

Magnetic Resonance of Mn²⁺-Doped LiF Crystals* †

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The electron paramagnetic resonance of Mn²⁺ in powdered LiF was observed at X-band and room temperatures for various impurity concentrations. The highest concentration was examined at K-band and low temperatures to obtain additional information regarding the distribution of Mn²⁺ ions which were introduced chemically into the lattice in small amounts. In the highest concentration, the K-band spectra indicate that part of the Mn²⁺ goes into the powder in the form of clusters of Mn and F which are antiferromagnetic at helium temperatures. NMR linewidth measurements on the lithium nuclei at low temperatures are qualitatively explained by the antiferromagnetism.

The room-temperature data from the more dilute samples exhibit not only the expected hyperfine splitting but also a superhyperfine splitting. The hyperfine interaction of the Mn²⁺ ion was determined to be $A_{\text{H}} = 90 \pm 2 \times 10^{-4} \text{ cm}^{-1}$, and the isotropic part of the superhyperfine interaction with each of the six fluorine nearest-neighbor nuclei was measured to be $A_s = 17.1 \pm 0.5 \times 10^{-4} \text{ cm}^{-1}$.

Comparisons between K-band spectra from chemically prepared powdered samples and single crystals grown from the melt indicate that the melt method is unsuitable for obtaining the solid solution required to examine the superhyperfine spectra.

INTRODUCTION

THE paramagnetic resonance of Mn²⁺ substitutional impurities in ZnF₂ was observed by Tinkham¹ to have superposed on the usual Mn²⁺ hyperfine spectrum an additional splitting due to the interaction of the Mn²⁺ electrons with the nuclear spins of the fluorine nearest neighbors. This interaction has been termed a "superhyperfine" interaction to distinguish it from the hyperfine interaction which is a term customarily reserved for the interaction of the paramagnetic electrons with the nucleus of their own ion. As a result of Tinkham's observation of the superhyperfine interaction several publications² have appeared bearing on the analysis of the superhyperfine interaction. Closely allied to the paramagnetic resonance observations of Tinkham's, in that the observations both complement and supplement Tinkham's observations, are the measurements of the nuclear magnetic resonance of F in MnF₂ at temperatures immediately above the antiferromagnetic transition temperature.³

In our experiment we have observed the superhyperfine interaction of the Mn²⁺ electrons with the F nuclei in LiF doped with Mn²⁺. The phenomena appears on the microwave spectrum of the Mn²⁺ as a splitting of each of the six hyperfine lines into seven superhyperfine lines due to the interaction of the *d*-shell electrons

of Mn²⁺ with the nearest neighbor F nuclei. The splitting into seven lines and the over-all spectrum is such that we interpret the Mn²⁺ to reside in the lattice substitutionally at Li⁺ site in the dilute samples. The local symmetry of the Mn²⁺ in the LiF lattice is higher than in the ZnF₂ lattice, being cubic rather than orthorhombic. It must be noted, however, that charge-compensating positive-ion vacancies would lower the symmetry, a fact that has been discussed by Watkins.⁴ Since the results which exhibit the superhyperfine interaction are based on measurements on powders, we are unable to distinguish the effects of lattice vacancies, as their angular dependence is washed out by the angular averaging the spectrometer performs on a powder. The broadening of the hyperfine lines is, in part, attributable to these effects.

Measurements have also been performed on commercially grown Mn²⁺-doped single crystals of LiF in an attempt to determine both the isotropic and anisotropic parts of the superhyperfine constant A_s . The resulting spectra indicated that the manganese ions tend to migrate into "clusters of MnF₂"⁵ as the melt is being cooled and hence only a single broad resonance was detected. This behavior is consistent with observations made in this laboratory while growing Mn²⁺ doped LiCl₂ crystals. It was found necessary to quench the melt quite rapidly in order to have the Mn²⁺ ions introduced substitutionally into the LiCl₂ lattice.

Since only in the dilute powdered samples were we able to achieve a solid solution, additional measurements were made in an effort to determine more about the Mn²⁺ distribution in the more concentrated polycrystalline samples. NMR linewidth measurements

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† A preliminary announcement of the present experiment appears in the J. Chem. Phys. **38**, 571-572 (1963).

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¹ M. Tinkham, Proc. Roy. Soc. (London) **A235**, 535 (1956).

² M. Tinkham, Proc. Roy. Soc. (London) **A236**, 549 (1956);

A. Mukherji and T. P. Das, Phys. Rev. **111**, 1479 (1958); F.

Keffer, T. Oguchi, W. O'Sullivan, and J. Yamashita, *ibid.* **115**,

1553 (1959); A. M. Clogston, J. P. Gordon, V. Jaccarino, M.

Peter, and L. R. Walker, *ibid.* **117**, 1222 (1960).

³ R. G. Shulman and V. Jaccarino, Phys. Rev. **103**, 1126 (1956).

⁴ G. D. Watkins, Phys. Rev. **113**, 79 (1959).

⁵ D. A. Jennings, thesis, University of Colorado, 1962 (to be published).

TABLE I. The values of the g factor of Mn^{55} , the hyperfine interaction parameter for Mn^{55} (designated as A^{55}) and the isotropic superhyperfine interaction parameter A_s for Mn^{55} are given for various compounds.

Crystal	g	A^{55}	A_s	Reference
ZnF ₂	2.002±0.005	-96.27±2.8		Tinkham ^a
ZnF ₂		-90.76±0.3	16.56±0.19	Clogston ^b
MgO	2.0016±0.001	-81.2±0.5		Low ^c
CaF ₂	2.0013±0.001	-95.4±1		Low ^c
KCdF ₃	2.002±0.002	-92.6±0.9	15.8±0.5	Ogawa ^d
SrS	2.0009±0.0005	-75.4±0.2		Manekov ^e
BaF ₂	2.0009±0.0010	-90.6±1		Drumheller ^f
LiF	2.0018±0.0010	-90.1±2	17.1±0.5	This experiment

^a See Refs. (1) and (2).

^b See Ref. (2).

^c See Ref. (8).

^d S. Ogawa, J. Phys. Soc. Japan 14, 1475 (1960).

^e A. A. Manekov and A. M. Prokhorov, Zh. Exptim. i Teor. Fiz. 40, 1606 (1961) [English transl.: Soviet Phys.—JETP 13, 1129 (1961).]

^f J. Drumheller, J. Chem. Phys. 38, 970 (1963).

were performed on the Li and F nuclei as a function of Mn^{2+} concentration and temperature. These measurements were complemented by measurements on the paramagnetic spectrum at 77° and 4.2°K with a K -band spectrometer.

The X -band measurements indicate that for the smaller concentration, the Mn^{2+} ions go into the lattice substitutionally for the lithium ions. The K -band and NMR measurements indicate that for higher concentrations, the Mn^{2+} ions combine with F ions and form clusters which exhibit features of an antiferromagnet at 4.2°K.

Spectrum for Dilute Concentrations

The spin Hamiltonian appropriate to a Mn^{2+} ion in the ground $(3d^5)^6S$ state in a cubic crystalline field is^{6,1,2}

$$H = g\beta H \cdot S + AS \cdot I_{Mn} + \sum_{i=1}^6 S \cdot A^i \cdot I_{F_i} + \frac{1}{6}a[S_x^4 + S_y^4 + S_z^4 - \frac{1}{3}S(S+1)(3S^2 + 3S - 1)] + \sum_j S \cdot B^j \cdot S_j - g_{Mn}\beta_n H \cdot I_{Mn} - g_F\beta_n \sum_{i=1}^6 H \cdot I_{F_i} \quad (1)$$

g , g_{Mn} , and g_F are the Mn^{2+} , manganese nuclear, and fluorine nuclear g factors. β and β_n are the Bohr and nuclear magnetons. The first term represents the interaction of the Mn^{2+} spin with the external field H (~ 3000 G for X band, 8400 G for K band), the second term the interaction of the Mn^{2+} ionic electrons with the Mn^{2+} nucleus (~ 100 G), the third term the superhyperfine interaction of the Mn^{2+} electrons with the six nearest-neighbor F nuclear spins I_{F_i} (~ 20 G), the fourth term represents the interaction of the Mn^{2+}

⁶ W. G. Penney and R. Schlapp, Phys. Rev. 41, 194 (1932); See also W. Low, *ibid.* 105, 793 (1957).

ion with the cubic field (~ 25 G), the fifth term the spin interaction of the Mn^{2+} spin with other Mn^{2+} spins, S_j . This term includes dipole-dipole as well as exchange effects and is completely negligible in crystals where the Mn^{2+} concentration is small. The last two terms are the Zeeman terms for the Mn and F nuclei, respectively. It must be observed that in the case where there is a departure of the local crystalline field from cubic symmetry the crystalline, interaction is quadratic in the spin S of the Mn^{2+} ion rather than quartic, being then of the form:

$S \cdot D \cdot S$.

We ignore the fifth term. In a coordinate system in which the direction of H is picked as the Z -direction, the axis of quantization, the energy eigenvalues of the Hamiltonian (1) are then:

$$E(M, m_{Mn}, m_F) = g\beta HM + AMm_{Mn} + \sum_{i=1}^6 \langle M m_{F_i} | S \cdot A^i \cdot I_{F_i} | M m_{F_i} \rangle + \frac{1}{6}a \langle M | S_x^4 + S_y^4 + S_z^4 - \frac{1}{3}S(S+1)(3S^2 + 3S - 1) | M \rangle + (A^2/2g\beta H) \{ M[I(I+1) - m_{Mn}^2] - m_{Mn}[S(S+1) - M^2] \} - g_{Mn}\beta_n H m_{Mn} - g_F\beta_n H \sum_{i=1}^6 m_{F_i} \quad (2)$$

M is the electronic magnetic quantum number of the Mn^{2+} , m_{Mn} is the nuclear quantum number of the Mn nucleus, and

$$M_F = (\sum_{i=1}^6 m_{F_i})$$

is the sum of the nuclear magnetic quantum numbers of the six F nuclei nearest the Mn^{2+} . The fifth term on

TABLE II. NMR linewidth (in gauss) of F and Li in Mn²⁺:LiF.

Nucleus	Sample	77°K		4°K		Nominal 1.5°K	
		Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
F	10%	5.5	7.0	4.0	99.1	4.0(1.57°)	264.0
F	1%	5.3	5.2	5.9	33.2	6.0(1.57°)	87.7
F	0.1%	6.3	4.9	6.1	11.5	6.9(1.71°)	28.2
F	0.01%	6.1	4.9	6.3	5.9	5.5(1.65°)	10.1
Li	10%	6.0	10.3	11.1	175	22 (1.51°)	465
Li	1%	6.1	5.8	6.6	58.2	8.7(1.51°)	154
Li	0.1%	6.3	5.1	6.4	19.0	6.7(1.49°)	49.3
Li	0.01%	6.5	5.0	6.8	7.7	6.9(1.70°)	16.3

the right-hand side is the hyperfine interaction to second order.

Using published values of the energy eigenvalues for the fourth term⁷ and taking the angular average of the energy eigenvalue of the total Hamiltonian (2) appropriate for the spectrum of the powder we obtain finally the transition energies

$$\begin{aligned}
 E_{\frac{1}{2} \rightarrow -\frac{1}{2}} &= E_0 + 7E_1 + E_2 \left[\left(\frac{3}{4} - m_{Mn}^2 \right) + 4m_{Mn} \right], \\
 E_{\frac{1}{2} \rightarrow \frac{1}{2}} &= E_0 + 29E_1 + E_2 \left[\left(\frac{3}{4} - m_{Mn}^2 \right) + 2m_{Mn} \right], \\
 E_{\frac{3}{2} \rightarrow -\frac{1}{2}} &= E_0 + 22E_1 + E_2 \left[\left(\frac{3}{4} - m_{Mn}^2 \right) + 0 \right], \\
 E_{\frac{3}{2} \rightarrow \frac{1}{2}} &= E_0 + 29E_1 + E_2 \left[\left(\frac{3}{4} - m_{Mn}^2 \right) - 2m_{Mn} \right], \\
 E_{\frac{5}{2} \rightarrow -\frac{1}{2}} &= E_0 + 7E_1 + E_2 \left[\left(\frac{3}{4} - m_{Mn}^2 \right) - 4m_{Mn} \right],
 \end{aligned} \quad (3)$$

where

$$\begin{aligned}
 E_0 &= (g\beta H + Am_{Mn} + A_s m_F), \\
 E_1 &= \frac{1}{3} (a^2/g\beta H) \quad \text{and} \quad E_2 = (A^2/2g\beta H).
 \end{aligned}$$

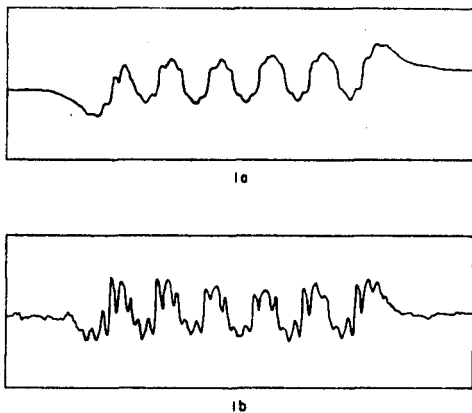


FIG. 1. The X-band microwave spectra of Mn²⁺ showing the electronic $\frac{1}{2} \rightarrow -\frac{1}{2}$ transitions exhibiting the superhyperfine lines that result from the interaction of the Mn²⁺ nucleus, the Mn electrons and the fluorine nucleus in (a) 1% nominal Mn²⁺ molar concentration in LiF. The abscissa is the derivative of the microwave absorption and the ordinate the magnetic field. (b) A 0.1% nominal Mn²⁺ molar concentration in LiF.

⁷ E. De L. Kronig and C. J. Bouwkamp, *Physica* **6**, 290 (1939).

The term involving E_0 is the most important term in Eq. (3) in that it determines the main features of the spectrum. The term involving $g\beta H$ specifies the interaction of the Mn²⁺ electronic moment with the applied field, H . The term Am_{Mn} splits the electronic transitions into six lines, the hyperfine lines. Each of these lines is split by the interaction with the fluorine nuclei into seven superhyperfine lines corresponding to $m_F = 3, 2, 1, 0, -1, -2, -3$ having relative intensities 1, 6, 15, 20, 15, 6, 1, respectively. A_s is the isotropic component of the Mn²⁺ electron-F nucleus magnetic interaction tensor.

The term E_1 in Eq. (3) is insignificant in that it makes an immeasurable contribution to the frequency of the various transitions since a is of the order of 20 G. However, it is important to mention that the energies of the satellite lines depended linearly on a prior to the angular averaging while the central line ($\frac{1}{2} \leftarrow -\frac{1}{2}$) had a quadratic dependence. Thus the detailed features of the X-band spectrum appearing in Fig. 1 are due to the $\frac{1}{2} \leftarrow -\frac{1}{2}$ transitions while the satellite lines contribute to the broad features. The effect of the E_2 term does not modify the powder spectrum in a significant way.

The K-band spectrum also showed the superhyperfine splitting but the lines are not resolved as well due to the increased effective magnetic moment which is proportional to the Boltzmann factor. The factor $\mathbf{u} \cdot \mathbf{H}_{K\text{-band}}$ in $e(\mathbf{u} \cdot \mathbf{H}/kT)$ is about three times as great as $\mathbf{u} \cdot \mathbf{H}_{X\text{-band}}$.

The experimental results are presented in Table I and are compared with data on other crystals containing Mn²⁺ impurities.

Discussion of Higher Concentration

NMR linewidths were also measured as part of the investigation. The width of nuclear resonance lines may be due to the broadening by the radio-frequency field, by the spin lattice relaxation, by the spin-spin relaxation, by external magnetic field inhomogeneities, by the local field, etc. The temperature-dependent part

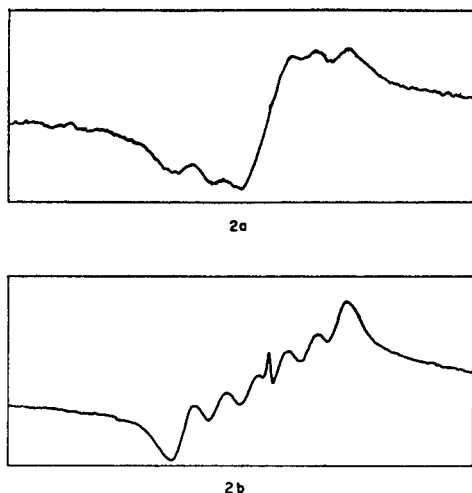


FIG. 2. (a) *K*-band microwave spectrum of 10% nominal Mn^{2+} molar concentration in LiF at 77°K; (b) the remaining paramagnetic spectrum after "MnF clusters" have gone antiferromagnetic at 4.2°K (The sharp spike near the center of (b) is due to a condensate on a mica window.) The abscissa is the derivative of the microwave absorption and the ordinate the magnetic field.

of the local H field is from the temperature dependence of the time-average magnetic moment of the magnetic electrons of the paramagnetic impurities, in this case the Mn^{2+} ions. Existing theories predict that this part is proportional to the inverse of the temperature. The behavior of the lithium nuclei is qualitatively as expected; however, the behavior of the observed fluorine linewidths is very different from that which is predicted by the usual theories. As is shown in Table II, the fluorine nuclear resonance linewidth remains essentially constant as one proceeds to the lowest temperature. This constancy is partially explained by assuming that part of the crystal is in some form of MnF_2 and thus is in the antiferromagnetic state at the lower temperatures. Hence the Larmor frequency of the F nuclei in these MnF_2 clusters is shifted out of the range of the spectrometer.

This same hypothesis is given further credence by the *K*-band paramagnetic spectrum behavior at low temperatures, in the case of the 10% concentration. In Fig. 2(a) is a recording of the derivatives of the absorption curve for this sample at 77°K where the paramagnetic susceptibility is near its maximum for pure MnF_2 . Figure 2(b) shows a spectrum of the same sample at 4.2°K, by comparing the areas under the broad lines and the narrower hyperfine lines, it is estimated that 40% of the sample was in the antiferromagnetic state at 4.2°K, hence out of the spec-

trometer range. [The existing theories indicate that to first order, the shift is $(2H_0 H_a)^{1/2}$. For MnF_2 in the pure state this is about 10^6 G and hence well outside the range of either spectrometer.]

EXPERIMENTAL

The sample of LiF containing Mn^{2+} as an impurity was obtained by precipitation with NH_4F from a water solution of LiCl and $MnCl_2$. The precipitate was separated from the water solution by suction filtration and was washed with water and dried. The amount of Mn^{2+} in the crystal was determined by controlling the amount of $MnCl_2$ in the initial water solution. The mole fraction of Mn^{2+} in the crystal appears to be less by a factor of 10 than the mole fraction of Mn^{2+} in the initial water solution.

An *X*-band spectrometer was used for the work at room temperature, and the low temperature measurements were performed with a *K*-band system since this waveguide size could easily fit into a Dewar. The *X*-band spectrometer was powered by a 2K25 Klystron.

For the *X*-band measurements the sample was contained in a cylindrical cavity ($Q \sim 14\,000$) operating in the TE₀₁₁ mode. The transmitted microwave power was detected and amplified using standard phase-sensitive amplification. Automatic frequency regulation was obtained by locking in on the sample cavity by means of 290-kc/sec alternating voltage applied to the reflector and the 290-kc/sec transmitted microwave power crystal detected, amplified, phase detected and fed back as dc voltage to the reflector power supply. The 6-in. magnet used was provided with a slow sweep as well as an audio-frequency modulation. The slowest sweep provided was 1000 G/h.

The *K*-band spectrometer differed from the *X*-band principally in that either a reflection type cavity or shorted section of waveguide was used. Power was supplied by an EMI 960 Klystron. The AFC frequency was 10 kc/sec, referenced to either the sample cavity, or a cavity wave meter when the shorted waveguide was used. A 12-in. magnet with a 3-in. gap to accommodate the Dewar was used for both *K*-band and NMR measurements. The NMR measurements were made by conventional circuits using a marginal oscillator and a phase detector.

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