Cornell University
Ithaca, New York 14850

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Hydrostatic Pressure Behavior of the Exchange Fields in $\text{MnF}_2:\text{Fe}^{2+}$ *

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Abstract

We have determined the pressure dependence of both impurity and host exchange fields in $\text{MnF}_2:\text{Fe}^{2+}$ by measuring the frequency shifts of far infrared active modes in $\text{MnF}_2:\text{Fe}^{2+}$, MnF_2 , and $\text{ZnF}_2:\text{Fe}^{2+}$ at pressures up to 7.1 kbar.

The far infrared active localized magnetic mode in $\text{MnF}_2:\text{Fe}^{2+}$ at 94.9 cm^{-1} is a direct probe of the magnetic exchange and crystalline anisotropy energies at the Fe^{2+} ion site.¹ The frequency of this mode is given in the molecular field approximation by

$$\omega_{\text{LM}} = 2S J'_{\text{eff}} + 3D' + \omega_A', \quad (1)$$

where J'_{eff} is the effective total exchange constant between Fe^{2+} and its first and second Mn^{2+} neighbors ($J' > 0$ for anti-ferromagnetic coupling), S is the host lattice spin, D' the

uniaxial anisotropy constant, and ω'_A the small ($< 1 \text{ cm}^{-1}$) dipole-dipole anisotropy. A similar probe of the magnetic parameters of Mn^{2+} is provided by the antiferromagnetic resonance,² which occurs in the pure crystal at a frequency

$$\omega_{\text{AFMR}} = (4S Z_2 J_2 \cdot \omega_A)^{\frac{1}{2}}, \quad (2)$$

where ω_A is primarily dipole-dipole anisotropy and J_2 is the exchange between Mn^{2+} and its second nearest neighbors. Because the second neighbor exchange is dominant in the pure crystal, the value obtained from AFMR measurements is an excellent approximation to the total effective Mn^{2+} - Mn^{2+} exchange.

By measuring the shifts in frequency of these modes as a function of hydrostatic pressure it is possible to determine spectroscopically the lattice dependence of the effective exchange acting on each of the two ions, provided there exists some independent measure of the anisotropy contributions. Since the dipole-dipole terms ω_A and ω'_A are simple functions of the interatomic spacings, their pressure dependence is readily calculated by using the compressibility data of Benedek and Kushida.³ In order to isolate the pressure behavior of the more complex anisotropy term D' , we have also measured the pressure dependence of the paramagnetic resonance spectrum of the isomorphous crystal $\text{ZnF}_2:\text{Fe}^{2+}$.

In $\text{ZnF}_2:\text{Fe}^{2+}$ the fivefold spin degeneracy in the ground orbital state of Fe^{2+} is lifted solely by the crystalline anisotropy (in the absence of an applied field). Analysis of the spin Hamiltonian⁴ predicts magnetic dipole active lines in the far infrared with frequencies given by

$$\begin{aligned}\omega_A &= 3(D + E) \\ \omega_B &= 3(D - E) + \Delta,\end{aligned}\tag{3}$$

where D and E are the uniaxial and orthorhombic anisotropy constants and $\Delta = 3E^2/D$, and we have used the convention that D and E are positive. The energy separations of the spin manifold are shown in Fig. 2. We have observed these lines at $\omega_A = 26.9 \text{ cm}^{-1}$ and $\omega_B = 23.0 \text{ cm}^{-1}$ at zero pressure; this result permits determination of precise values for D and E in $\text{ZnF}_2:\text{Fe}^{2+}$: $D = 8.29 \pm .04 \text{ cm}^{-1}$, $E = 0.67 \pm .04 \text{ cm}^{-1}$.

The center frequency shifts versus pressure of the local mode in $\text{MnF}_2:\text{Fe}^{2+}$ and the EPR lines in $\text{ZnF}_2:\text{Fe}^{2+}$ are shown in Figure 2. The shifts are linear with pressure to within the limits of the measurements. The slopes $\partial\omega/\partial p$ as well as the original center frequencies for all the modes are listed in Table I. The frequency shift of the AFMR was so small (0.15 cm^{-1} at 7.1 kbars) that it was measured only at the highest pressure.

The measurements were made on single crystals of MnF_2 , $\text{MnF}_2:\text{Fe}^{2+}$ (1.1 at.%), and $\text{ZnF}_2:\text{Fe}^{2+}$ (.6 at.%); the impurity concentrations were determined by atomic absorption analysis. High pressures at 4.2°K were obtained by cooling the helium gas used as pressurizing medium at constant volume below its freezing point; the maximum 4.2° pressure was 7.1 kbar. Subsequent lower pressures were obtained by heating the sample cell above the melting point of the helium and releasing the desired amount of gas through an external valve. Frequency measurements were made with both Michelson and lamellar interferometers, and detection was performed by a He^3 -cooled doped germanium bolometer.

The calculation of the pressure derivative of D in $\text{ZnF}_2:\text{Fe}^{2+}$ follows directly from (3) and the measured values of $\partial\omega/\partial p$, with the result $\partial D/\partial p = -.033 \pm .005 \text{ cm}^{-1}/\text{kbar}$. If we then assume that the uniaxial anisotropy energies in the similar hosts ZnF_2 and MnF_2 have identical pressure dependence we can immediately extract the pressure derivative of the effective impurity exchange for Fe^{2+} from (1):

$$\partial J'_{\text{eff}}/\partial p = .046 \pm .005 \text{ cm}^{-1}/\text{kbar}.$$

The pressure dependence of the effective exchange for Mn^{2+} is readily calculated to be $\partial J_{\text{eff}}/\partial p = 0.040 \pm .005 \text{ cm}^{-1}/\text{kbar}$.

The results can be presented in a more suggestive fashion if we define a "magnetic Gruneisen constant" which measures

the relative change in effective exchange with volume:

$$\gamma_J = \frac{-\partial \ln J}{\partial \ln V} = \frac{1}{J} \frac{\partial J}{\partial p} \cdot \frac{1}{K}, \text{ where}$$

K is the compressibility. If the local compressibility about the impurity is assumed to be identical to that in the host, the experimental results may be expressed as

$$\gamma_J(\text{Mn}^{2+} - \text{Mn}^{2+}) = 3.45 \pm 0.4$$

$$\gamma_J(\text{Fe}^{2+} - \text{Mn}^{2+}) = 2.8 \pm 0.4$$

Here we have used the value for $J'_{\text{eff}} = 13.7 \text{ cm}^{-1}$, a result obtained from (1) by taking $\omega_A' = 0.8 \text{ cm}^{-1}$ and $D' = 8.6$.⁵

The precision of the reported value for $\partial J'_{\text{eff}}/\partial p$ is limited by the assumption that $\partial D/\partial p$ is the same for $\text{ZnF}_2:\text{Fe}^{2+}$ and $\text{MnF}_2:\text{Fe}^{2+}$. A good test is precluded by the lack of compressibility data for ZnF_2 . We expect the agreement to be good, however, for several reasons: 1) very similar values for D at zero pressure (8.3 cm^{-1} for $\text{ZnF}_2:\text{Fe}^{2+}$, 8.6 cm^{-1} for $\text{MnF}_2:\text{Fe}^{2+}$)⁵, 2) nearly identical lattice constants and the existence of phase changes in both at similar pressures,⁶ and 3) the qualitative agreement with experiment given by a simple crystal field calculation for $\partial D/\partial p$ and $\partial E/\partial p$ in $\text{ZnF}_2:\text{Fe}^{2+}$ using the MnF_2 compressibility data.

Our value of $\gamma_J(\text{Mn}^{2+} - \text{Mn}^{2+})$ is very close to the result obtained for the relative change in the Néel temperature with

volume, found by Benedek and Kushida² to be $\gamma_{T_N} = \frac{\partial \ln T_N}{\partial \ln V} = 3.6 \pm 0.3$. These quantities are expected to be the same from both molecular field theory and more sophisticated treatments,⁷ which indicates that our microscopic analysis gives good agreement with results based on a bulk property of the crystal. On the other hand, the value of $\gamma_J(\text{Fe}^{2+} - \text{Mn}^{2+})$, which is obtainable only from microscopic measurements, is significantly lower. The possibility that the difference is due to a change in the local compressibility is unlikely, since the ionic radii and masses of Mn^{2+} and Fe^{2+} are very similar. We therefore conclude that the variation of the effective impurity-host superexchange interaction with ionic separation is significantly less than that of the host-host interaction.

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~~References~~

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1. WEBER R., Phys. Rev. Letters 21, 1260(1968).
 2. JOHNSON F. M. and NETHERCOT A. H. JR., Phys. Rev. 114, 705(1959).
 3. BENEDEK G. B. and KUSHIDA T., Phys. Rev. 118, 46(1960).
 4. TINKHAM M., Proc. Roy. Soc. A236, 535(1956).
 5. LOWE M. A., MISETICH A., and ABELEDO C. R., Journ. de Phys. 32, C1-1068 (1971).
 6. DANDEKAR D. P. and JAMIESON J. C., Trans. Amer. Crystal. Assoc. 5, 19 (1969).
 7. SMART J. S., Phys. and Chem. Solids 11, 97 (1959).

Absorption Line	P=0 Center Frequency (cm^{-1})	$\frac{\partial \omega_0}{\partial p} (\text{cm}^{-1}/\text{kbar})$
$\omega_{\text{AFMR}}(\text{MnF}_2)$	$8.69 \pm .01$	$.021 \pm .002$
$\omega_{\text{LM}}(\text{MnF}_2:\text{Fe}^{2+})$	$94.90 \pm .05$	$.13 \pm .01$
$\omega_{\text{A}}(\text{ZnF}_2:\text{Fe}^{2+})$	$26.90 \pm .05$	$-.044 \pm .010$
$\omega_{\text{B}}(\text{ZnF}_2:\text{Fe}^{2+})$	$23.00 \pm .05$	$-.15 \pm .02$

Figure Captions

Fig. 1: Energy level diagram of the low-lying spin manifold in $\text{ZnF}_2:\text{Fe}^{2+}$. The level values were determined from our measurements of ω_A and ω_B .

Fig. 2: Pressure induced center frequency shifts for the local mode in $\text{MnF}_2:\text{Fe}^{2+}$ and the EPR spectrum in $\text{ZnF}_2:\text{Fe}^{2+}$.

Table I. Summary of experimental results

ZnF₂ : Fe²⁺ Spin Manifold

Energy (cm⁻¹)

$$33.5 \text{ ————— } 4D_0 + 2\Delta$$

$$27.0 \text{ ————— } 3(D_0 + E_0) + \Delta$$

$$23.0 \text{ ————— } 3(D_0 - E_0) + \Delta$$

$$\omega_A = 3(D_0 + E_0)$$

$$\omega_B = 3(D_0 - E_0) + \Delta$$

$$\begin{array}{c} 0.16 \\ 0 \end{array} \text{ ————— } \begin{array}{c} \Delta = 3E_0^2/D_0 \\ 0 \end{array}$$

ω_A

ω_B

Figure 1

Figure 2