Fe¹⁺ AND Fe²⁺ HYPERFINE FIELDS IN MgO AND CaO

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Hyperfine interactions have been measured for Fe¹⁺ and Fe²⁺ in MgO and CaO. The core polarization fields per spin moment are -127 kOe/μ_B for both Fe¹⁺ and Fe²⁺.

Multiple charge states have been observed in the Mössbauer spectra of ⁵⁷Co -doped MgO [1,2] and CaO [2] crystals. In this letter we report the observation of magnetic field-induced hyperfine structure in Fe¹⁺ and Fe²⁺ in MgO and CaO. From the measured hyperfine fields, we derive the core polarization fields, using calculated values for the orbital contribution to the hyperfine interaction in the crystal-field split ground state. We also present evidence for paramagnetic relaxation effects in Fe²⁺ in MgO in small external fields, which may be related to the zero-field splitting of the Fe²⁺ line into a doublet at 14°K [3].

The ground term of the ferrous ion is 3d⁶, ⁵D which is split in a cubic crystalline field into a lower orbital triplet (⁵T_{2g}) and an upper orbital doublet (⁵E_g). The triplet is further split by spin-orbit coupling so that at 4.2°K, only a triply degenerate state (effective S' = 1) is populated. The degeneracy of this state is lifted by a linear Zeeman interaction with an applied magnetic field. In Fe¹⁺, the ground term is 3d⁷, ⁴F which splits in a cubic crystalline field into two orbitally degenerate triplets and an orbital singlet with an orbital triplet lying lowest. The spin orbit coupling leaves a Kramers' doublet lowest.

The experimental spectra at 4.2°K and different external magnetic fields, H₀, show that the Fe¹⁺ splitting increases while the Fe²⁺ splitting

Fig. 1. Hyperfine field H_h as a function of external longitudinal fields at 4.2°K for Fe¹⁺ (upper) and Fe²⁺ (lower). The solid curves are calculated assuming thermal averages (eq. (1)).

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decreases with H_0 . From these splittings we measure the actual field at the nucleus H_n , where

$$H_n = H_{\text{hf}}^S BS \left(\frac{g\mu_B H_0}{kT} \right) \pm H_0, \quad (1)$$

BS is the Brillouin function for a spin S and H_{hf}^S is the saturation hyperfine field. From the data at large H_0/T ($BS \approx 1$), we find that $H_{\text{hf}}^S = +20$ kOe and -120 kOe for Fe^{1+} and Fe^{2+} respectively. The solid curves in fig. 1 are from eq. (1) and the above values of H_{hf}^S . In the case of Fe^{2+} , ($S' = 1$, $g = 3.428$) [4], the hyperfine structure appears for anomalously small values of H_0 and the deviation of the data from the theoretical curve indicates slow paramagnetic relaxation effects. For Fe^{1+} ($S' = \frac{1}{2}$, $g = 4.15$) [5] the deviation at the highest fields may reflect a field dependence of H_{hf}^S due to mixing of the ground and higher levels by the applied magnetic field.

The hyperfine field at the nucleus may be written as a sum of core polarization, orbital and dipolar contributions. In terms of the electronic state

$$H_{\text{hf}}^S = (H_C/2S) S \langle S_z \rangle + 2\mu_B k \langle r^{-3} \rangle \langle L_z \rangle + \frac{1}{2}\mu_B k \langle r^{-3} \rangle [3 \langle L_z^2 \rangle - L(L+1)] \langle S_z \rangle, \quad (2)$$

where $H_C/2S$ is the core polarization field per spin moment, k is the orbital reduction factor, and the expectation values refer to the $L = 2$, $S = 2$ basis for Fe^{2+} and the $L = 3$, $S = \frac{3}{2}$ basis for Fe^{1+} . The cubic site symmetry allows the calculation of the second and third terms of the second member of eq. (2) [6] and extraction of $H_C/2S$ from the measured H_{hf}^S , using calculated values of $\langle r^{-3} \rangle$ [7] and k values from EPR measurements [4, 5]*; the second and third terms are $+254$ and $+6$ kOe for Fe^{2+} and $+231$ and 0 kOe for Fe^{1+} , giving $H_C/2S = -127$ kOe/ μ_B for both Fe^{1+} and Fe^{2+} . The core polarization fields derived are in reasonably good agreement with the systematics of core polarization fields in the 3d transition metal ions [9].

The hyperfine spectrum in Fe^{2+} in MgO begins to appear at $H_0 \sim 250$ Oe and is fully developed at $H_0 \sim 800$ Oe. For these fields and at

* We note, however, that the k value (from EPR) appropriate to the moment is not necessarily the same as the k value appropriate to the hyperfine interaction because the former involves the expectation value of L_z while the latter involves the expectation value of $r^{-3}L_z$ [8] similar to the k value appropriate to spin-orbit coupling. The effect of increasing k on $H_C/2S$ may be calculated by noting that H_{orb} (in eq. (2) is proportional to k . Thus for Fe^{2+} , a 10% increase in k makes $H_C/2S = -133$ kOe/ μ_B .

4.2°K, all three levels of the ground triplet are populated and the spectrum is the superposition of the spectra for ions in each level. The $S_z' = 0$ level has a zero hyperfine interaction while the $S_z' = \pm 1$ levels have hyperfine interactions which are equal in magnitude and opposite in sign. In the limit of long relaxation time and external fields just large enough to quench the off-diagonal elements of the hyperfine interaction, we expect and observe a spectrum consisting of a single line superposed on a four line hyperfine spectrum with a splitting corresponding to H_{hf}^S and with relative intensities 3:1:4:1:3.

In CaO similar measurements give $H_{\text{hf}}^S = +28$ kOe and -235 kOe for Fe^{1+} and Fe^{2+} , respectively. Slow relaxation effects in external fields were observed for Fe^{2+} , but the deviations from eq. (1) were not as large as for Fe^{2+} in MgO. The high value of H_{hf}^S for Fe^{2+} in CaO results from a smaller orbital contribution in CaO than in MgO ($H_{\text{orb}} = +145$ kOe in CaO), if we assume that $H_C/2S$ is the same for CaO and MgO. Then we calculate from eq. (2) that $k \approx 0.5$ in CaO ($k \approx 0.8$ in MgO) [4] in substantial agreement with the EPR measurements of Shuskus [10]. A smaller value of k is generally associated with a higher degree of covalency in the ion-ligand bonds [7]. However, the isomer shifts in Fe^{2+} in MgO [1] and CaO [2] indicate *less* covalency in CaO. The smaller k value in CaO may therefore be due to a dynamical Jahn-Teller effect. As Ham [11] has discussed, such an effect can drastically reduce the value of k .

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