HYPERFINE INTERACTIONS IN $\text{MgF}_2:\text{Fe}^{2+}$ AND $\text{ZnF}_2:\text{Fe}^{2+}$ BY MÖSSBAUER SPECTROSCOPY

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Measurement of the magnetic hyperfine interaction in paramagnetic Fe^{2+} in ZnF_2 and MgF_2 by Mössbauer spectroscopy is reported. The results, -275 ± 3 kOe and -270 ± 3 kOe for $\text{ZnF}_2:\text{Fe}^{2+}$ and $\text{MgF}_2:\text{Fe}^{2+}$ respectively are compared with a previous analysis of hyperfine interactions in the rutile fluorides.

We report the measurement of the magnetic hyperfine interactions in Fe^{2+} in single crystals of MgF_2 and ZnF_2 using Mössbauer spectroscopy. In a previous letter [1], we presented an analysis of the hyperfine interactions in Fe^{2+} in the isomorphous crystals MnF_2 , ZnF_2 and FeF_2 , in which we showed that the large variation in the hyperfine fields could be ascribed to small changes in the electronic ground state of Fe^{2+} in the three crystals. We also used that analysis to evaluate the hyperfine interactions in $\text{MnF}_2:\text{Fe}^{2+}$ in the spin-flopped state in large magnetic fields at low temperature [2]. Recently, the spin-hamiltonian parameters of the low lying electronic states of Fe^{2+} in MgF_2 have been measured [3] using far infrared spectroscopy and thus provide a good opportunity for checking on the analysis of the hyperfine interactions.

The measurements [4] of the hyperfine interactions in $\text{MnF}_2:\text{Fe}^{2+}$ and FeF_2 analyzed in our previous letter were made at low temperatures where these materials are magnetically ordered. The value for $\text{ZnF}_2:\text{Fe}^{2+}$

was obtained [5] by Wertheim and Buchanan by extrapolation of the hyperfine fields from mixed $(\text{ZnF}_2)_x(\text{FeF}_2)_{1-x}$ crystals which were also magnetically ordered. As $\text{MgF}_2:\text{Fe}^{2+}$ is not magnetically ordered, we have measured the hyperfine interaction in the Fe^{2+} by applying large magnetic fields at low temperature to saturate the electronic moment. We have also made similar measurements in samples of $\text{ZnF}_2:\text{Fe}^{2+}$ to check if the hyperfine interaction in the paramagnetic region coincides with the result obtained from the linear extrapolation [5] to $x = 1$ from the ferromagnetic samples.

Sources of ^{57}Co in MgF_2 and ZnF_2 were prepared by depositing acid solutions on the appropriate single crystal faces and diffusing in HF atmosphere at 800°C . Sources were prepared on both c and a faces for both materials. Contrary to previous work [6] we found that the ^{57}Co entered the lattice predominantly as Co^{2+} , or at least decayed to give predominantly Fe^{2+} . The zero field spectra from 4.2 K to 300 K consist of quadrupole doublets (table 1) with appropriate intensities for the a and c faces, providing evidence that the ^{57}Co enters single crystal lattice sites. At low

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Table 1

	ZnF ₂ :Fe ²⁺	MgF ₂ :Fe ²⁺
$g_{\parallel}$ ^{a)}	2.25 ± 0.02	2.26 ± 0.02
D ^{a)} (cm ⁻¹)	-8.29	-8.69
E ^{a)} (cm ⁻¹)	-0.67	-0.44
ΔE_Q (mm/s)		
295 K	2.80	2.83
4.2 K	3.13	3.11
H_{hf} (kOe)	-275 ± 3	-270 ± 3

^{a)} See ref. [3].

temperatures an applied magnetic field induces a magnetic hyperfine interaction (fig. 1) for the applied field directed along the c axis in both MgF₂ and ZnF₂, but no magnetic hyperfine field for the applied field directed along the a axis as expected from the spin hamiltonian [3, 7]. The hyperfine field for $H_0 \parallel c \parallel \gamma$, does not follow a Brillouin function of the applied field and temperature, but rather the full hyperfine splitting is observed for applied fields as low as 3 kOe, indicating that for these fields and temperatures the nuclear Larmor precession time is long compared to the nuclear lifetime and to the relaxation time between the lowest lying electronic levels. The measurements at higher fields show that the hyperfine fields have a negative sign in both cases.

The hyperfine fields in Fe²⁺ in the rutile fluorides may be written [8]

$$H_{hf} = H_c + H_d + H_L, \quad (1)$$

Fig. 1. Mössbauer spectrum of MgF₂:Fe²⁺ single crystal at 4.2 K and $H_0 = 40$ kOe, with $H_0 \parallel c \parallel \gamma$.

where H_c is a core polarization term, H_L is an orbital contribution term and H_d is a dipolar term. In our previous letter we assumed that the differences in H_{hf} in Fe²⁺ in the rutile fluorides was due to changes in H_L . This latter term can be written as $H_L = 2\beta \langle S_z \rangle \langle r^{-3} \rangle (g_{\parallel} - 2)$. We were thus able to correlate, within the limits of experimental error, the values of H_{hf} with the measured values of $g_{\parallel}$. Since $g_{\parallel}$ for Fe²⁺ cannot be measured with equivalent precision in the magnetically concentrated systems as in the dilute ones such as Fe²⁺:ZnF₂ and Fe²⁺:MgF₂, it is relevant to extend our previous analysis to these systems where $g_{\parallel}$ is better known. Eq. (1) can be written as

$$H_{hf} = A + B(g_{\parallel} - 2) \quad (2)$$

and from our previous analysis $A = H_c + H_d = 540 \pm 24$ kOe and $B = 1000 \pm 10$ kOe. The assumption implicit in eq. (2) is that A and $\langle r^{-3} \rangle$ are the same for Fe²⁺ in all the members of the rutile fluoride series even though the fluoride host cation distances are slightly different. In Fe³⁺ Geschwind [9] has shown that the core polarization contribution [which is one of the terms which contributes to A in eq. (2)] is the same in different hosts where the metal-ligand distance changes from 1.85 to 2.40 Å. Hazony [10] has also analyzed the hyperfine interactions in a series of Fe²⁺ compounds assuming constant $\langle r^{-3} \rangle$.

We find (table 1) the respective experimental values to be $H_{hf} = -275 \pm 3$ kOe and -270 ± 3 kOe for ZnF₂:Fe²⁺ and MgF₂:Fe²⁺. These experimental values thus agree with those predicted by eq. (1), within the errors of measurement of the g -factors and the values A and B . We conclude that these results support the validity of the assumptions outlined above and the use of eq. (1) to analyze hyperfine interactions in Fe²⁺ in the rutile fluorides.

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