Magnetic Resonance of Mn\textsuperscript{2+}-Doped LiF Crystals\textsuperscript{*} \textsuperscript{†}

T. T. Chang,\textsuperscript{†} W. H. Tantilla, and J. S. Wells

University of Colorado, Boulder, Colorado

(Received 20 June 1963)

The electron paramagnetic resonance of Mn\textsuperscript{2+} 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 Mn\textsuperscript{2+} ions which were introduced chemically into the lattice in small amounts. In the highest concentration, the K-band spectra indicate that part of the Mn\textsuperscript{2+} 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 Mn\textsuperscript{2+} ion was determined to be $A_\text{eff}=90.4\pm2\times10^5$ cm\textsuperscript{-1}, and the isotropic part of the superhyperfine interaction with each of the six fluorine nearest-neighbor nuclei was measured to be $A_\text{i}=17.1\pm0.5\times10^5$ cm\textsuperscript{-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 Mn\textsuperscript{2+} substitutional impurities in ZnF\textsubscript{2} was observed by Tinkham\textsuperscript{1} to have superposed on the usual Mn\textsuperscript{2+} hyperfine spectrum an additional splitting due to the interaction of the Mn\textsuperscript{2+} 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 publications\textsuperscript{2} 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 MnF\textsubscript{2} at temperatures immediately above the antiferromagnetic transition temperature.\textsuperscript{3}

In our experiment we have observed the superhyperfine interaction of the Mn\textsuperscript{2+} electrons with the F nuclei in LiF doped with Mn\textsuperscript{2+}. The phenomena appears on the microwave spectrum of the Mn\textsuperscript{2+} as a splitting of each of the six hyperfine lines into seven superhyperfine lines due to the interaction of the d-shell electrons

\textsuperscript{*}This work was supported in part by a grant from the National Science Foundation and a contract from the U. S. Air Force Office of Scientific Research.


\textsuperscript{3}R. G. Shulman and V. Jaccarino, Phys. Rev. 103, 1126 (1956).
Table I. The values of the $g$ factor of Mn$^{2+}$, the hyperfine interaction parameter for Mn$^{2+}$ (designated as $A^{2+}$) and the isotropic superhyperfine interaction parameter $A_s$ for Mn$^{2+}$ are given for various compounds.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$g$</th>
<th>$A^{2+}$</th>
<th>$A_s$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnF$_2$</td>
<td>2.002±0.005</td>
<td>$-96.27±2.8$</td>
<td>16.56±0.19</td>
<td>Tinkham*</td>
</tr>
<tr>
<td>ZnF$_3$</td>
<td>2.0016±0.001</td>
<td>$-81.2±0.5$</td>
<td>16.56±0.19</td>
<td>Clugstonb</td>
</tr>
<tr>
<td>MgO</td>
<td>2.0013±0.001</td>
<td>$-95.4±1$</td>
<td>15.8±0.1</td>
<td>Low*</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>2.0012±0.002</td>
<td>$-92.6±0.9$</td>
<td>15.8±0.1</td>
<td>Low*</td>
</tr>
<tr>
<td>KCdF$_3$</td>
<td>2.0009±0.0005</td>
<td>$-75.4±0.2$</td>
<td>15.8±0.1</td>
<td>Ogawad</td>
</tr>
<tr>
<td>SrS</td>
<td>2.0009±0.0010</td>
<td>$-90.6±1$</td>
<td>15.8±0.1</td>
<td>Manenkov*</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>2.0019±0.0010</td>
<td>$-90.1±2$</td>
<td>17.1±0.3</td>
<td>Drumhellerf</td>
</tr>
</tbody>
</table>

* See Refs. (1) and (2).
+ See Ref. (2).
- See Ref. (8).
- W. G. Penney and R. Schlapp, Phys. Rev. 41, 194 (1932); See also W. Low, ibid. 105, 793 (1957).
Mn\textsuperscript{2+} Doped LiF Crystals

Table II. NMR linewidth (in gauss) of F and Li in Mn\textsuperscript{2+}:LiF.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>10%</td>
<td>5.5</td>
<td>7.0</td>
<td>4.0</td>
<td>99.1</td>
<td>4.0</td>
<td>264.0</td>
</tr>
<tr>
<td>F</td>
<td>1%</td>
<td>5.3</td>
<td>5.2</td>
<td>5.9</td>
<td>33.2</td>
<td>6.0</td>
<td>87.7</td>
</tr>
<tr>
<td>F</td>
<td>0.1%</td>
<td>6.3</td>
<td>4.9</td>
<td>6.1</td>
<td>11.5</td>
<td>6.9</td>
<td>28.2</td>
</tr>
<tr>
<td>F</td>
<td>0.01%</td>
<td>6.1</td>
<td>4.9</td>
<td>6.3</td>
<td>5.9</td>
<td>5.5</td>
<td>10.1</td>
</tr>
<tr>
<td>Li</td>
<td>10%</td>
<td>6.0</td>
<td>10.3</td>
<td>11.1</td>
<td>175</td>
<td>22</td>
<td>465</td>
</tr>
<tr>
<td>Li</td>
<td>1%</td>
<td>6.1</td>
<td>5.8</td>
<td>6.6</td>
<td>58.2</td>
<td>8.7</td>
<td>154</td>
</tr>
<tr>
<td>Li</td>
<td>0.1%</td>
<td>6.3</td>
<td>5.1</td>
<td>6.4</td>
<td>19.0</td>
<td>6.7</td>
<td>49.3</td>
</tr>
<tr>
<td>Li</td>
<td>0.01%</td>
<td>6.5</td>
<td>5.0</td>
<td>6.8</td>
<td>7.7</td>
<td>6.9</td>
<td>16.3</td>
</tr>
</tbody>
</table>

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

Using published values of the energy eigenvalues for the fourth term\textsuperscript{7} 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

\[
E_{l+1} = E_0 + \frac{1}{2} \varepsilon + \frac{1}{2} \varepsilon (a^2/\gamma H),
\]

\[
E_{l-1} = E_0 + 2\varepsilon + \frac{1}{2} \varepsilon (a^2/\gamma H),
\]

\[
E_{l-1} = E_0 + 2\varepsilon + \frac{1}{2} \varepsilon (a^2/\gamma H),
\]

\[
E_{l+1} = E_0 + \frac{1}{2} \varepsilon + \frac{1}{2} \varepsilon (a^2/\gamma H),
\]

where

\[
E_0 = (g\beta H + Am_{\text{Mn}} + Ax, m_F),
\]

\[
E_1 = \frac{1}{2} \varepsilon (a^2/\gamma H) \quad \text{and} \quad E_2 = (A^2/2g\beta H).
\]

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 Mn\textsuperscript{2+} electronic moment with the applied field, \(H\). The term \(Am_{\text{Mn}}\) 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. \(A_r\) is the isotropic component of the Mn\textsuperscript{2+} 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 \((3/2 - 1/2)\) had a quadratic dependence. Thus the detailed features of the X-band spectrum appearing in Fig. 1 are due to the \(3/2 - 1/2\) 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 \(\nu \cdot H_{\text{K-band}}\) in \(e(\nu \cdot H/kT)\) is about three times as great as \(\nu \cdot H_{\text{X-band}}\).

The experimental results are presented in Table I and are compared with data on other crystals containing Mn\textsuperscript{2+} 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

\[7\] E. De L. Kronig and C. J. Bouwkamp, Physica 6, 290 (1939).
FIG. 2. (a) K-band microwave spectrum of 10% nominal Mn
molar concentration in LiF at 77°K; (b) the remaining para-
magnetic spectrum after "MnF clusters" have gone antiferro-
magnetic 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.

The sample of LiF containing Mn\textsuperscript{2+} as an impurity
was obtained by precipitation with NH\textsubscript{4}F from a water
solution of LiCl and MnCl\textsubscript{2}. The precipitate was sepa-
rated from the water solution by suction filtration and
was washed with water and dried. The amount of Mn\textsuperscript{2+}
in the crystal was determined by controlling the amount of MnCl\textsubscript{2} in the initial water solution. The mole fraction of Mn\textsuperscript{2+} in the crystal appears to be less
by a factor of 10 than the mole fraction of Mn\textsuperscript{2+} in the
initial water solution.

An X-band spectrometer was used for the work at
room temperature, and the low temperature measure-
ments 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.

The same hypothesis is given further credence by the
X-band paramagnetic spectrum behavior at low
temperatures, in the case of the Mn\textsuperscript{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 ex-
pected; however, the behavior of the observed fluorine
linewidths is very different from that which is pre-
dicted by the usual theories. As is shown in Table II,
the fluorine nuclear resonance linewidth remains essen-
tially constant as one proceeds to the lowest tempera-
ture. This constancy is partially explained by assuming
that part of the crystal is in some form of MnF\textsubscript{2} and
thus is in the antiferromagnetic state at the lower
temperatures. Hence the Larmor frequency of the
F nuclei in these MnF\textsubscript{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\textsubscript{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 anti-
ferromagnetic state at 4.2°K, hence out of the spec-
trometer range. [The existing theories indicate that
to first order, the shift is \((2H_e H_a)\). For MnF\textsubscript{2} in the
pure state this is about 106 G and hence well outside
the range of either spectrometer.]

ACKNOWLEDGMENT

We wish to acknowledge discussions with Dr. James
Currin concerning some aspects of the analysis of the
spectrum.