Multiple Charge States, Hyperfine Interactions, and Relaxation Processes of Fe in $^{57}$Co-Doped MgO

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The Mössbauer spectra of cobalt-57-doped magnesium oxide have been studied between 1.3 and 550 K in external magnetic fields of up to 135 kOe for both single-crystal and polycrystalline samples. At room temperature and zero external magnetic field, the velocity spectrum is composed of three single lines, attributed to monovalent, divalent, and trivalent iron. In certain samples, for $T < 140$ K, the Fe$^{2+}$ line undergoes a transition to a quadrupole doublet with a splitting $\Delta E_Q = 0.30 \pm 0.02$ mm/sec, while in certain other samples, annealed differently, no doublet is observed down to 1.3 K. The first case is in quantitative agreement with a random-strain model proposed by Ham. The application of an external magnetic field induces a magnetic hyperfine interaction for the three charge states with saturation hyperfine fields of approximately $+20$, $-120$, and $-60$ kOe for Fe$^{1+}$, Fe$^{2+}$, and Fe$^{3+}$, respectively. From these values the core polarization contribution per spin is estimated to be $-127$ kOe/μB. Effects of slow paramagnetic relaxation for the Fe$^{2+}$ spectrum in the presence of an external magnetic field have been observed. In addition to the magnetic hyperfine interaction, an external magnetic field induces an Fe$^{2+}$ quadrupole interaction, as predicted by crystal-field theory. From the value of this interaction, $\Delta E_Q = 0.32$ mm/sec, the $^{57}$Fe nuclear quadrupole moment is estimated to be $+0.21$ b.

I. INTRODUCTION

A number of interesting phenomena are associated with the behavior of magnetic impurities in diamagnetic systems. Magnesium oxide provides a nearly ideal host because it has a simple cubic structure (NaCl type) and a Goldschmidt ionic radius close to that of the iron group (0.78 Å for Mg$^{2+}$). Small amounts of iron, for example, can be incorporated as impurities at substitutional sites, the divalent cation lying at the center of an octahedron of six oxygen ions. A powerful tool for investigating the iron impurity behavior in solids is provided by the Mössbauer technique because the impurity itself acts as a microscopic probe. These results may be correlated with data obtained by other techniques such as EPR spectroscopy. Here we present our investigation of the temperature and field dependence of the electric and magnetic hyperfine interactions of iron diffused into magnesium oxide. Three charge states corresponding to Fe$^{1+}$, Fe$^{2+}$, and Fe$^{3+}$ were observed in MgO by means of their respective isomer shifts. The quadrupole interaction reflects the charge symmetry seen by the nucleus but, as will be seen for the Fe$^{2+}$ ion, a cooperative distortion of the lattice is not required for the observation of quadrupole splitting. It can appear because of local departures from cubic symmetry produced by random strains in the crystal or by the application of an external magnetic field which reduces the symmetry. Such a quadrupole interaction, having no lattice contribution, has proved useful in estimating the value of the nuclear quadrupole moment. An external magnetic field may also induce a magnetic hyperfine field. This field may be considered as the sum of three contributions: core polarization, orbital, and dipolar. While the last two terms may be calculated using crystal-field theory, the first one is less accessible. We will show how the core-polarization term can be derived from the experimental saturation hyperfine fields and how their values tend to confirm the systematics observed in iron-series salts.

II. EXPERIMENTAL PROCEDURE

The Mössbauer experiments were carried out, using a constant acceleration electromechanical drive system...
together with a multichannel analyzer for collecting and storing the data. The temperature range of investigation extended from 1.3 to 550 K. The magnetic fields were produced by a wire-wound water-cooled solenoid producing up to 5 kOe, a 150-kOe water-cooled Bitter solenoid or a NbSn superconducting magnet capable of operating in the persistent mode up to 75 kOe. All experiments were performed using the longitudinal configuration (field parallel to the γ-ray propagation direction).

An aqueous solution of $^{57}$CoCl$_2$ was deposited onto the (100) surfaces of the single-crystal samples. For most of the results presented here, the doped crystals were annealed at 1200°C in air for 24 h followed by slow cooling. Powder pellets were made by pressing the powder and subsequent heating at 1200°C in air for 24 h. $^{57}$CoCl$_2$ was then deposited and annealed under the same conditions as for the single crystals. Sources prepared in this way will be subsequently referred to as source A. The effects of various annealing conditions, such as higher temperature (source B), quenching, hydrogen atmosphere (source C), or vacuum were also studied. By recording Mössbauer spectra of samples annealed under various conditions, we have observed that the diffusion process occurred only after heating 4 h at 800°C in air. The strength of each source was typically about 1 mC ($\sim$10 μg Co) deposited on a 4-sq mm spot. The resonant absorber was nonmagnetic sodium ferrocyanide which exhibits an unsplit narrow line; the absorber was kept at room temperature and in zero external field in all experiments.

### III. EXPERIMENTAL RESULTS

Room-temperature velocity spectra of $^{57}$Co-doped MgO, both single crystals and powder pellets (source A), are shown in Fig. 1. Each spectrum is characterized by three lines, the positions of which relative to zero velocity are given in Table I. From these positions and from the isomer-shift systematics, we assign these lines to Fe$^{1+}$, Fe$^{2+}$, and Fe$^{3+}$. The room-temperature intensity ratio Fe$^{2+}$/Fe$^{3+}$ in the type-A samples was found to be $\sim$0.2 for single crystals and $\sim$0.6 for powder pellets, while the ratio Fe$^{3+}$/Fe$^{2+}$ was approximately 0.15 in both samples. The identification of these lines was supported by other experimental evidence which we shall describe later. The origin of the different charge states will be discussed in Sec. IV A.

The relative line intensities were strongly influenced by various heat treatments. For example, heating at 1500°C in air for 48 h (source B) slightly increased the intensity of the 3+ line but almost completely removed the 1+ line. A hydrogen atmosphere (source C) produced an intense line at zero velocity with respect to sodium ferrocyanide (Fig. 2). Rapid quenching to room temperature greatly changed the relative intensities, as shown in Fig. 3 for a type-A pressed-powder pellet. In this case the 1+ line increased at the expense of the 2+ line while the 3+ line was unaffected, the integrated area of the spectrum did not vary, thus indicating a change in the relative concentration of the 1+ and 2+ states. Experiments at various temperatures indicated a strong temperature dependence for the intensity of the 1+ line which decreased with an increasing temperature and almost vanished at 550 K as shown in Fig. 4 for a powder pellet. The same temperature dependence can be seen by comparing the single-crystal spectra of Figs. 1 and 5. The Fe$^{2+}$ and Fe$^{3+}$ line intensities were much less sensitive to changes in temperature. The second-order Doppler shift

![Fig. 1. Typical room-temperature spectra of MgO single-crystal and powder-pellet sources annealed at 1200°C (type A). Solid lines are drawn through the points.](image1)

![Fig. 2. Room-temperature spectrum of MgO single-crystal source annealed in hydrogen (type C).](image2)

![Fig. 3. Room-temperature spectrum of MgO powder pellet source annealed in hydrogen (type C).](image3)

![Fig. 4. Room-temperature spectrum of MgO single-crystal source annealed in hydrogen (type C).](image4)

![Fig. 5. Room-temperature spectrum of MgO powder pellet source annealed in hydrogen (type C).](image5)

### Table I. Isomer shifts (mm/sec) versus sodium ferrocyanide (kept at 300°C) of the Fe$^{2+}$, Fe$^{3+}$, and Fe$^{4+}$ lines in cobalt-57-doped MgO. Single crystals and powder pellets gave the same values within experimental errors.

<table>
<thead>
<tr>
<th>$T$°K</th>
<th>Fe$^{2+}$</th>
<th>Fe$^{3+}$</th>
<th>Fe$^{4+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-1.55±0.03</td>
<td>-1.10±0.02</td>
<td>-0.50±0.05</td>
</tr>
<tr>
<td>77</td>
<td>-1.78±0.03</td>
<td>-1.23±0.02</td>
<td>-0.62±0.05</td>
</tr>
</tbody>
</table>


between 300 and 77°K was larger for the 1+ line than for the 2+ line (Table I), suggesting that different Debye temperatures \( \Theta_D \) are associated with each charge state. We can derive \( \Theta_D \) from the temperature dependence of the line intensities. Our results for a powder pellet give \( \Theta_D \approx 400 \) and \( \approx 150°K \) for Fe\(^{2+}\) and Fe\(^{3+}\), respectively. The large difference between the two values will be discussed later in relation to the origin of the multiple charge states. Because the Fe\(^{3+}\) line was relatively weak, no attempt was made here to study in detail its Mössbauer parameters [see Ref. 1(a)].

Debye temperatures can also be derived from the second-order Doppler-shift values, although this method is not very sensitive. However, the larger second-order Doppler shift observed for Fe\(^{1+}\) compared with Fe\(^{2+}\) is qualitatively explained by the above values of the respective Debye temperatures.

A characteristic feature of the type-A samples is the sudden broadening of the Fe\(^{2+}\) line which occurs at 14°K in both single crystals and powder pellets. Figure 5 shows the resonance spectrum of an MgO single-crystal sample where a resolved doublet is observed at 6°K. The quadrupole splitting is \( \Delta E_Q = \frac{1}{2}e q Q = 0.30 \pm 0.02 \text{ mm/sec} \). This substantially agrees with the value (0.33 mm/sec) observed in MgO absorbers by Leider and Pipkorn. In the case of a powder pellet, the doublet is poorly resolved but the broadening of the Fe\(^{2+}\) line corresponds to \( \Delta E_Q = 0.35 \pm 0.05 \text{ mm/sec} \). The temperature dependence of the transition undergone by the Fe\(^{3+}\) state has been observed to be quite sharp in both single crystals and pellets of type A. In order to investigate this behavior, we have recorded the counting rate at the Fe\(^{3+}\) line position when an MgO crystal goes through the transition. In Fig. 6, we compare this counting rate to the (constant) value recorded at the Fe\(^{1+}\) position. The sharp decrease observed is due to the sudden broadening of the Fe\(^{2+}\) line occurring within approximately 2°K. The origin of this quadrupole coupling and its temperature dependence will be discussed later in terms of Ham's model. However, for the MgO crystals of type B, annealed at 1500 instead of 1200°C, no resolved doublet was observed at temperatures as low as 1.5°K, but only a slight broadening (Fig. 7, linewidth=0.43 mm/sec at 6°K compared to 0.35 mm/sec at 77°K).

Some experimental spectra at 4.2°K and at different external magnetic fields \( H_s \) are shown in Fig. 8 for the type-A single crystals. These display mainly Fe\(^{1+}\) and Fe\(^{2+}\) states, and the corresponding hyperfine structures are resolved. Because of the longitudinal configuration, the \( \Delta m=0 \) lines did not appear and each

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MULTIPLE CHARGE STATES OF Fe IN 57Co-DOPED MgO

The ionic state gave rise to a four-line spectrum. From the external field dependence of the hyperfine splitting at constant temperature, we found that the hyperfine fields induced at the nuclei of Fe$^{3+}$ and Fe$^{2+}$ were of opposite signs. The observed saturation hyperfine fields are $-120$ kOe for Fe$^{2+}$ and $+20$ kOe for Fe$^{3+}$. With samples exhibiting a strong Fe$^{3+}$ line, we measured a saturation hyperfine field of $-560$ kOe for Fe$^{3+}$. The Fe$^{2+}$ hyperfine structure appeared for very small fields ($H_{o} \approx 50$ kOe) and became fully developed ($H_{hf} = -120$ kOe) for $H_{o} \approx 800$ Oe. For these small applied fields, the Fe$^{3+}$ line was almost unchanged. The type-A powder pellets exhibited the same behavior except for the fact that the $\Delta m=0$ lines did not vanish completely as might be expected. For the type-B single crystals, the Fe$^{3+}$ saturation field had the same value $-120$ kOe, but the hyperfine field did not begin to appear until about $H_{o} \approx 5$ kOe, depending upon the heat treatment of the crystal.

In addition to the magnetic hyperfine structure, an external magnetic field induced a quadrupole interaction for the Fe$^{2+}$ spectrum in both types A and B sources. This is more clearly seen in a type-B single crystal where the Fe$^{3+}$ and Fe$^{2+}$ states are very weak. Figure 9 shows this case. An applied magnetic field $H_{o}=50$ kOe gives a quadrupole interaction $\Delta E_{Q} = e^{2}q'Q = -0.32 \pm 0.05$ mm/sec at $4.2^\circ$K. Moreover, we observed that when the magnetic-field direction was changed from [100] to [111], the quadrupole interaction changed sign but had the same magnitude. This interaction was positive for the [111] direction. The same features appeared in iron-doped MgO.

IV. DISCUSSION

A. Multiple Charge States

The room-temperature spectra of $^{57}$Co-doped MgO consist of three single lines (Fig. 1) that have been identified on the basis of their isomer shifts$^{7,11}$ as due to

![Figure 8](image.png)

FIG. 8. Fe$^{2+}$ and Fe$^{3+}$ hyperfine interactions induced at $4.2^\circ$K by various external magnetic fields $H_{o}$ in an MgO single-crystal source (type A). The induced quadrupole interaction has been omitted from the stick diagrams, as has the splitting of $2H_{o}$ between $J=+1$ and $J=-1$ states for the low $H_{o}$ values.

induced by an external magnetic field showing both magnetic and quadrupole hyperfine interactions isomer shift (-1.10 mm/sec relative to sodium ferrous compound (used as a source). Our measurements indicate -1.15 mm/sec relative to stainless steel. This reduced value correspond to a ~10% covalent bond according to these calculations. The covalent character of the bonding has also been noted by EPR measurements.

Although the previous charge-state identification is the most straightforward explanation of the observed spectra, we must consider other possibilities, such as the presence of an asymmetric quadrupole doublet superimposed upon a single line. In the latter case the doublet would be centered about the Fe$^{2+}$ line position, the two components corresponding to our designations Fe$^{3+}$ and Fe$^{2+}$. An asymmetric doublet can result from an asymmetric Debye-Waller factor (Gol’danskii effect). In this case a rotation of the crystal should produce a relative change in the component intensities. Such a change was not observed experimentally. Moreover, we observed (Fig. 4) that the asymmetry of this doublet decreased as the temperature was raised contrary to what would have been expected on the basis of a Gol’danskii effect; therefore, we have ruled out such an interpretation. An asymmetric doublet might also result from electronic spin-lattice relaxation as described by Blume. In this case, raising the temperature would decrease the asymmetry of the quadrupole pattern as observed here (Fig. 4); but the relaxation effect would also produce a broadening of the lines. Our spectra did not show any significant broadening within the experimental errors in a temperature range from 20 to 550 K.

Additional evidence for the existence of Fe$^{+}$ and Fe$^{2+}$ is provided by the effect of various heat treatments which produced strong changes in the relative intensities of these two lines (Figs. 2, 3, and 7). For instance, heating the crystal in air at very high temperature (source B) increased the Fe$^{2+}$ line and decreased the Fe$^{3+}$, as would be expected from the oxidation process. Further evidence to support our designation of the charge states will be given later by the sign and magnitude of the external field induced hyperfine fields. Assuming the superposition of the Fe$^{2+}$ and Fe$^{3+}$ major charge states, the spectra were separated by computer curve fitting (Fig. 8) and the values of the core-polarization fields which were derived are in agreement with other measurements of these quantities. Moreover, the suppression of the Fe$^{3+}$ state by appropriate heat treatment caused the Fe$^{2+}$ hyperfine structure to vanish, leaving only the Fe$^{3+}$ pattern (Fig. 9).

It must be pointed out that all three charge states associated with point defects have been observed in the EPR study of MgO. The EPR work also indicates Co$^{3+}$ and Co$^{2+}$, which are in fact the ions first stabilized in our sources. Multiple charge states have also been revealed in the Mösßbauer investigation of several other compounds doped with $^{57}$Co. Fe$^{2+}$ was reported in NaCl$^{18}$ and Cu$_2$O$^{19}$ with an isomer shift of about -2 mm/sec relative to stainless steel. We observe -1.6 mm/sec in MgO and -1.7 mm/sec in CuO$^{20}$ for Fe$^{2+}$ relative to stainless steel. The trivalent state has been seen in $^{57}$Co-doped MgO$^{20}$ and iron-doped MgO absorbers.

The monovalent charge state could be explained in terms of oxygen vacancies. But if such were the origin, the electric-field symmetry about the Fe nucleus would have been strongly altered and a quadrupole doublet instead of a single line would have been observed. Instead of having an oxygen vacancy, one could imagine a hydroxyl group replacing an oxygen ion thus balancing the Fe$^{3+}$ charge state while not strongly affecting the symmetry about the iron nucleus. This hypothesis is supported by different observations. First, it has been shown both theoretically and experimentally by

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infrared spectroscopy\textsuperscript{23} that hydroxyl groups persist in appreciable amounts in MgO even after heating at high temperature and are located mainly near the surface. As a confirmation, we observed a strong decrease in the Fe\(^{2+}\) line by heating the crystal to higher temperatures (Fig. 7) where one would expect that many of the hydroxyl ions would be evaporated while the cobalt ions would be diffused deeper into the crystal. Most of the \(\gamma\) rays which we counted in our experiments originated near the surface of the crystal; while in the absorbers,\textsuperscript{24,25} where the impurity ions were distributed uniformly throughout the sample volume, no Fe\(^{2+}\) line was observed. Other attempts\textsuperscript{26,27} to observe Fe\(^{2+}\) in MgO sources failed when the samples were prepared by firing a solution of \(^{57}\text{Co}\) chloride and magnesium nitrate. Here again, not only the surface, but the whole volume of the sample was involved. Furthermore, we observed that the Fe\(^{2+}\) line always had a stronger intensity in the powder pellet (Fig. 1) where the surface area is larger than in the single crystal. This surface effect could also account for the lower Debye temperature observed for Fe\(^{2+}\) as compared with Fe\(^{2+}\).

The trivalent charge state has an isomer shift which is characteristic of ferric systems\textsuperscript{7} (Table I). The amount of Fe\(^{3+}\) in the crystal can be slightly increased by raising the annealing temperature, suggesting an oxidation of the cobalt ions from Fe\(^{2+}\) to Fe\(^{3+}\). The same feature was observed by Wertz \textit{et al.} in their EPR experiments.\textsuperscript{17} Such a trivalent state, exhibiting a single line, was observed by Wertheim in an early study of \(^{57}\text{Co}\)-doped MgO.\textsuperscript{28} In the ion-doped absorbers the trivalent state was also observed,\textsuperscript{24,25} but instead of a single line a quadrupole doublet with a large splitting (0.74 mm/sec in Ref. 6) is present. This quadrupole splitting has been attributed to a charge-compensating cation vacancy.\textsuperscript{29} Wertheim\textsuperscript{30} has proposed an explanation for higher charge states such as Fe\(^{3+}\) which would explain the difference of behavior of sources and absorbers. The trivalent state may be obtained as a result of the aftereffects of the electron-capture decay of \(^{57}\text{Co}\),\textsuperscript{31} which can produce multiply ionized atoms. These charge states may be observed provided that their lifetimes are of the order of or greater than \(\sim 10^{-7}\) sec, which is the lifetime of the \(^{57}\text{Fe}\), 14.4-keV level. However, Triftshäuser and Craig\textsuperscript{32,33} performing delayed coincidence measurements, did not observe any time-dependent effects in magnetic insulators, and concluded that the multiple charge states are not related to electron-capture aftereffects within the time realm of their experiments. They interpreted the Fe\(^{3+}\) state in CoO as resulting from nonequivalent sites due to deviations from stoichiometry. At this point it is not possible from our measurements to decide which (if either) mechanism is responsible for the observed Fe\(^{3+}\) line in the MgO sources.

When an MgO sample was prepared by heating in a hydrogen atmosphere, the room-temperature Mössbauer spectrum consisted mainly of a line at zero velocity relative to sodium ferrocyanide (Fig. 2). This line may be attributed to a low-spin ferrous ion. This is hard to understand in a cubic material, but it seems likely that heating in hydrogen destroys the local cubic symmetry by creating vacancies or inserting interstitial hydrogen atoms mainly in the crystal surface. We also noticed that a small external magnetic field (~3 kOe) did not affect the zero velocity line, apart from the broadening corresponding to the applied field. Such a low-spin state has, for example, been reported in hydrogen-fired \(^{57}\text{Co}\)-doped SrTiO\(_3\).\textsuperscript{25}

\section*{B. Fe\(^{3+}\) Strain-Induced Quadrupole Interaction}

The onset of an Fe\(^{3+}\) low-temperature quadrupole splitting observed in this cubic material (Fig. 5) in the absence of an external magnetic field was first interpreted by Ham\textsuperscript{3} on the basis of crystal-field theory. This comes about as a result of the electric field gradient produced at the \(^{57}\text{Fe}\) nucleus by the valence electrons of Fe\(^{3+}\) combined with random strains in the crystal which remove the electronic degeneracy of the ground-state triplet. The ground state of the ferrous ion is \(3d^6\, 1D\), with \(L = 2\) and \(S = 2\). In MgO, this ion is at the center of an octahedron of nearest-neighbor oxygen ions. Therefore, the crystalline cubic field splits the ground term into a lower-orbital triplet and an upper-orbital doublet, separated by 10 \(Dq\).\textsuperscript{14} The orbital triplet, which behaves as an \(L = 1\) manifold because of the \(t_{2g} - \pi\) equivalence,\textsuperscript{35} is further split by the spin-orbit interaction into a number of levels of which a \(\Gamma_{4g}\) triplet is lowest, with an effective \(J' = 1\) (Fig. 10). In the presence of an arbitrary static strain\textsuperscript{28} (strain splitting small compared to spin-orbit coupling) the threefold degeneracy may be lifted. Each electronic eigenstate may be written as

\[|\psi\rangle = a|\xi\rangle + b|\eta\rangle + c|\zeta\rangle,\tag{1}\]

where \(|\xi\rangle, |\eta\rangle,\) and \(|\zeta\rangle\) transform, respectively, like \(y_3, x\zeta, xy,\) and \(a, b, c\) are real coefficients.\textsuperscript{2} The quadrupole splitting due to the interaction between the nuclear quadrupole moment \(Q\) of \(^{57}\text{Fe}\) and the electronic state \(|\psi\rangle\) was calculated by Ham and is given by

\[\Delta E_Q = 3[c_2^2+(\xi^2)(16c_2^2-9c_2^2)(a^2b^2+b^2c^2+c^2a^2)]^{1/2},\tag{2}\]

where \(c_2\) and \(c_5\) are coefficients of the quadrupole operator. Using point-charge crystal-field model, \(c_2\) and \(c_5\) are

\textsuperscript{24} K. R. Reddy (private communication).
\textsuperscript{28} V. G. Bhide and H. C. Bhasin, Phys. Rev. 159, 586 (1967).
are shown to be related by

$$-3e_0 = 4e_2 = \frac{3}{35}(r^{-3}) (1-R) e^2 Q/I(2I-1).$$  (3)

Here \((r^{-3})\) refers to the expectation value using one electron \(d\) orbitals, \((1-R)\) represents the Sternheimer shielding,\(^{20}\) and \(I\) is the excited-state nuclear spin. Therefore, Eq. (2) yields

$$\Delta E_Q = \frac{1}{35}(r^{-3}) (1-R) e^2 Q,$$  (4)

for \(I = \frac{3}{2}\). Since Eq. (4) is independent of the coefficients \(a, b, c\), the magnitude of \(\Delta E_Q\) is the same for the three \(|\psi\rangle\) states, but the orientation of the electric field gradient at the iron nucleus depends on the state. Therefore a quadrupole splitting will be observed at temperatures sufficiently low that the relaxation time \(\tau\) for transitions among the three electronic states \(|\psi\rangle\) is long compared to \(\hbar/\Delta E_Q\). From Eq. (4), Ham derived a splitting \(\Delta E_Q = 0.44\) mm/sec using \(Q = 0.29\) \(\text{b}^{20}\) and reducing Freeman and Watson’s estimate\(^{31}\) of \((r^{-3})(1-R) = 3.3\) a.u. for the Fe\(^{2+}\) free ion by \(-20\%\) to take into account the combined effect of covalent bonding and dynamic quenching. Experimentally, we observed \(\Delta E_Q = 0.30 \pm 0.02\) mm/sec at 6°K for a type-A single crystal and \(0.35 \pm 0.05\) mm/sec for a powder pellet. These experimental values of the quadrupole splitting are smaller than predicted. As Ham\(^{3}\) pointed out, this may be evidence that Ingall’s value\(^{20}\) for \(Q\) is somewhat too high. In fact, recently, two independent evaluations of \(Q\) for \(\text{ferrous}\) compounds concluded that \(Q = 0.20\) \(\text{b}^{22}\) and \(0.18\) \(\text{b}^{23}\) yielding a theoretical splitting \((\sim 0.30\) mm/sec) in very good agreement\(^{1,6}\) with the experimental value.

The disappearance of the Fe\(^{2+}\) quadrupole doublet above 14°K has been attributed by Ham\(^{3}\) to motional narrowing resulting from rapid transitions among the three strain-split electronic states of each Fe\(^{2+}\) ion. Tjon and Blume\(^{34}\) have also derived an expression for the Mössbauer line shape in the presence of an electric field gradient which fluctuates randomly among the \(x, y,\) and \(z\) axes. Their results agree with the motional narrowing observed here. Ham inferred a relaxation time \(\tau = \hbar/\Delta E_Q \sim 5 \times 10^{-8}\) sec among the three \(\Gamma_6\) components at 14°K. Ruling out a direct process for phonon-induced transitions because of the small strain splitting \((\sim 10^{-2}\) cm\(^{-1}\)), he proposed that relaxation occurs by an Orbach mechanism involving the next spin-orbit level of Fe\(^{2+}\). He calculated that the energy separation would have to be reduced from the free ion value 200–95 cm\(^{-1}\). Covalent bonding and Jahn-Teller effect can be responsible for such a reduction. Following Ham’s calculation, the temperature dependence of the quadrupole splitting,\(^{6}\) far infrared spectroscopy,\(^{35}\) and spin-resonance measurements\(^{36}\) have confirmed this value for the energy separation.

As we mentioned previously, the type-\(B\) MgO samples which were annealed in air at 1500° instead of 1200°C do not exhibit an Fe\(^{2+}\) quadrupole doublet at temperatures down to 1.5°K. Since we observed here only a single line for Fe\(^{2+}\), we need to assume fast relaxation between the electronic levels. This point will be discussed in more detail in Sec. IV D.

C. Fe\(^{2+}\) Magnetic-Field-Induced Quadrupole Interaction

As mentioned earlier, a quadrupole interaction \(\Delta E_Q' = \frac{1}{2}Q = 0.32 \pm 0.05\) mm/sec was observed when an external magnetic field was applied.\(^{1,6}\) The origin of this interaction is completely independent from the strain-induced quadrupole coupling previously described. It was first pointed out by Marshall\(^{37}\) who suggested that it is due to the spin-orbit coupling which produces an asymmetrical charge cloud, since the orbital angular momentum is not completely quenched in the ferrous state. The theory of this magnetically induced quadrupole interaction has been worked out by several authors.\(^{3-5}\) This shows that the electric field gradient has an axial symmetry and is collinear with the magnetic field. Such a quadrupole interaction in a cubic material has been observed in the magnetically ordered compounds CoO,\(^{20}\) NiO,\(^{38}\) MnO,\(^{39}\) and FeCr\(_2\)S\(_4\),\(^{3,40}\) below their ordering temperatures. In all these cases, it is the exchange field which induces the quadrupole interaction, while in the case of MgO,\(^{4,5}\) it is the externally applied
magnetic field which is responsible for the observed quadrupole splitting.

The magnetic field lifts the degeneracy of the spin-orbit triplet \( \Gamma_{\alpha} \) and, if the field is large enough, the strain splitting (~4 \( \times 10^{-2} \) cm\(^{-1}\)) becomes negligible compared with the Zeeman splitting (~9 cm\(^{-1}\) for \( H_0=50 \) kOe). Then the electronic eigenstates are no longer determined by the strain (Eq. 1), but are the eigenstates of \( J'_{\alpha} \) with \( J'_{\alpha}=0 \) and ±1 (\( \alpha \) in the direction of \( H_0 \)). Each state will again produce an electric field gradient. Using crystal-field theory, Ham\(^3\) arrived at an interaction,

\[
\Delta E_q' = e\rho Q = 3[c_0 + (4c_3 - 3c_5)] \times (a_x^2 a_y^2 + a_x a_y^2 + a_x^2 a_z^2),
\]

(5)

for the \( J'_{\alpha}=\pm 1 \) states, where \( a_x, a_y, \) and \( a_z \) denote the direction cosines of \( H_0 \) with respect to the cubic axes. For the state with \( J'_{\alpha}=0 \), there is no hyperfine field at the nucleus. Therefore, the spectrum will appear as a quadrupole doublet with a splitting identical to that obtained by substituting \( a_x, a_y, \) and \( a_z \) in Eq. (2). For \( H_0 \) along [100] or [111], \( \Delta E_q' \) is given by +3\( c_5 \) and +4\( c_5 \), respectively. If the relationship (3) still holds, we see that the quadrupole interaction will have the same magnitude, given by Eq. (4), but with opposite signs for \( H_0 \) along [100] or [111]. This is precisely what we have observed, as shown in Fig. 9. At \( H_0=50 \) kOe and \( T=4.2^\circ \)K only the lowest state \( J'_{\alpha}=-1 \) of the triplet is appreciably populated and a splitting \( \Delta E_q'=0.32 \) mm/sec is observed. In addition, from Eq. (3) we see that the coefficient \( c_3 \) is negative while \( c_5 \) is positive. Therefore the interaction should be positive when \( H_0 \) is along [111], negative for [100]. Again this is in agreement with the observations.\(^1,6\)

It is worth pointing out that this quadrupole interaction can be used to get an estimate of the nuclear quadrupole moment \( Q \) of \(^{57}\)Fe since there is no lattice contribution to the electric field gradient which arises solely from the electronic charge distribution. The experimental value for the magnetically induced quadrupole interaction gives \( Q=+0.21 \) b in agreement with recent evaluations.\(^2,3\)

**D. \( \text{Fe}^{2+} \) Magnetic Hyperfine Interaction**

We shall now discuss the \( \text{Fe}^{2+} \) magnetic hyperfine interaction induced at the iron nucleus by an external magnetic field. For a paramagnet we may write the observed field at the nucleus \( H_n \) as

\[
H_n = H_0 \pm H_{hf},
\]

(6)

where \( H_0 \) is the external applied field and \( H_{hf} \) is the field at the nucleus due to the atomic electrons in the sample. The \( \text{Fe}^{2+} \) observed spectrum will here depend on whether the relaxation rate among the three electronic states \( J'_{\alpha}=\pm 1, 0, -1 \) is fast or slow compared with the Larmor precession time of the nucleus. This is illustrated in Fig. 11. In the first case, fast relaxation, the hyperfine field seen by the nucleus is the thermal average of the contributions of the three levels

\[
H_{hf}=H_{hf} B J'(gB H_0/kT),
\]

(7)

where \( H_{hf} \) is the saturation hyperfine field, \( B J' \) is a Brillouin function for an effective spin \( J' \), and \( g \) is the electronic \( g \) factor. The spectrum should then consist of four lines (longitudinal configuration) with a splitting corresponding to \( H_0-H_{hf} \). The solid curve in Fig. 12 represents this case for \( J'=1 \) and \( H_{hf}=-120 \) kOe at \( T=4.2^\circ \)K. On the other hand if the relaxation rate is slow, there is no average over the three states and each contribution may be seen separately; the states \( J'_{\alpha}=\pm 1 \) give rise to hyperfine fields of equal magnitude but with opposite signs. The state \( J'_{\alpha}=0 \) gives only a central quadrupole split doublet. Therefore we expect the spectrum to be the superposition of the three patterns (Fig. 11), the outermost lines of the \( J'_{\alpha}=\pm 1 \) states being now separated by \( H_{hf}=\pm H_0 \), respectively. As \( H_0 \) increases the splitting between the electronic levels becomes greater while the relative line intensities vary due to changes in the Boltzmann distribution. This is the last case which is observed (Fig. 8). The experimental values of \( H_{hf} \) for various \( H_0 \) at \( T=4.2^\circ \)K are shown in Fig. 12 for both type-A and -B MgO samples. We get a best fit with \( H_{hf}=-120 \) kOe. The dashed lines in Fig. 12 represent the theoretical values assuming slow relaxation: one line at \( H_{hf}=0 \) corresponding to...
The experimental values of $H_{hf}$ in the foregoing discussion were all made at 4.2°K. It is of interest to study the temperature dependence of the magnetic hyperfine structure induced by a given field in order to see if the motional narrowing observed for the strain induced quadrupole coupling occurs also for the magnetic hyperfine pattern, since the same mechanism is involved. As may be seen in Fig. 6 for the quadrupole coupling. Actually, a difference of about 1°K is expected for the transition temperature in the two cases because the relaxation time necessary to narrow the hyperfine splitting ($\tau = h/\Delta E_q$) is different from that necessary to narrow the quadrupole splitting, ($\tau = h/\Delta E_{q}$). The constancy of $H_{hf}$ below ~12°K and its sudden disappearance above this temperature are in agreement with Ham's interpretation.5

In samples $A$, the hyperfine field begins to appear at $H_o \sim 250$ Oe and reaches its saturation value (~120 kOe) for $H_o \sim 800$ Oe where the Brillouin function $R_1$ is only ~0.04. The reason why the magnetic hyperfine structure is not observed here for $H_o < 250$ Oe was suggested by Ham.2 The strain splitting of the ground-state triplet (~10^{-2} cm^{-1}) is at least one order of magnitude greater than the hyperfine interaction. Therefore, the strains in the crystal prevent observation of the hyperfine structure. By increasing the external magnetic field, the hyperfine structure appears when the strain splitting becomes negligible in comparison with the Zeeman splitting. From the value $H_o \sim 250$ Oe, Ham derived an estimate (4X10^{-2} cm^{-1}) for the typical amount of strain splitting in the MgO crystals. This value agrees with estimates from paramagnetic resonance studies.41,42

We have confirmed this interpretation by applying uniaxial stress which increases the amount of strain in the crystal. In particular the strain produced by a pressure of 2600 kg/cm^2 wiped out the magnetic hyperfine structure induced by an external field $H_o = 1$ kOe.44 Details of these measurements will be published elsewhere.

For the type-$B$ sources heated at 1500°C, the magnetic hyperfine structure began to appear at $H_o \sim 5$ kOe and reached its saturation value at $H_o \sim 10$ kOe. The heat treatment was responsible for this behavior since both $A$ and $B$ sources came from the same single crystal. Also, the $B$ samples did not exhibit a low-temperature quadrupole splitting in zero magnetic field. These results suggest that in these samples the relaxation rate for low external magnetic field is faster than in the $A$ samples. The nature of this rapid relaxation is not well understood. On the basis of spin-lattice relaxation, the relaxation rate should be temperature-dependent and field-independent. Using Eq. (9) in Ref. 2 and the fact that we observed a hyperfine field at 4.2°K and $H_o \geq 5$ kOe we should observe the strain-induced quadrupole interaction at 1.5°K because the relaxation time $\tau$ increases by a factor of ~10 when $T$ goes from 4.2 to 1.5°K. This increase in $\tau$ should allow the observation of the quadrupole splitting since the relaxation time associated with the quadrupole interaction is approximately three times the one associated with the magnetic hyperfine structure. With respect to the field dependence of the magnetic hyperfine interaction, the fact that it began to appear only at $H_o \sim 5$ kOe may be due to a field-dependent relaxation mechanism. This cannot be explained by spin-lattice relaxation since the dominant term is a field-independent Orbach process.2

Another alternative, consistent with our observation,
would be a spin-spin relaxation mechanism which is field-dependent ($\tau$ decreases with an increase of $H_0$) and temperature-independent.

In samples $A$, the threshold field, $H_0 \approx 250$ Oe, at which the magnetic hyperfine structure appeared was used in order to give an estimate of the strain splitting in the crystal. In samples $B$, this threshold field was $\approx 5$ kOe. But, since we do not know whether the absence of magnetic hyperfine structure below 5 kOe is due to the strain or to fast relaxation, we are able only to derive an upper limit ($\approx 1$ cm$^{-1}$) for the strain splitting in samples $B$. In fact, it is even possible that the amount of strain there is smaller than in the samples $A$. This could be checked by EPR spectroscopy.

The hyperfine field at the nucleus may be written as a sum of terms

$$H_{hf} = H_{cp} + H_{orb} + H_{dif},$$

where $H_{cp}$, $H_{orb}$, and $H_{dif}$ are the core-polarization, orbital, and dipolar contributions. In terms of the electronic state,

$$H_{hf} = 2[H_{cp}/2(S_a)_{-1,0]} + 2\mu_b h_0 (r^{-3}) \langle L_a \rangle$$

$$+ \frac{1}{2} \mu_b h_0 (r^{-3}) [3 \langle L_a^2 \rangle - L(L+1)] (S_a),$$

where $H_{cp}/2(S_a)$ is the core-polarization field per spin, the expectation values refer to the $L=2, S=2$ basis, and $h_0$ is an orbital hyperfine reduction factor. It must be remembered that the orbital reduction factor $h_0$ appropriate to the hyperfine interaction is not necessarily the same as the orbital Zeeman reduction factor $h_0$ observed for example in EPR spectroscopy. This is discussed in more detail in the Appendix.

The orbital and dipolar contributions in Eq. (9) may be calculated. Using the observed value of $H_{hf}$ we may therefore derive the core-polarization term, $H_{cp}$. In order to calculate the expectation values for Eq. (9) it is more appropriate, since we apply an external magnetic field, to take the eigenstates of the electronic state, $\langle L_a S_a \rangle$ as our electron basis functions. They are easily written, using the appropriate Clebsch-Gordan coefficients, as linear combinations of the functions $| L_a S_a \rangle$

$$\Phi(J' = +1) = \sqrt{(6/10)} | 1, 2 \rangle$$

$$- \sqrt{(4/10)} | 0, 0 \rangle + \sqrt{(2/10)} | 1, 0 \rangle,$$

$$\Phi(J' = 0) = \sqrt{(3/10)} | 1, -1 \rangle$$

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which are connected with the previous real wave functions (Eq. 1). For example, if the field direction $\alpha$

$$\Phi(J' = +1) = (i/\sqrt{2}) | 1, -1 \rangle + (1/\sqrt{2}) | 1, 1 \rangle,$$

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</tr>
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The expectation values $\frac{H_{cp}}{2(S_a)}$ and $\frac{H_{dif}}{2(S_a)}$ are found equal to $\pm \frac{1}{2}$ and $\pm \frac{3}{2}$, respectively, for $J' = \pm 1$. For $J' = 0$, both are zero. Using these values and the saturation hyperfine field $H_{hf}$ we may now calculate the core-polarization term $H_{cp}$ (Eq. 9). Values for $r^{-3}$ have been calculated by Freeman and Watson. Within certain assumptions it is possible to derive the hyperfine reduction factor $h_0$ from the measured EPR spectroscopy. This is discussed in more detail in the Appendix.

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$$\Phi(J' = -1) = (i/\sqrt{2}) | 1, -1 \rangle - (1/\sqrt{2}) | 1, 1 \rangle.$$
was observed despite an increase of $H_{cp}/T$ by a factor of $\sim 3$. The change in the value of $H_{cp}$ at very high fields may reflect an external field dependence of $H_{hf}$ due to mixing of the ground and higher levels by the applied magnetic field.

It is difficult to give an accurate value of $H_{hf}$ corresponding to $H_{o}=0$ because of the changes in $H_{hf}$ with $H_{o}$. Assuming different criteria for the extrapolation, we get $H_{hf}$ values that range from $\pm 15$ to $\pm 20$ kOe. Using the latter value for $H_{hf}$ and an analysis similar to that for Fe$^{3+}$, we obtain a value of $-127$ kOe/$\mu_B$ for the core-polarization field per spin, assuming $k_{hf}=k_{cp}$. These results are summarized in Table III.

V. CONCLUSIONS

Using the Mössbauer technique we have observed the presence of three different charge states, Fe$^{2+}$, Fe$^{3+}$, and Fe$^{4+}$ in $^{57}$Co-doped MgO. The relative intensities of the resonance lines corresponding to the various charge states were sensitive to the manner in which the samples were prepared as well as to the temperature during the Mössbauer experiment. The origin of Fe$^{4+}$ has been attributed to a surface process in which hydroxyl groups replace oxygen ions in the MgO lattice. At low temperatures, ($T<14^\circ$K) an Fe$^{4+}$ strain-induced quadrupole splitting (0.30 mm/sec) was generally observed because of slow spin-lattice relaxation, in agreement with Ham’s strain model. Depending upon the heat treatment some samples exhibited faster electronic relaxation and this quadrupole doublet was not observed in such samples. When a large enough external magnetic field was applied (Zeeman splitting greater than strain splitting) and Fe$^{4+}$ quadrupole splitting was induced by the field, in agreement with theoretical predictions. From this quadrupole interaction we estimate the nuclear quadrupole moment of $^{57}$Fe to be $+0.21$ b. An external field also induced a magnetic hyperfine structure for all three charge states. From the measured hyperfine field we derived the core-polarization contribution to the hyperfine field, using calculated values for the orbital and dipolar contributions. We found in both Fe$^{2+}$ and Fe$^{3+}$ a core-polarization field per spin of $-127$ kOe/$\mu_B$, in agreement with the systematics of these terms in the 3$d$ transition metal ions. A case of slow paramagnetic relaxation in a ferrous compound is illustrated by the behavior of the external field dependence of the induced hyperfine field.

TABLE III. Derivation of the Fe$^{3+}$ core-polarization contribution to the hyperfine field. It is assumed $k_{hf}=k_{cp}=k$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$</td>
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<td>$(r^{-1})$</td>
<td>4.5 a.u.</td>
</tr>
<tr>
<td>$H_{hf}$</td>
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<tr>
<td>$k$</td>
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<tr>
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<tr>
<td>$H_{dip}$</td>
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<tr>
<td>$H_{cp}$</td>
<td>$-211$ kOe</td>
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ACKNOWLEDGMENTS

The authors are deeply indebted to F. S. Ham for many enlightening discussions concerning his work and for many suggestions as well. They are also grateful to A. J. Freeman, G. R. Hoy, D. N. Pipkorn, H. C. Praddaude, B. B. Schwartz, and J. Träff for stimulating discussions and to U. Ganiel, G. R. Hoy, and D. N. Pipkorn for communicating their work prior to publication. The invaluable help of R. Katz and J. Träff for data analysis and the technical assistance of W. Mosby are gratefully acknowledged. One of us (J. C.) would like to thank Professor B. Lax and Professor A. J. Freeman for their hospitality at the Francis Bitter National Magnet Laboratory and Professor L. Néel and Professor E. F. Bertaut for making possible the leave of absence from the Centre d’Etudes Nucléaires de Grenoble.

APPENDIX

Covalency and dynamic Jahn-Teller effects are known to reduce the purely ionic value of the angular momentum of paramagnetic ions in crystals. It is usually assumed that the Zeeman reduction factor (from EPR spectroscopy, for example) is the same as the hyperfine reduction factor. However, this is not generally the case as we will discuss here, because the former involves the expectation value of \( L \) while the latter involves the expectation value of \( \frac{1}{2}L^2 \).

We have to evaluate in both cases the contribution due to dynamic Jahn-Teller effect (JT) and to covalency (cov). The total reduction factor can be approximated by

\[
\kappa_{\text{ze}} = \kappa_{\text{ze}}^{\text{JT}} \kappa_{\text{ze}}^{\text{cov}}
\]

for Zeeman effect (EPR); and

\[
\kappa_{\text{hf}} = \kappa_{\text{hf}}^{\text{JT}} \kappa_{\text{hf}}^{\text{cov}}
\]

for the hyperfine interaction. Since the dynamic Jahn-Teller effect is mainly a property of the nuclear wave function, we expect its reduction effect to be independent of the electronic operator evaluated for a given pair of basis functions. Therefore \( \kappa_{\text{ze}}^{\text{JT}} = \kappa_{\text{hf}}^{\text{JT}} \).

In order to get expressions for the covalent reduction factors, \( \kappa_{\text{ze}}^{\text{cov}} \) and \( \kappa_{\text{hf}}^{\text{cov}} \), we write simple molecular orbitals for the paramagnetic electron wave functions:

\[
\psi_{xx} = \mathcal{S}_e (d_{xx} - \lambda_e \Delta_{xx})
\]

and

\[
\psi_{yz} = \mathcal{S}_e (d_{yz} - \lambda_e \Delta_{yz}),
\]

where \( d_{xx} \) and \( d_{yz} \) are Fe\(^{2+}d\) orbitals, \( \Delta_{xx} \) and \( \Delta_{yz} \) are the linear combinations of ligand (oxygen) orbitals of the appropriate symmetry, \( \lambda_e \) is the covalency parameter. The normalization factor \( \mathcal{S}_e \) is given by

\[
\mathcal{S}_e = \left(1 - 2\lambda_e S_e + \lambda_e^2\right)^{-1/2} = 1 + \lambda_e S_e - \left(\lambda_e^2/2\right),
\]

where \( S_e \) is the overlap between the metal and ligand wave functions, \( S_e = \left<d_{xx}, | \Delta_{xx}\right> \).

The covalent Zeeman reduction factor is defined by

\[
\kappa_{\text{ze}}^{\text{cov}} = \frac{\left<d_{xx} | \Delta_{xx}\right>}{\left<d_{xx}, | \Delta_{xx}\right>} = \mathcal{S}_e \left(1 - 2\lambda_e S_e + \frac{1}{2}\lambda_e^2\right).
\]

In the same way, the covalent hyperfine reduction factor is given by

\[
\kappa_{\text{hf}}^{\text{cov}} = \frac{\left<d_{xx} | r^{-3}L| \Delta_{xx}\right>}{\left<d_{xx}, | r^{-3}L| \Delta_{xx}\right>} = \mathcal{S}_e \left[1 - 2\lambda_e \left(\frac{\Delta_{xx}}{r^{-3}L}\right) + \frac{1}{2}\lambda_e^2 \left(\frac{\Delta_{xx}}{r^{-3}L}\right)^2\right].
\]

In order to understand the difference between \( \kappa_{\text{ze}}^{\text{cov}} \) and \( \kappa_{\text{hf}}^{\text{cov}} \) we have to consider the matrix element between metal \( d \) and ligand \( \Delta \) wave functions. In the Zeeman case, Eq. (A5), the integral is proportional to the overlap, and, in general, cannot be neglected. In the hyperfine case, Eq. (A6), it is greatly reduced by the factor \( r^{-3} \) which is small at the ligand site and can be neglected. Therefore, Eq. (A6) reduces to

\[
\kappa_{\text{hf}}^{\text{cov}} = \mathcal{S}_e \lambda^2.
\]

Similar conclusions have been obtained for the matrix elements of the spin-orbit coupling.

If we expand \( \mathcal{S}_e \) and retain only quadratic terms in \( \lambda_e \) and \( S_e \), we get

\[
\kappa_{\text{ze}}^{\text{cov}} \sim 1 - \left(\lambda_e^2/2\right)
\]

and

\[
\kappa_{\text{hf}}^{\text{cov}} \sim 1 + 2\lambda_e S_e - \lambda_e^2.
\]

Of the two effects, dynamic Jahn-Teller and covalency, we do not know which is the dominant one. If the covalency effect is negligible, then \( \kappa_{\text{ze}}^{\text{cov}} = \kappa_{\text{hf}}^{\text{cov}} = \kappa_{\text{JT}} \) and we can use the EPR reduction factor for the hyperfine calculations (see column 2 of Table III). On the other hand, if the dynamic Jahn-Teller effect is negligible \( (\kappa_{\text{JT}} = 1) \), the covalency parameter \( \lambda_e \) can be derived from Eq. (A8) by measuring \( \kappa_{\text{ze}} \) (by EPR spectroscopy). Using a computed value \( S_e = 0.055 \) and inserting \( \lambda_e \) in Eq. (A9) we get an estimate of \( \kappa_{\text{hf}} \). For \( \kappa_{\text{ze}} = 0.814 \) we get \( \kappa_{\text{hf}} = 0.7 \) and the third column in Table II shows the value derived for the core-polarization contribution to the hyperfine field.

Our conclusion is that the covalent contribution to the Zeeman reduction factor is different from the contribution to the hyperfine reduction factor, but it is possible to calculate one once we know the other.

\[\text{We used a program written by L. D. Kandel, M. C. G. Passeggi, and T. Buch, University of Chile to calculate overlap integrals.}\]