Mössbauer Spectroscopy Study of the Spin-Flop Transition in Fe-Doped MnF_2

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Measurements of the hyperfine interaction in Fe^{++} in MnF_2 in external fields above the spin-flop field at 4.2 K are reported and a value of $g_{\perp} = 2.13$ is derived, in good agreement with theory.

I. INTRODUCTION

Below 67.3 K MnF_2 is a uniaxial antiferromagnet with spins aligned along the c axis. At helium temperatures and in applied magnetic fields H_0 greater than 93 kOe along the c axis, the spins flop into the basal plane.¹ Ferrous ions may be grown substitutionally in single crystals of MnF_2 . Because of the greater single-ion anisotropy of Fe^{++} as compared with that of Mn^{++} , the spin-flop field H_{sf} increases with iron concentration and is 105 kOe for 1% Fe: MnF_2 .²

Hyperfine interactions in Fe^{++} -doped MnF_2 at 4.2 K and zero applied field have been reported by Wertheim *et al.*,³ who found that the saturation magnetic hyperfine field at ^{57}Fe nuclei H_{hf} in Fe: MnF_2 is 227.5 kOe. In this paper we report Mössbauer measurements of hyperfine interactions in single crystals of Fe-doped MnF_2 at 4.2 K and in external magnetic fields above and below the spin-flop transition. From the change in the magnetic hyperfine field in going through the spin flop, we derive a value for $g_{\perp}$ which we compare with the value derived using parameters measured in FeF_2 .

II. EXPERIMENTAL RESULTS

Single crystals of Fe^{++} -doped MnF_2 were grown from a melt of MnF_2 and isotopically enriched FeF_2

by Optovac, Inc. The single crystals were oriented and thin (6–10 mil) slices were cut perpendicular to the c axis. Mössbauer spectra were taken in a conventional constant-acceleration spectrometer operating in the normalized mode. Measurements for $H_0 \leq 75$ kOe were made in a superconducting solenoid. Spectra at higher fields were obtained using a Bitter solenoid.

At $T = 4.2$ K and $H_0 = 0$ and for γ rays propagating parallel to the c axis, we observe a spectrum consisting of three lines ($\Delta m = 0$ lines are forbidden and the two inner lines are superimposed) which yields the magnetic hyperfine field $H_{hf} \leq 228$ kOe $\parallel c$ and the electric quadrupole splitting parameters $V_{zz}(\perp c) = -2.80$ mm/sec and $\eta = 0.5$. For $H_0 \parallel c$ but less than H_{sf} we observe a spectrum which is the superposition of spectra corresponding to the two sublattices, one with an effective field at the nucleus $H_n = H_{hf} + H_0$ and the other with $H_n = H_{hf} - H_0$. For H_0 greater than H_{sf} , the spectrum changes dramatically due to the appearance of the $\Delta m = 0$ lines and may be interpreted in terms of the magnetic field at the nucleus $\mathbf{H}_n = \mathbf{H}_0 + \mathbf{H}_{hf}$, with $\mathbf{H}_0 \parallel c$ and $\mathbf{H}_{hf} \perp c$ (Fig. 1). In MnF_2 , there are two crystallographic sites for the transition-metal ions, oriented at 90° with respect to each other and with equivalent orthorhombic symmetry. The principal axes

FIG. 1. Mössbauer spectrum of a single crystal of 1% $\text{Fe}^{2+}:\text{MnF}_2$ in an external magnetic field of 111.4 kOe $\parallel c$. Gamma-ray propagation is also $\parallel c$.

of the electric field gradient V_{zz} for Fe^{2+} in these sites are $[110]$ for one sublattice and $[\bar{1}\bar{1}0]$ for the other. If the spins flop to a $[100]$ direction, the angle between V_{zz} and the magnetic hyperfine field is the same for both sites and we expect a simple six-line spectrum. If the spins flop to a $[110]$ direction, then for one site $V_{zz} \perp H_{\text{hf}}$ and for the other site $V_{zz} \parallel H_{\text{hf}}$ and we expect a superposition of two spectra. Furthermore, because of the orthorhombic local symmetry, H_{hf} should not be the same for both sites. The superposition of two spectra is in fact expected for the spins lying in any direction other than $[100]$. From comparisons of the observed spectrum (Fig. 1) with calculated spectra, we hypothesize a two-domain model, in which one domain has spins oriented along $[100]$, and the other domain has spins not oriented along $[100]$, but probably $[110]$. We then have three superimposed spectra all with $V_{zz} = -2.8$ mm/sec and $\eta = 0.5$ and with $H_{\text{hf}} = -320$ kOe for spins along $[100]$ and $H_{\text{hf}} = -340$ kOe for spins along $[110] \perp V_{zz}$ and -260 kOe for spins along $[110] \parallel V_{zz}$.

III. DISCUSSION

The magnetic hyperfine field at the nucleus in Fe^{2+} in MnF_2 may be written⁴

$$H_{\text{hf}} = H_c + H_L + H_D$$

where H_c is the core polarization term, H_L is the orbital contribution term, and H_D is the dipolar term. The value of H_{hf} above the spin flop depends on the direction of the spins on the basal plane. In going through the spin flop H_c does not change⁵ and so the difference between $H_{\text{hf}}^<$ and $H_{\text{hf}}^>$ is due to changes in the values of H_L and H_D . Therefore,

$$\Delta H_{\text{hf}} = H_{\text{hf}}^> - H_{\text{hf}}^< = \Delta H_D + \Delta H_L.$$

ΔH_D for Fe^{2+} in MnF_2 is estimated using the wave function for the ground state of Fe^{2+} in MnF_2 given by Johnson and Ingalls.⁶ When the spins flop to the $[100]$ direction, we obtain $\Delta H_D = +30$ kOe. Since $\Delta H_{\text{hf}} = -320 + 228 = -92$ kOe, we obtain $\Delta H_L = -122$ kOe. When the spins flop to the $[110]$ direction we have two values of H_{hf} corresponding to the two orientations relative to V_{zz} . For $H_{\text{hf}} \parallel V_{zz}$ we calculate $\Delta H_D = +78$ and then get $\Delta H_L = -110$. For $H_{\text{hf}} \perp V_{zz}$ we calculate $\Delta H_D = 0$ and get $\Delta H_L = -112$. ΔH_L is related to the g factors by the expression

$$\Delta H_{L_i} = 2\beta \langle r^{-3} \rangle S(g_i - g_{\parallel}),$$

where g_i is the component of the gyromagnetic factor in the direction of H_{hf} in the flopped phase (i.e., $\perp c$) and $g_{\parallel}$ is that $\parallel$ to c . From our data we obtain $g_{\parallel} - g_i = +0.13 \pm 0.01$ for the three different cases. $g_{\parallel}$ for Fe^{2+} in MnF_2 has been measured by far-infrared spectroscopy^{7,8} giving $g_{\parallel} = 2.30$, hence $g_{\perp} = g_i = 2.17$. These values for g may be compared with values calculated using crystal-field theory and parameters obtained from optical and Mössbauer experiments.⁶ These parameters include the spin-orbit coupling and the crystal-field splittings. We calculate $g_{\parallel} - g_i = +0.16$ for spins parallel to V_{zz} and $g_{\parallel} - g_i = +0.15$ for spins perpendicular to V_{zz} in good agreement with the experimental results.

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‡ Supported by the U.S. Air Force Office of Scientific Research.

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