ANALYSIS OF HYPERFINE INTERACTIONS OF Fe^{2+} IN FeF_2 , MnF_2 AND ZnF_2 *

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Analysis of magnetic hyperfine interactions of Fe^{2+} in FeF_2 , $\text{Fe}^{2+}:\text{MnF}_2$ and $\text{Fe}^{2+}:\text{ZnF}_2$ yields a core polarization hyperfine field $H_c = -514 \pm 30$ kOe and a value of $\langle r^{-3} \rangle_{\text{eff}} = 3.9 \pm 0.4$ au.

FeF_2 , MnF_2 and ZnF_2 all crystallize in the rutile fluoride structure and have very similar metal ion-fluorine distances [1]. One would therefore expect that the local environment of Fe^{2+} in doped MnF_2 and ZnF_2 would be similar to that in FeF_2 and the Fe^{2+} ion would have a similar electronic structure in all three hosts. Indeed, this has been shown by several experiments†. On the other hand, Mössbauer spectroscopy has shown a large variation in the magnetic hyperfine field for Fe^{2+} in the three hosts, viz., -329 kOe in FeF_2 , -227 kOe in MnF_2 and -276 kOe in ZnF_2 (table 1). As we show below, this variation can be attributed to small changes in the Fe^{2+} orbital moment and provides a sensitive measure of those differences. For example, we recently studied the hyperfine interactions in Fe^{2+} in antiferromagnetic MnF_2

Table 1
Parameters for FeF_2 , $\text{Fe}^{2+}:\text{MnF}_2$ and $\text{Fe}^{2+}:\text{ZnF}_2$

Host	H_{hf} (kOe)	$g_{\parallel}$	ΔE_Q (mm/sec)
FeF_2	-329	2.21	2.85
$\text{Fe}^{2+}:\text{MnF}_2$	-227	2.30	2.80
$\text{Fe}^{2+}:\text{ZnF}_2$	-276	2.24	3.13

above and below the spin-flop transition at 4.2°K [5], i.e., above and below ≈ 95 kOe along the c axis at which field the spins change their orientation from antiparallel along the c axis to antiparallel perpendicular to the c axis. The hyperfine field changed from -227 kOe for the orientation parallel to c to a value of the order of -330 kOe for the orientation perpendicular to c (depending on the orientation of the spin in the c plane with respect to the a axis). We found that the observed hyperfine fields could be successfully correlated with the values of $g_{\parallel}$ and $g_{\perp}$ for Fe^{2+} in MnF_2 [5].

The magnetic hyperfine field in Fe^{2+} may be written as [6]

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

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† The single ion anisotropy constant of Fe^{2+} in MnF_2 has a value which is very close to that of Fe^{2+} in FeF_2 [2]. The electronic spectrum of Fe^{2+} in MnF_2 is similar to that of FeF_2 [3].

where H_c is a core polarization term, H_L is an orbital contribution term and H_D is a dipolar term. The variation in H_{hf} in Fe^{2+} in the three hosts could be due to variations in all three terms, however, we will maintain that all the variation is due to changes in H_L . Firstly, because the three hosts have the same ligands and structures and have metal–ligand distances which are very similar, we can assume that H_c is the same in all three cases. Secondly, as shown by Johnson [6], H_D is proportional to the electric field gradient. The values of the quadrupole splitting in the three cases at 4.2°K (table 1) are 2.85 [4], 2.80 [5] and 3.13 [8] mm/sec for FeF_2 , MnF_2 and ZnF_2 respectively. These values are within 10% of each other. In FeF_2 Johnson and Ingalls have estimated $H_D = -26$ kOe, therefore the corresponding variations in H_D can be no greater than ≈ 3 kOe. This leaves the orbital term H_L , which can be written (for the applied field or sublattice magnetization along the c axis) [6]

$$H_L = 2\beta\langle S \rangle(g_{\parallel} - 2)\langle r^{-3} \rangle_{eff} \quad (2)$$

$g_{\parallel}$ has been measured in the three hosts by different methods. In FeF_2 , Lines' analysis gives $g_{\parallel} = 2.21$ [9]; in $Fe^{2+}:MnF_2$, far-infrared measurements by Weber [10] and Bernstein et al. [11] give $g_{\parallel} = 2.30$; in $Fe^{2+}:ZnF_2$ ESR measurements by Tinkham [12] give $g_{\parallel} = 2.24$. These values are tabulated in table 1.

Combining eqs. (1) and (2), we write

$$H_{hf} = A + B(g_{\parallel} - 2), \quad (3)$$

with $A = H_c + H_D$ and $B = 2\beta\langle r^{-3} \rangle_{eff}\langle S_z \rangle$ and assuming, for reasons presented above, that A and B are the same for the three cases. Using the measured values of H_{hf} and $g_{\parallel}$, we obtain $A = 540 \pm 25$ kOe and $B = 1000 \pm 10$ kOe which yield $H_c = -514 \pm 30$ kOe and $\langle r^{-3} \rangle_{eff} = 3.9 \pm 0.4$ au. This value of H_c for Fe^{2+} is in good agreement with other calculated and experimental values. Watson and Freeman [13] calculate $H_c = -550$ kOe; in FeF_2 , Johnson and Ingalls [7] obtain

$H_c = -518 \pm 250$ kOe; in ionic cubic $KMgF_3$ Frankel et al. [14] obtain -495 ± 25 kOe; and recently Hazony [15] has shown that for a series of ionic Fe^{2+} compounds, $H_c \approx -530$ kOe.

The value of $\langle r^{-3} \rangle_{eff}$ that we obtain is higher than that estimated by Johnson and Ingalls [7] and Hazony [15] for FeF_2 (3.0 au). The difference may be due to inaccuracies in the values of $g_{\parallel}$. For our value of $\langle r^{-3} \rangle_{eff}$ to be in better agreement with the other values would require $g_{\parallel} \approx 2.19$ for FeF_2 , for which $g_{\parallel}$ has been reported with less precision than in the other cases.

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