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Stress-Induced Angular Momentum Quenching in MgO :Fe^{2+} as Observed by Mössbauer Spectroscopy

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Under the influence of a suitable uniaxial stress, the quenching of the electronic angular momentum of the low-lying threefold degenerate Γ_{5g} level of Fe^{2+} in cubic MgO has been observed by Mössbauer spectroscopy. The result is consistent with Ham's model for the appearance of a quadrupole doublet at low temperatures. A value for the strain coefficient of Fe^{2+} in MgO has been obtained: $G_{11}=585$ cm^{-1}.

I. INTRODUCTION

At $T\lesssim 14$°K in the absence of external magnetic fields, the experimental Mössbauer spectrum of Fe^{2+} in cubic MgO consists of a quadrupole doublet.[1,2] Ham[3] has proposed that this doublet is to be expected at suitably low temperatures on the basis of crystal field theory including the effect of random strains in the crystal. The ground state of the ferrous ion in octahedral symmetry is $3d^6\ {}^5D$ with $L=2$ and $S=2$ (Fig. 1). The crystalline electric field splits the ground term into an orbital triplet and an orbital doublet separated by $\sim 10^4$ cm^{-1}, with the triplet lying lowest. The fivefold spin degenerate orbital triplet is further split by the spin-orbit interaction into a number of levels of which a Γ_{5g} triplet is lowest, with an effective $J'=1$. The effect of random strains is to raise the

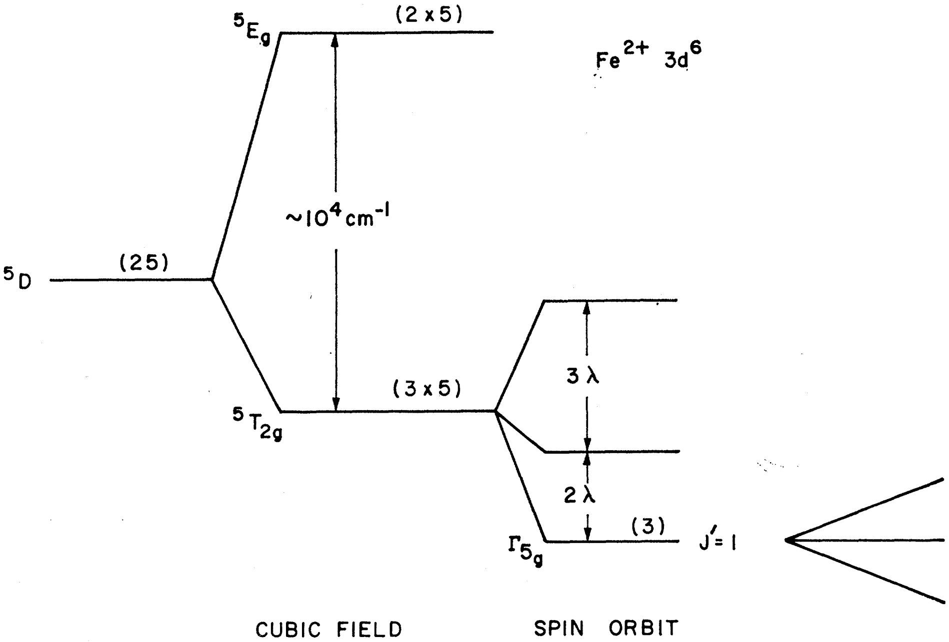

FIG. 1. Energy-level scheme of the Fe^{2+} ^5D term.

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[1] H. R. Leider and D. N. Pipkorn, Phys. Rev. **165**, 494 (1968).

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threefold degeneracy. Following Ham[3] each electronic eigenstate may then be written

$$|\psi\rangle = a|\xi\rangle + b|\eta\rangle + c|\zeta\rangle,$$

where $|\xi\rangle$, $|\eta\rangle$, and $|\zeta\rangle$ transform as yz, zx, and xy, respectively, and a, b, and c are real coefficients. Ham calculated the quadrupole interaction for the state $|\psi\rangle$ and obtained

$$\Delta E_Q = 3[C_3^2 + \tfrac{1}{3}(16C_5^2 - 9C_3^2)(a^2b^2 + b^2c^2 + c^2a^2)]^{1/2}, \quad (1)$$

where C_3 and C_5 are coefficients of the quadrupole interaction operator. C_3 and C_5 are related by crystal field theory, viz.,

$$-3C_3 = 4C_5; \quad (2)$$

hence the magnitude of the quadrupole splitting is independent of the coefficients a, b, and c (but the orientation of the field gradient does depend on the state). Using a point-charge crystal field model, Ham obtained

$$\Delta E_Q = (1/35)\langle r^{-3}\rangle(1-R)e^2Q, \quad (3)$$

where $\langle r^{-3}\rangle$ is the expectation value using one electron $3d$ orbitals, $(1-R)$ is the Sternheimer shielding, and Q is the quadrupole moment of the $I=\frac{3}{2}$ first excited state of ^{57}Fe. The collapse of the doublet above 14°K is due to motional narrowing resulting from rapid electronic transitions between the three strain-split Fe^{2+} states, which occur by an Orbach process[3] via the next higher-lying spin-orbit level at 95 cm^{-1}.[4]

The magnitude of the strain splitting may be obtained from the magnitude of the external field H_0 necessary for the onset of magnetic hyperfine structure in the Mössbauer spectrum. For a typical $\mathrm{MgO{:}Fe^{2+}}$ sample, this threshold value is $H_0=250$ Oe,[2] which with the g value of 3.428[5] corresponds to a strain splitting of $\sim 4\times 10^{-2}$ cm^{-1}. For larger values of the external field such that the magnetic splitting is larger than the strain splitting, the system behaves as a triplet with wave functions which may be characterized by $J_z'=\pm 1, 0$. Besides structure due to the interaction of the nucleus with the external field, paramagnetic and quadrupole hyperfine structure is observed for the $J_z'=\pm 1$ states while only quadrupole hyperfine structure is observed for the $J_z'=0$ state. The paramagnetic hyperfine structure is also motionally narrowed at $T>14$°K.[2]

Uniaxial stress applied perpendicular to the external magnetic field mixes the J_z' levels, and for large enough stress, again quenches the angular momentum. This is illustrated in Fig. 2. In this case the paramagnetic hyperfine splitting vanishes, leaving the quadrupole splitting and the direct interaction of the nucleus with

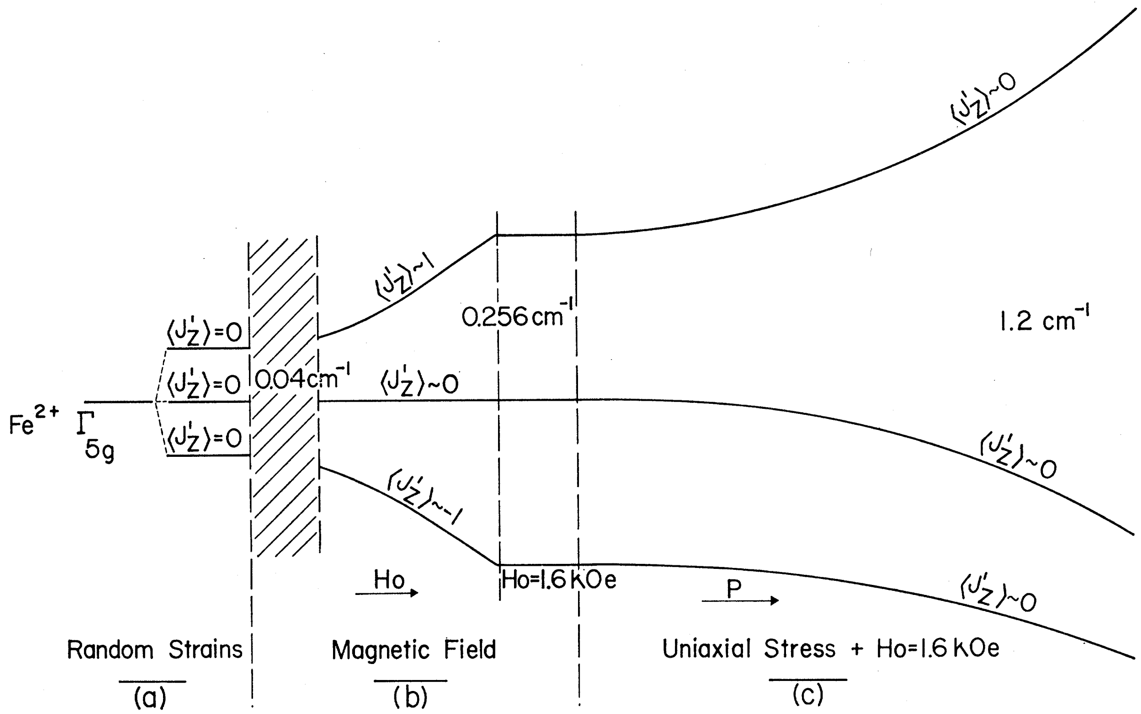

FIG. 2. Splitting of the Γ_{5g} energy level of Fe^{2+} in MgO produced by (a) random strains, (b) random strains and external field H_0, (c) random strains and external field H_0 and uniaxial stress P. Paramagnetic hyperfine structure is observed for (b), but vanishes for (a) and (c).

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[4] J. Y. Wong, Phys. Rev. **168**, 337 (1968).

[5] W. Low and M. Weger, Phys. Rev. **118**, 1130 (1960).

the external field. In this paper we report the observation by Mössbauer spectroscopy of the quenching of the orbital angular momentum. The experiment consists of observing the Fe^{2+} paramagnetic hyperfine structure as a function of increasing externally applied stress for the case where the stress is perpendicular to the applied field and the magnitude of the field is such that the magnetic splitting is much larger than the random strain splitting.

In Sec. II, we discuss experimental details, in Sec. III, we present the experimental results, and in Sec. IV, we discuss the results.

II. EXPERIMENTAL DETAILS

The Mössbauer measurements were made using a conventional constant acceleration electromechanical drive system together with a multichannel analyzer for collecting and storing the data. The sodium ferrocyanide room-temperature absorber was moved outside the Dewar. The source consisted of an MgO single crystal, one [100] face of which was coated with $^{57}CoCl_2$ and subsequently annealed at 1200°C for 24 h. The source exhibited Fe^{1+}, Fe^{2+}, and Fe^{3+} charge states.[2] At 4.2°K and in an external field $\sim$1 kOe, the Fe^{1+} spectrum consisted of a broadened single line, while the Fe^{3+} spectrum showed magnetic hyperfine structure. This structure overlapped the Fe^{2+} spectrum, but as the Fe^{3+} spectrum was insensitive to pressure over the range of pressures used in this experiment, changes in the Fe^{2+} spectrum were readily observed.

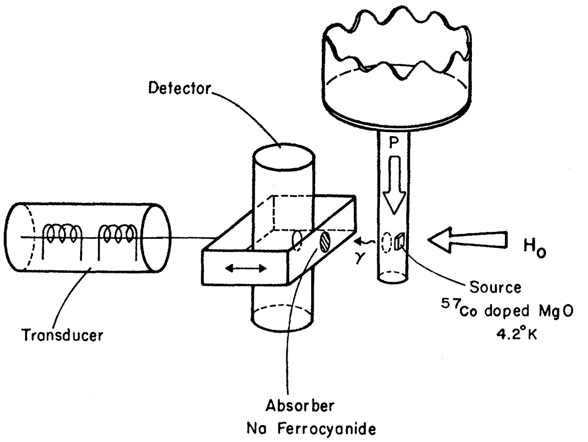
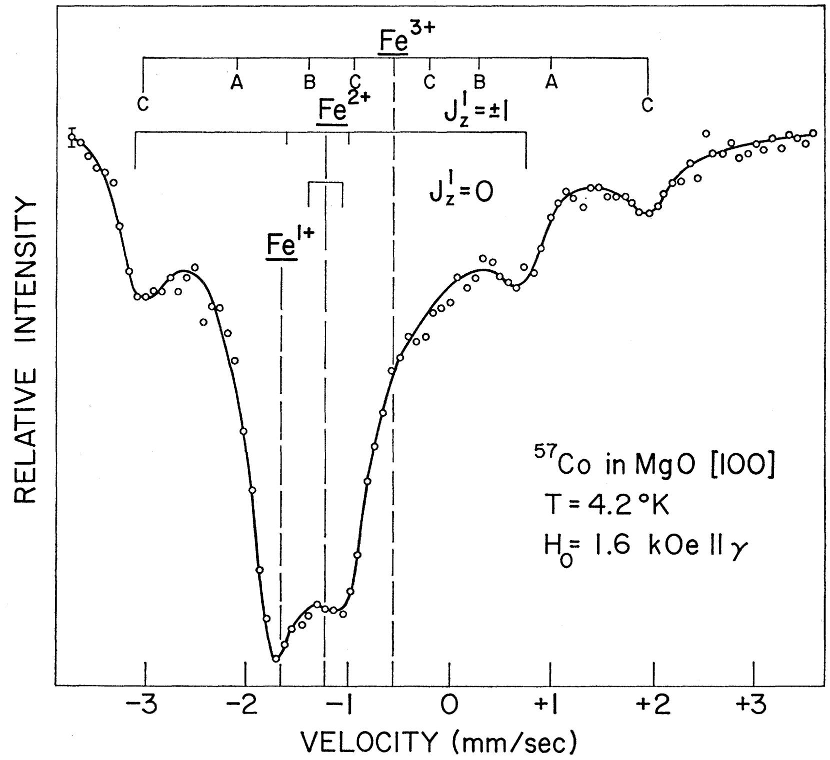


FIG. 3. Experimental arrangement. The pressure P is applied at right angles to the external field H_0 and the γ-ray observation direction.

Longitudinal magnetic fields up to 2 kOe were produced by a small water-cooled wire-wound solenoid fitted with a soft iron pole piece of 2 in. diam. The external stress was produced by a pneumatic cylinder and was transmitted to the sample at 4.2°K by a stainless-steel rod. The experiments were performed with the external magnetic field and γ-ray propagation directions parallel to [100] and the stress direction at right angles (Fig. 3).

FIG. 4. Velocity spectrum of the ^{57}Co-doped MgO source at 4.2°K and in an external field of 1.6 kOe. The effect of the external field has been omitted in the stick diagrams for the Fe^{2+} $J_z'=\pm1$, and $J_z'=0$ states. The stick diagram for Fe^{3+} indicates the lines in this velocity interval and A, B, and C are defined in Fig. 5.



III. RESULTS

The charge states 1+, 2+, and 3+ were clearly visible in the room-temperature spectrum.[2] Figure 4 shows the spectrum for the source at 4.2°K in a longitudinal magnetic field of 1.6 kOe. The Fe^{1+} line is unsplit, while the Fe^{2+} line shows magnetic hyperfine structure corresponding to an effective hyperfine field of −120 kOe for the $J_z'=\pm1$ states.[2] A field of 1.6 kOe corresponds to an electronic splitting of only 0.256 cm^{-1}, so that at 4.2°K all three states are populated. The positions of the lines corresponding to Fe^{3+} were obtained from spectra at higher velocity (Fig. 5) where the other Fe^{3+} lines are clearly visible. The spectra in transverse and longitudinal magnetic fields indicate three superimposed Fe^{3+} spectra, corresponding roughly to $|S_z\rangle=|\pm\frac{5}{2}\rangle$, $|\pm\frac{3}{2}\rangle$, and $|\pm\frac{1}{2}\rangle$. The values of the hyperfine fields, 540, 340, and 155 kOe, respectively, indicate some mixing of these "pure" states which is probably due to charge compensation. The line assignments were checked by making measurements at very low magnetic fields. The Fe^{2+} line does not show magnetic hyperfine structure until $H_0\approx250$ Oe but the Fe^{3+} line is split in smaller fields.

Figure 6 shows the Mössbauer spectra for the MgO source at 4.2°K in an external field of 1.6 kOe and at various values of external stress. The outermost Fe^{2+} hyperfine line positions are indicated by α and β and the disappearance of these lines with increasing stress is easily observable. The residual intensity at α and β is due to an Fe^{3+} contribution. Changes in the Fe^{3+} and Fe^{1+} spectra are not observed for these values of stress, as the latter is a Kramers's doublet, and the former, being an S-state ion, is much less sensitive to stress. Also, for values of P up to 3250 kg/cm^2 we did not detect any change in the value of the Fe^{2+} zero-field quadrupole splitting, as would be expected from Ham's result[3] that this splitting is independent of the amount of strain in the crystal as long as the stress does not appreciably mix the Γ_{5g} ground state with the excited electronic states. In the absence of random strains the Fe^{2+} hyperfine lines would shift smoothly into the center as a function of the applied stress, when the

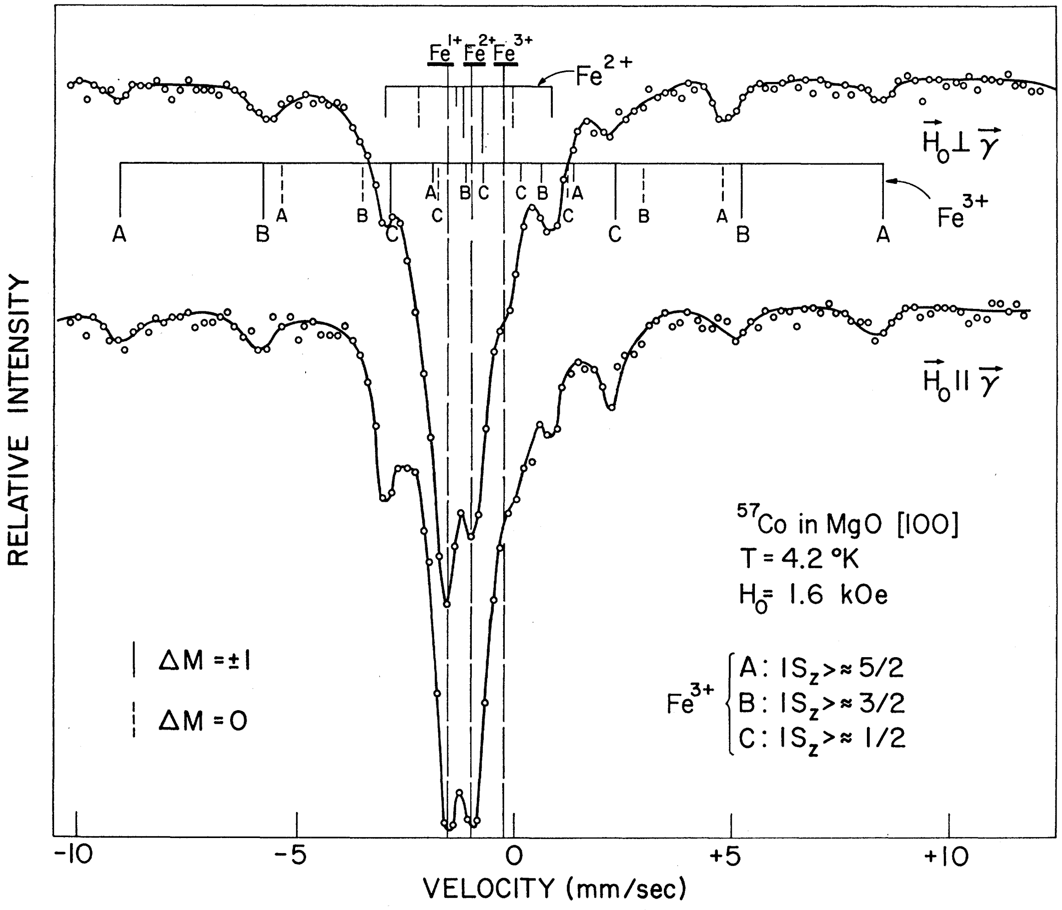


FIG. 5. Higher-velocity spectrum of the ^{57}Co-doped MgO source at 4.2°K and in an external field of 1.6 kOe, showing the paramagnetic hyperfine structure in the Fe^{3+} spectrum. The lines labeled A, B, and C refer to the states which can be roughly characterized as $|S_z\rangle=\pm\frac{5}{2}$, $\pm\frac{3}{2}$, and $\pm\frac{1}{2}$, respectively.

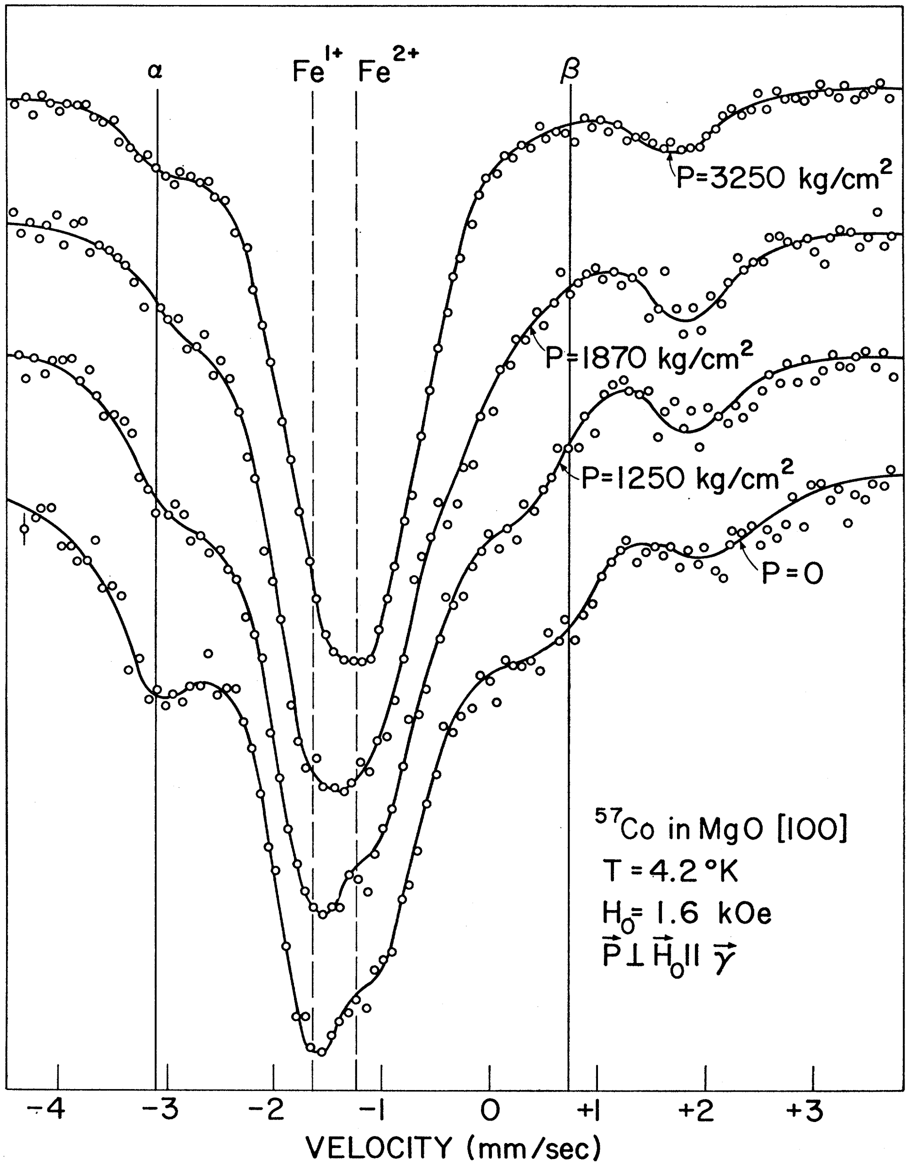


FIG. 6. Velocity spectra of ^{57}Co-doped MgO at 4.2°K and in an external field of 1.6 kOe for various values of applied pressure P. α and β indicate the positions of outermost hyperfine lines in the Fe^{2+} spectrum.

stress splitting becomes of the same order or larger than the magnetic splitting. Because of the distribution of random strain splittings,[6] the hyperfine field in various Fe^{2+} ions will collapse at different values of applied stress. Thus we observed a gradual decrease of intensity in the outermost Fe^{2+} hyperfine lines accompanied by an increase in the intensity at the center of the spectrum.

IV. DISCUSSION

The effect of uniaxial stress applied perpendicular to the external field on the Γ_{5g} electronic ground state of Fe^{2+} in MgO may be described by the simple spin Hamiltonian

$$\mathcal{H}=g\beta H_0S_z+D[S_x^2-\tfrac{1}{3}S(S+1)], \qquad (4)$$

where D is the tetragonal distortion parameter representing the effect of the stress P. The magnitude of D is related to P by

$$D=G_{11}P/(c_{11}-c_{12}), \qquad (5)$$

where G_{11} is the strain coefficient for Fe^{2+} in MgO and c_{11} and c_{12} are the stiffness constants for the MgO host. The eigenvalues of the Hamiltonian [Eq. (4)] for the effective $J'=1$ manifold are

$$\begin{gathered}\tfrac{1}{3}D,\\ -\tfrac{1}{6}D\pm[(\tfrac{1}{2}D)^2+(g\beta H_0)^2]^{1/2}.\end{gathered} \qquad (6)$$

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[6] D. H. McMahon, Phys. Rev. **134**, A128 (1964).

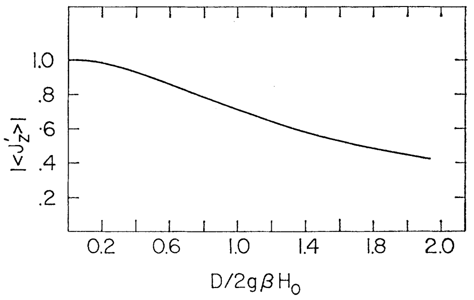

FIG. 7. Nonzero $|\langle J_z' \rangle|$ for the eigenfunctions of the Hamiltonian in Eq. (4) plotted as a function of $D/2g\beta H_0$.

The magnetic hyperfine interaction is at least two orders of magnitude smaller than the two terms in Eq. (4), for the magnitudes of $g\beta H_0$ and D used in this experiment. Thus the magnetic hyperfine interaction may be treated as a first-order perturbation, and the effective hyperfine field is

$$H_{hf} = A\langle J_z' \rangle. \tag{7}$$

The value of $\langle J_z' \rangle$ for the eigenfunctions of the Hamiltonian [Eq. (4)] are

$$\langle J_z' \rangle = 0$$

and

$$\langle J_z' \rangle = \pm \frac{X}{(D/2g\beta H_0)^2 + X}, \tag{8}$$

where

$$X = 1 - [(D/2g\beta H_0)^2 + 1]^{1/2}.$$

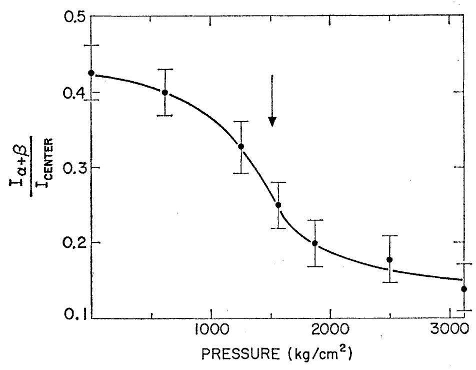

FIG. 8. Ratio of the intensities at the positions α and β of Fig. 6 to the intensity in the center of the Fe^{1+} and Fe^{2+} spectra plotted as a function of applied stress. The solid line is drawn through the points. The arrow indicates the pressure for which $|\langle J_z' \rangle|$ has fallen to $\simeq 0.78$ (see text).

Figure 7 shows the nonzero $|\langle J_z' \rangle|$ plotted as a function of $D/2g\beta H_0$. We can use the stress dependence of the intensity of the outer hyperfine lines to provide a rough criterion for determining the magnitude of the stress splitting. If we measure the intensity at the position of the hyperfine lines at zero stress, the intensity will fall to approximately $\frac{1}{2}$ its initial value and will be changing most rapidly for $|\langle J_z' \rangle| \simeq 0.78$ which from Fig. 7 corresponds to $D/2g\beta H_0 = 0.80$.

Figure 8 shows the ratio $I_{\alpha+\beta}/I_{\text{center}}$ of the intensity at the positions of the outer hyperfine lines of the Fe^{2+} spectrum, α and β of Fig. 6, to the intensity at the center of the spectrum as a function of applied stress and for $H_0 = 1.6$ kOe. Since most of the intensity at the center comes from the unchanging Fe^{1+} and Fe^{2+} ($J_z' = 0$) contributions, changes in this ratio reflect mainly changes in the magnitude of the Fe^{2+} magnetic hyperfine lines. The greatest rate of change occurs for $P \approx 1500$ kg/cm^2. From the preceding paragraph, this value of P corresponds to $\frac{1}{2}D \approx 0.8 g\beta H_0 = 0.205$ cm^{-1}. Inserting D and P into Eq. (5), and using $c_{11} - c_{12} = 2.147 \times 10^6$ kg/cm^2,[7] we obtain

$$G_{11} = 585 \text{ cm}^{-1}.$$

This value is consistent with other reported values of G_{11} for Fe^{2+} in MgO as shown in Table I.

TABLE I. Values of G_{11} for Fe^{2+} in MgO.

G_{11} (cm^{-1})	Method	Reference
800	EPR	a
650	Acoustic	b
647	Acoustic	c
585	Mössbauer	This work

[a] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).
[b] N. S. Shiren, Bull. Am. Phys. Soc. **7**, 29 (1962).
[c] M. F. Lewis and A. M. Stoneham, Phys. Rev. **164**, 271 (1967).

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[7] A. L. Schalow, A. H. Piksis, and S. Sugano, Phys. Rev. **122**, 1469 (1961).