Below 67.3 K MnF₂ is a uniaxial antiferromagnet with spins aligned along the c axis. At helium temperatures and in applied magnetic fields $H_o$ greater than 93 kOe along the c axis, the spins flop into the basal plane. Ferrous ions may be grown substitutionally in single crystals of MnF₂. Because of the greater single-ion anisotropy of Fe²⁺ as compared with that of Mn²⁺, the spin-flop field $H_{sf}$ increases with iron concentration and is 105 kOe for 1% Fe:MnF₂.

Hyperfine interactions in Fe²⁺-doped MnF₂ at 4.2 K and zero applied field have been reported by Wertheim et al., who found that the saturation magnetic hyperfine field at $^{57}$Fe nuclei $H_{hf}$ in Fe:MnF₂ is 227.5 kOe. In this paper we report Mössbauer measurements of hyperfine interactions in single crystals of Fe-doped MnF₂ 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 $g_\perp = 2.13$ is derived, in good agreement with theory.

II. EXPERIMENTAL RESULTS

Single crystals of Fe²⁺-doped MnF₂ were grown from a melt of MnF₂ and isotopically enriched FeF₂ 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 $H_o < 75$ kOe were made in a superconducting solenoid. Spectra at higher fields were obtained using a Bitter solenoid.

At $T=4.2$ K and $H_o=0$ 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 $H_{hf} = 228$ kOe || c and the electric quadrupole splitting parameters $V_{zz}(\perp c) = -2.80$ mm/sec and $\eta = 0.5$. For $H_o || c$ 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 $H_n = H_{hf} + H_o$ and the other with $H_n = H_{hf} - H_o$. For $H_o$ 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 $H_n = H_o + H_{hf}$, with $H_o || c$ and $H_{hf} \perp c$ (Fig. 1). In MnF₂, 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
of the electric field gradient $V_{zz}$ for Fe$^{+\ +}$ in these sites are [110] for one sublattice and [110] 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 $V_{zz} \parallel H_{hf}$ and for the other site $V_{zz} \perp H_{hf}$ 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 $H_{hf} = -320$ kOe for spins along [100] and $H_{hf} = -340$ 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$^{+\ +}$ in MnF$_2$ may be written

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

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 change and so the difference between $H_{hf}^c$ and $H_{hf}^s$ is due to changes in the values of $H_L$ and $H_D$. Therefore,

$$\Delta H_{hf} = H_{hf}^s - H_{hf}^c = \Delta H_D + \Delta H_L.$$

$\Delta H_D$ for Fe$^{+\ +}$ in MnF$_2$ is estimated using the wave function for the ground state of Fe$^{+\ +}$ in MnF$_2$ given by Johnson and Ingalls. When the spins flop to the [100] direction, we obtain $\Delta H_D = +30$ kOe. Since $\Delta H_{hf} = -320 + 228 = -92$ 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 $H_{hf} || V_{zz}$ we calculate $\Delta H_D = +78$ and then get $\Delta H_L = -110$. For $H_{hf} \perp V_{zz}$ we calculate $\Delta H_D = 0$ and get $\Delta H_L = -112$. $\Delta H_L$ is related to the $g$ factors by the expression

$$\Delta H_L = 2\beta(\gamma^2)S(g_{||} - g_{\parallel}),$$

where $g_{||}$ 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 $|| c$. From our data we obtain $g_{||} - g_{\parallel} = +0.13 \pm 0.01$ for the three different cases. $g_{||}$ for Fe$^{+\ +}$ in MnF$_2$ has been measured by far-infrared spectroscopy giving $g_{||} = 2.30$, hence $g_{\parallel} = g_{||} = 2.17$. These values for $g$ may be compared with values calculated using crystal-field theory and parameters obtained from optical and Mössbauer experiments. These parameters include the spin-orbit coupling and the crystal-field splittings. We calculate $g_{||} - g_{\parallel} = +0.16$ for spins parallel to $V_{zz}$ and $g_{||} - g_{\parallel} = +0.15$ for spins perpendicular to $V_{zz}$ in good agreement with the experimental results.

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$\Delta H_D$ is proportional to the iron magnetic moment which does not change when the spins flop at low temperature.
\[ T. Bernstein, A. Missetich, and B. Lax (unpublished). \]