**Fe**^1+ AND **Fe**^2+ HYPERFINE FIELDS IN **MgO** AND **CaO**

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Received 15 June 1967

Hyperfine interactions have been measured for Fe**^1+** and Fe**^2+** in MgO and CaO. The core polarization fields per spin moment are -127 kOe/μ_B for both Fe**^1+** and Fe**^2+**.

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 Fe**^1+** and Fe**^2+** 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 Fe**^2+** in MgO in small external fields, which may be related to the zero-field splitting of the Fe**^2+** line into a doublet at 14ºK [3].

The ground term of the ferrous ion is 3d^6, 5D which is split in a cubic crystalline field into a lower orbital triplet (5T^2_g) and an upper orbital doublet (5E_g). The triplet is further split by spin-orbit coupling so that at 4.2ºK, 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 Fe**^1+**, the ground term is 3d^7, 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 4.2ºK and different external magnetic fields, H_O, show that the Fe**^1+** splitting increases while the Fe**^2+** splitting decreases.

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*On leave from the Centre d'Etudes Nucléaires, Grenoble, Supported by CEA, France.
†Supported by the U.S. Air Force Office of Scientific Research.
decreases with \( H_0 \). From these splittings we measure the actual field at the nucleus \( H_n \), where

\[
H_n = H_{hf} B_S \left( \frac{\mu_B H_0}{k_B T} \right) + H_0. \tag{1}
\]

\( B_S \) is the Brillouin function for a spin \( S \) and \( H_{hf}^B \) is the saturation hyperfine field. From the data at large \( T = 1 \), we find that \( H_{hf}^B = +20 \text{ kOe} \) and \(-120 \text{ kOe} \) for \( \text{Fe}^{1+} \) and \( \text{Fe}^{2+} \) respectively. The solid curves in fig. 1 are from eq. (1) and the above values of \( H_{hf}^B \). In the case of \( \text{Fe}^{2+} \), \( S^+ = \frac{3}{2}, g = 3.426 \) [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 \( \text{Fe}^{1+} \) \( (S^+ = \frac{1}{2}, g = 4.15) \) [5] the deviation at the highest fields may reflect a field dependence of \( H_{hf}^B \) 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

\[
H_{hf}^B = H_{hf}^c S (S_z^2) + 2 \beta H_{orb} \langle r^{-3} \rangle \langle L_z \rangle +
\]

\[
\frac{1}{2} H_{hf}^s \beta^s k^s \langle r^{-3} \rangle [3 (\langle L_z \rangle^2 - \langle L \rangle^2)] \langle S_z \rangle, \tag{2}
\]

where \( H_{hf}^c \) 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 \( \text{Fe}^{2+} \) and the \( L = 3, S = \frac{3}{2} \) basis for \( \text{Fe}^{1+} \). The cubic site symmetry allows the calculation of the second and third terms of the second member of eq. (2) [6] and extraction of \( H_{hf}^c \) from the measured \( H_{hf}^B \), 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 \( +6 \text{ kOe} \) for \( \text{Fe}^{2+} \) and \( +231 \) and \( 0 \text{ kOe} \) for \( \text{Fe}^{1+} \), giving \( H_{hf}^c = -123 \text{ kOe} \mu_B \beta H_0 \) for both \( \text{Fe}^{1+} \) and \( \text{Fe}^{2+} \). 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 \( \text{Fe}^{2+} \) in MgO begins to appear at \( H_0 \approx 250 \text{ Oe} \) and is fully developed at \( H_0 \approx 800 \text{ Oe} \) 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 \( r^{-3} L_z \) 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 \( H_{hf}^c/2S \) may be calculated by noting that \( \frac{H_{hf}^c}{2S} \) (in eq. (2)) is proportional to \( k \). Thus for \( \text{Fe}^{2+} \), a 10% increase in \( k \) makes \( H_{hf}^c/2S = -133 \text{ kOe}/\mu_B \).

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 \( S^+_z = 1 \) 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 \( H_{hf}^c \) and with relative intensities 3:1:4:1:3.

In CaO similar measurements give \( H_{hf}^c = +28 \text{ kOe} \) and \(-235 \text{ kOe} \) for \( \text{Fe}^{1+} \) and \( \text{Fe}^{2+} \), respectively. Slow relaxation effects in external fields were observed for \( \text{Fe}^{2+} \), but the deviations from eq. (1) were not as large as for \( \text{Fe}^{2+} \) in MgO. The high value of \( H_{hf}^c \) for \( \text{Fe}^{2+} \) in CaO results from a smaller orbital contribution in CaO than in MgO \( (H_{orb} = +145 \text{ kOe} \) in CaO, if we assume that \( H_{hf}^c \) is the same for CaO and MgO). Then we calculate from eq. (2) that \( k = 0.5 \) in CaO \( (k \approx 0.8 \text{ in MgO}) \) [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 \( \text{Fe}^{2+} \) 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 \( k \).

We are pleased to thank M. Blume, J. G. Dash, A. J. Freeman, P. S. Ham, A. Missetich, D. N. Pipkorn, H. C. Praddaude and H. H. Wickman for stimulating discussions.