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Mössbauer Effect in Iron under Very High Pressure*†

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The Mössbauer spectrum of Fe^{57} in iron metal has been measured at pressures up to 240 kbar at room temperature. Below 130 kbar the spectrum consists of the normal six lines characteristic of ferromagnetic, body-centered-cubic iron. The internal magnetic field H at the nucleus decreases linearly with volume; $\partial(H/H_o)/\partial(V/V_o)=0.34\pm0.01$, where H_o and V_o are the field and volume at atmospheric pressure. The center of gravity of the spectrum shifts with pressure, indicating an increase in s-electron density at the nucleus. The initial variation, -8.3×10^{-5} cm sec^{-1} kbar^{-1}, is consistent with scaling the $4s$ wave function with volume, while at higher pressures the variation is slower. Above 130 kbar a seventh line appears near the center of the spectrum due to the transformation of part of the iron source to the hexagonal-close-packed high-pressure phase. With increasing pressure this line becomes more intense and the split spectrum disappears, although the transformation is sluggish. From the absence of splitting and from the observed linewidth we conclude that the internal field in the hexagonal phase is 0 ± 3 kg. There may be a small broadening due to electric quadrupole interactions in the hexagonal lattice. The isomer shift of the hexagonal phase relative to the cubic phase is -0.017 cm/sec, indicating that the s-electron density is greater in the hexagonal phase. The pressure dependence of the shift in the hexagonal phase is very slight and is not consistent with scaling the $4s$ wave function with volume. Apparatus and experimental techniques that were developed for measuring the Mössbauer spectra of sources under pressure are described.

I. INTRODUCTION

THE properties of solids have been studied much less extensively as functions of pressure than of temperature. This lack of measurements under pressure is especially great in the very high-pressure region where the larger changes in the interatomic spacing will be reflected in larger changes of the properties. Several reasons why few high-pressure studies have been done can be given. Generation of very high pressures, containment of the sample in the high-pressure region, and determination of the pressure are difficult. Measurements of the properties are greatly complicated by the nature of the pressure generating apparatus.

In recent years apparatus has been developed for electrical resistance[1] and x-ray diffraction[2] measurements at very high pressures. This apparatus, utilizing tapered, work-hardened Carboloy pistons of small flat size and compressive support of the taper, is capable of generating pressures in excess of 500 kbar in volumes of about 0.2 mm^3. At these pressures sizeable volume changes occur in all materials, e.g., 19% for iron, 12% for rhodium, and 41% for cesium chloride.

The Mössbauer effect[3–6] has made possible important new experiments on the properties of solids under high pressures. By measurement of the Mössbauer spectrum of a source under pressure, information may be obtained about the pressure dependence of the magnetic field and electric-field gradient at the nucleus, the electron density at the nucleus, and the lattice properties through the second-order Doppler shift and the recoilless fraction. Discontinuities in some of these properties can occur at a phase transition.

Some advantages of using the Mössbauer effect to study the pressure dependence of the properties of materials may be noted. The shift and splitting of the spectrum can be determined with high accuracy making it possible to measure relatively small changes in these properties. Small sources can be made compatible with the size limitations imposed by the pressure cell. Many experiments can be done without applying fields which is made difficult by the pressure apparatus. No leads need to be connected to the sample although a window to transmit gamma rays out of the cell must be devised. However, there are suitable Mössbauer isotopes only for some elements.

Iron is a material of great theoretical and practical interest and Fe^{57} is one of the best isotopes for studying the Mössbauer effect. At atmospheric pressure and room-temperature iron has the body-centered-cubic structure (bcc, α iron). It is ferromagnetic up to the Curie temperature 770°C. At 910°C it transforms to a face-centered-cubic phase (fcc, γ iron). The α-γ transition has been traced as a function of pressure to 500°C and 95 kbar.[7] In recent years shock wave[8] and electrical resistance[9] measurements have revealed a phase transi-

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[1] H. G. Drickamer and A. S. Balchan, *Modern Very High Pressure Techniques*, edited by R. H. Wentorf, Jr. (Butterworth Scientific Publishers, Inc., Washington, 1962), p. 25.

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tion at 130 kbar and 25°C. The phase boundary between α iron and the high-pressure phase has been traced as a function of pressure and appears to meet the α-γ phase boundary in a triple point.[10] X-ray diffraction measurements at high pressure by Jamieson and Lawson[11] suggested that the high-pressure phase is hexagonal close-packed (hcp). Recent x-ray measurements by Clendenen and Drickamer[12] show that this phase is indeed hcp. The lattice parameters were measured to 300 kbar in the bcc phase and from 150 to 400 kbar in the hcp phase. The measurements in the bcc phase above 130 kbar are possible because the transition can be quite sluggish in some cases. The compressibility decreases with increasing pressure as expected. The pressure volume relation is of the form $-\Delta V/V_0 = ap - bp^2$. The volume change at the transition is 2.2% at 150 kbar and slightly larger at higher pressures. The c/a ratio in the hcp phase decreases with pressure from 1.643 at 150 kbar to 1.580 at 400 kbar.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental arrangement is sketched in Fig. 1. Pressure was applied to the Mössbauer source in the pressure cell by the hydraulic press. The 14.4-keV Fe^{57} gamma rays from the source were detected by a krypton-filled proportional counter with a wide beryllium window. A stainless-steel absorber containing Fe^{57} was moved relative to the source by a mechanical motion device utilizing a constant velocity cam and a variable speed drive. This motion introduces a Doppler shift between the emission spectrum and the single absorption line. By measuring the counting rate as a function of velocity the energy spectrum of the gamma rays from the source was determined. The variations of the shifts, splittings, and intensities of the lines of the spectrum gave information about the effect of pressure on the properties of the iron.

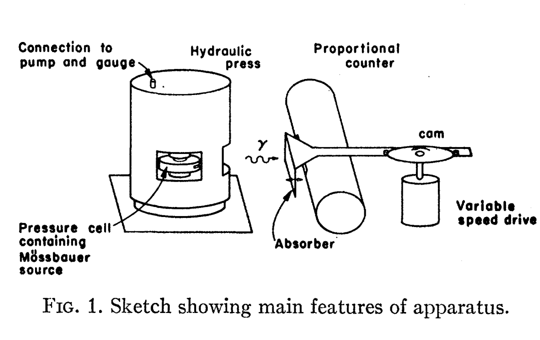

FIG. 1. Sketch showing main features of apparatus.

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A. Pressure Cell

The pressure cell used in these experiments was an adaption of electrical resistance and x-ray diffraction cells. Detailed descriptions of these are given in the literature[1,2] and only a brief description of the principles involved and the changes required for Mössbauer measurements are given here.

The sample was pressed between Carboloy pistons in the shape of truncated cones. The center parts of the flats on the pistons were stressed beyond the yield point but could not yield because they were supported by massive amounts of Carboloy (Bridgman's principle of massive support). The sample was prevented from extruding out from between the piston flats by a thin gasket of boron (mixed with 15% lithium hydride). This material showed a high degree of internal friction and friction with the pistons. The whole system can be described as a series of concentric pressure cells each one containing the one inside it and each one strong enough to support the pressure gradient across it.

Two important features of the pressure cell are the small flat size and the compressive support of the tapered parts of the pistons. This additional support extends the pressure range obtainable by supporting both the pistons and the gasket material. These features also make it possible to work harden the flats on the pistons by pressing a pyrophyllite pellet to a high enough pressure to dent the flats but not crack them. When reground the centers of the flats are work hardened and the obtainable pressure range is greatly extended.

A cross section of the pressure cell is shown in Fig. 2. The flats of the pistons were aligned with the window by shims placed between the bottom of the cylinder and the steel jacket on the bottom piston. The pyrophyllite pellets were 0.872 in. diam and the tapers were cut to

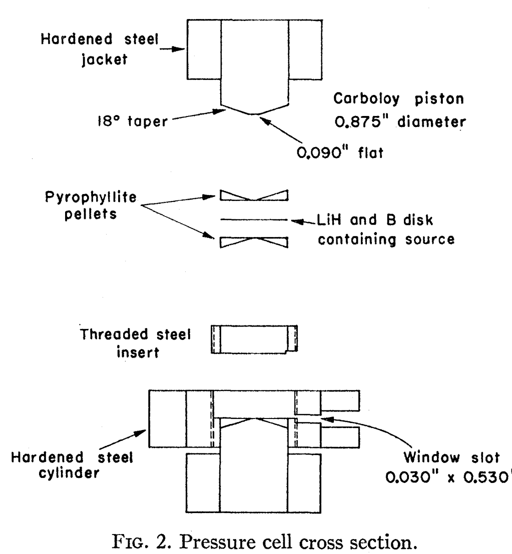

FIG. 2. Pressure cell cross section.

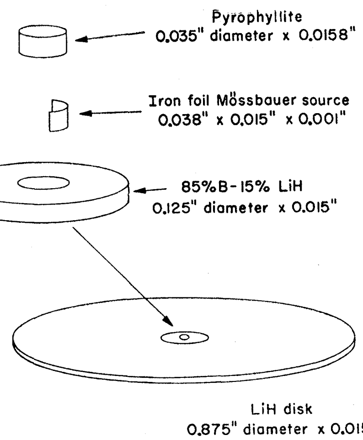

FIG. 3. Disk of lithium hydride and boron containing Mössbauer source. The details of the center are shown in enlarged view.

fit the pistons. The flat sides of the pellets were sanded until coplanar with the piston flats. Figure 3 shows the disk of lithium hydride and boron which contained the source. These materials have high transmission for the gamma rays as well as good pressure properties. The cell loading procedure is quite critical and must be done with care to obtain reproducible results. The hydraulic press used is described in Ref. 1. The press was operated by a hand pump, and the applied force was measured with an accurate Bourdon gage.

A pressure calibration curve was obtained by measuring transitions in bismuth at 25 and 87 kbar, titanium at 85, iron at 130, and lead at 160 kbar. The transitions were determined as discontinuities in electrical resistance. The pressure was linear in applied force over this range. The pressure versus applied force curves at higher pressures are known to be roughly logarithmic from the x-ray and electrical resistance work.[1,2] To relate the pressure above 175 kbar to the applied force we have therefore used a logarithmic curve joined smoothly to the linear function below 175 kbar.

The calibration is less certain than the electrical or x-ray calibrations because of the long times involved (of the order of days) at each pressure and because no marker could be used as in the x-ray apparatus.

B. Sources and Absorber

The 14.4-keV excited state of Fe^{57} is populated by the 270-day half-life electron capture decay of Co^{57}. Sources were prepared by electroplating Co^{57} on a small ribbon of Armco iron. They were heated in hydrogen to reduce any oxides and vacuum annealed to distribute the Co^{57} throughout the iron. The absorber used consisted of stainless steel containing 4.9 mg/cm^2 iron enriched to 25% Fe^{57}. This absorber had a single absorption line, and with a source of Co^{57} in stainless steel the maximum absorption corrected for background was 55%. All measurements were made with source and absorber at room temperature.

C. Analysis of Data

At each pressure the spectrum was measured repeatedly (usually 6 to 12 times) until several hundred thousand counts were accumulated at each velocity. The increments of velocity used were 0.01 cm/sec for the split spectra and 0.005 cm/sec for the single line spectra. The counting rate at 1.5 cm/sec (i.e., large enough to destroy all resonance absorption) was measured periodically to provide a base line for correcting the counting rate, when necessary, for small variations of source geometry in the pressure cell, slight drifts in the electronics, and source decay.

Typically about half of the counting rate in the 14.4-keV channel from a source in the pressure cell was background due to the 122-keV gamma rays. This was higher than the normal 10 to 20% for a source not in the pressure cell because of absorption of the 14.4-keV gamma rays in the boron and lithium hydride. There was also additional background due to x rays emitted following absorption of 122-keV gamma rays in the tungsten in the pistons. A correction for the background was made in the spectra shown in Figs. 4–6.

The centers, widths, and amplitudes of the lines were determined by making least-square fits of Lorentzian lines to the data. While the lines are not strictly Lorentzian the fits are reasonably good and are adequate for measuring relative changes of the parameters.

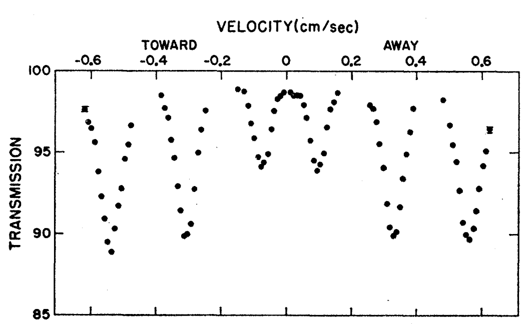

FIG. 4. Mössbauer spectrum of iron at atmospheric pressure. 100 corresponds to transmission in absence of Mössbauer absorption.

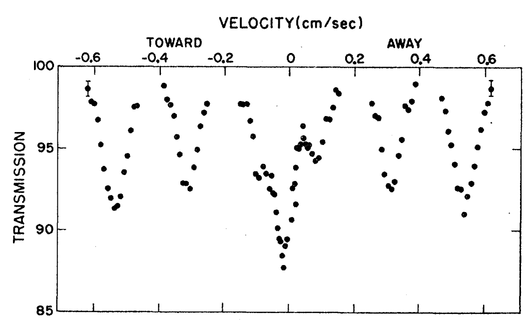

FIG. 5. Mössbauer spectrum of iron at 145 kbar.

III. RESULTS

Figure 4 shows the Mössbauer spectrum of iron at atmospheric pressure. The statistical errors of the data points are indicated. As the pressure increases the splitting decreases and the center of gravity shifts in the negative direction corresponding to increasing s-electron density in the source.

Above 130 kbar a new line appears in the spectrum (Fig. 5) corresponding to iron in the hcp phase. The shift of this line relative to the spectrum of the bcc phase is -0.017 cm/sec indicating that the s-electron density is greater in the hexagonal phase. As the pressure is raised the intensity of this line increases and the split spectrum disappears (Fig. 6). A pressure well above 130 kilobars, typically 170–200 kbar, is needed to transform most of the source. The shift of this line with pressure is very slight.

Figures 7 and 9 show results for the center of gravity ϵ and splitting of the spectra as functions of pressure. The splitting is presented as the ratio of the internal magnetic field H to H_0, its value at one atmosphere. The estimated uncertainties in the determinations of ϵ and H are similar to the spread between the points in the figures.

Two other Mössbauer experiments on iron under pressure have been reported. Pound *et al.*[13] have made an accurate measurement of the pressure shift up to 3 kbar. In their experiments a fluid pressure transmitter was used, and the pressures were truly hydrostatic and could be measured accurately. Their result is

$$\Delta\epsilon/\Delta P = (-7.98\pm0.31)\times10^{-5}\ \text{cm sec}^{-1}\ \text{kbar}^{-1}. \qquad (1)$$

A linear extrapolation of this to higher pressures is

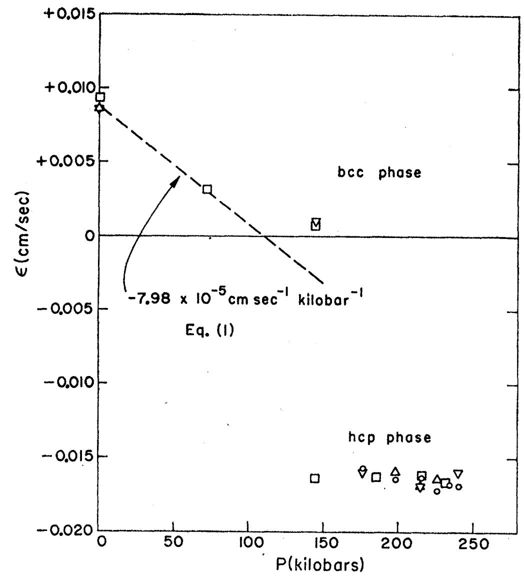

FIG. 7. Center of gravity of Mössbauer spectrum versus pressure. The line labeled Eq. (1) is an extrapolation of the data in Ref. 13.

shown in Fig. 7. Converting Eq. (1) to volume using the compressibility of iron at low pressure $(-\Delta V/V_0\Delta P = 5.95\times10^{-4}\ \text{kbar}^{-1})$ one obtains

$$\partial\epsilon/\partial(V/V_0) = 0.134\ \text{cm/sec}. \qquad (2)$$

In Fig. 8 our results are plotted versus fractional volume change using the x-ray data of Clendenen and Drickamer.[12] While there is no reason for ϵ to be a linear function of volume over such a great range of volume change, the extrapolation is in reasonable agreement with our data.

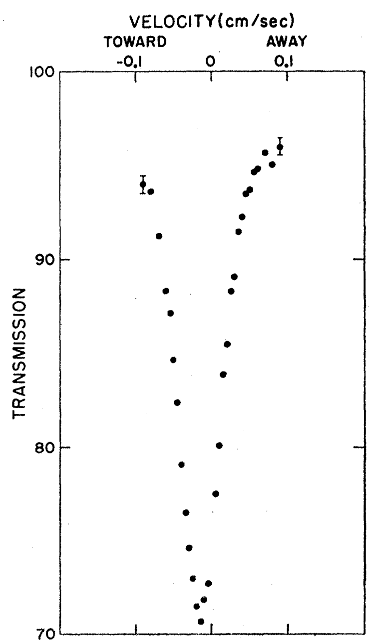

FIG. 6. Mössbauer spectrum of iron at 216 kbar.

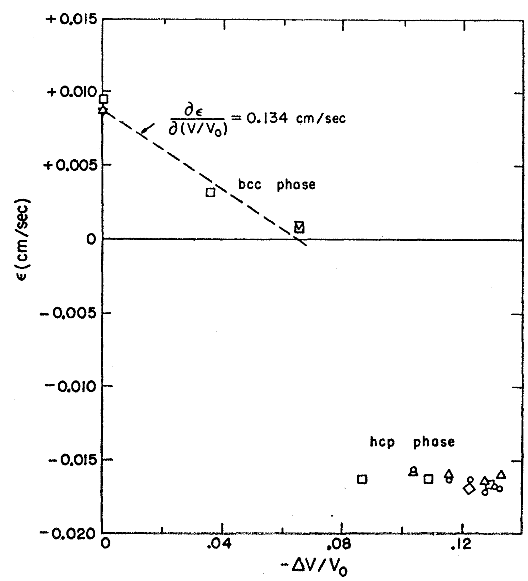

FIG. 8. Center of gravity of Mössbauer spectrum versus volume change. The broken line is an extrapolation of the data of Ref. 13.

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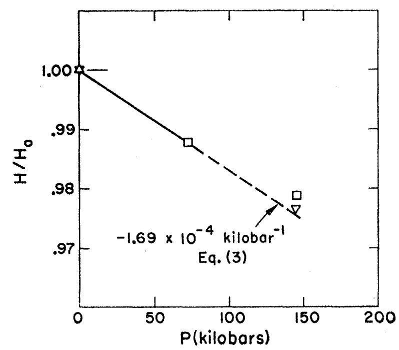

FIG. 9. Magnetic field at the nucleus versus pressure (α phase). The line labeled Eq. (3) is obtained from the data in Ref. 15.

Nicol and Jura[14] have measured the Mössbauer spectrum of iron up to 140 kbar using Bridgman anvils. Their results for the shift and splitting in the α phase agree with ours within experimental error. Their source was partially transformed to the hcp phase at 140 kbar. They report the shift of the Mössbauer line of this phase as (-0.0127 ± 0.0064) cm/sec which agrees with our value within experimental error.

Litster and Benedek[15] have measured the internal field in Fe to 65 kbar by nuclear magnetic resonance in a belt-type apparatus. Their sample was surrounded by silver chloride. This may produce more nearly hydrostatic pressures than those in our experiments. Their pressure calibration was more precise than ours due to the availability of well known transitions in Bi, Tl, and Ba in the pressure range to 65 kbar. They obtain

$$\partial\nu/\partial P|_{25.5^\circ\mathrm{C}}=(-7.67\pm0.22)\ \mathrm{kc\ kbar}^{-1}$$

where ν is the resonance frequency. This result can be written

$$\Delta H/H_0\Delta P=(-1.69\pm0.05)\times10^{-4}\ \mathrm{kbar}^{-1}. \tag{3}$$

A linear extrapolation of (3) to 150 kbar is shown in Fig. 9.

In Fig. 10 our data are plotted versus fractional volume change using the data of Ref. 12. Within the accuracy of the data we obtain a linear fit of the form

$$\partial(H/H_0)/\partial(V/V_0)=0.34\pm0.01. \tag{4}$$

The error given does not include a possible systematic error due to uncertainties in the pressure calibration.

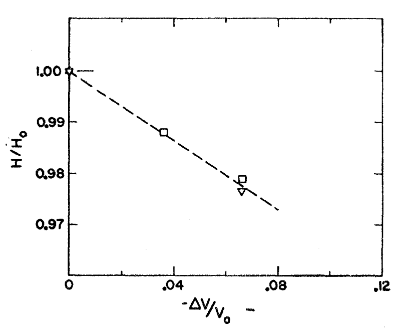

FIG. 10. Magnetic field at the nucleus versus volume change (α phase).

IV. DISCUSSION

A. Isomer Shift

The center of gravity of the spectrum is determined by the second-order Doppler shift which is proportional to the mean-square velocity of the atoms, and by the isomer shift which is proportional to the s-electron density at the nuclei. It can easily be shown that the effect of pressure on the second-order Doppler shift is small.[16]

The main effect of pressure must be a change in the isomer shift as a result of an increase in the electron density at the nucleus. An estimate of the contributions of the $4s$ and inner s electrons can be made from the work of Walker *et al.*[17] Using free-ion Hartree-Fock wave functions and the Fermi-Segrè-Goudsmit formula, they derive a plot of s-electron density at the nucleus versus number of $4s$ electrons per atom for various numbers of $3d$ electrons. They arrive at a calibration for the isomer shift in terms of electron density by associating the calculated electron density for the configuration $3d^6$ and $3d^5$ with the measured shifts for the most ionic divalent and trivalent compounds, respectively. Variation of the number of $3d$ electrons has small effect on the $1s$ and $2s$ densities at the nucleus but sizeable effects on the $3s$ and $4s$ due to shielding. The shielding of the inner s electrons by the $4s$ electrons is neglected (Watson's calculations for $3d^n$ and $3d^{n-2}\,4s^2$ show this effect to be small).[18] The measured shift for iron and the fact that there are eight electrons per atom lead to the configuration $3d^74s$.

If we assume that the only effect of changing the volume is to change the scale but not the shape of the $4s$ wave function, the volume dependence of the isomer shift can be found from the line $3d^74s^x$. The shift produced by one $4s$ electron occupying a volume V_0 is -0.14 cm/sec. Decreasing the volume by the small fraction $\Delta V/V_0$ is equivalent to adding that fraction of one $4s$ electron to the configuration $3d^74s$. The corresponding shift can be written

$$\Delta\epsilon=-0.14(-\Delta V/V_0)\ \mathrm{cm/sec}. \tag{5}$$

Comparing the data of the present experiment with Eqs. (2) and (5) we conclude that the main effect in the α phase is an increase in $4s$ density proportional to the increase in volume. At the higher pressures the variation appears to be slightly less which may indicate

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[15] J. D. Litster and G. B. Benedek, J. Appl. Phys. **34**, 688 (1963).
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[18] R. E. Watson, Phys. Rev. **119**, 1934 (1960).

that for larger volume changes scaling alone is not sufficient, shielding cannot be neglected completely, or that the $3d$ electrons may be slightly affected (especially those near the bottom of the band which are shown by band calculations[19] to be more extended than atomic $3d$ electrons).

In the hcp phase the isomer shift shows only very slight pressure dependence. The volume change over the pressure range 150 to 240 kbar is about 4% and Eq. (5) would imply a shift of -0.0056 cm/sec. Thus scaling the $4s$ wave function alone will not explain the data. Either the $4s$ wave functions are not sensitive to the volume change or there is a canceling effect due to changes in the $3d$ wave function. This lack of shift may be related to the anisotropy of the compressibility of the hcp phase. Most of the volume change is due to a decrease in the c axis with only small decreases in the a axes.[12]

The shift in the hcp phase relative to the α phase is -0.017 cm/sec. This is much larger (about 4 times) than would be expected on the basis of the volume change (2.2%) and Eq. (5) alone. We can estimate the change in the number of $4s$ electrons by using the data of Walker *et al.*[17] for the configuration $3d^{8-x}4s^x$. The measured shift corresponds to x changing from 1 to 1.06.

The explanation of this shift must be related to the difference in band structure of the two phases. An increase of the $4s$ density of states, decrease in the $3d$ density of states, or a lowering of the energy of the $4s$ band with respect to the $3d$ band would cause a shift in the proper direction. A change of shape of the $3d$ wave functions will also cause a shift through shielding of the $3s$ electrons.

Part of the shift may also arise as a result of the transition from a ferromagnetic phase to a paramagnetic phase. Preston *et al.*[6] observed a shift of -0.001 cm/sec at the Curie temperature in Fe. They found an additional shift of -0.003 cm/sec at the α-γ transition. The volume decrease at this transition is 1% so Eq. (5) would predict a shift of -0.0014 cm/sec. Results not in disagreement with these have been obtained for γ iron precipitates in copper by Gonser *et al.*[20,21] They found a difference of (-0.0027 ± 0.0030) cm/sec between the center of gravity of the γ precipitate and α iron. A difference of about (-0.002 ± 0.002) cm/sec was observed between the paramagnetic phase above the Néel temperature and the antiferromagnetic phase.

Comparison can also be made with the data of Johnson *et al.*[22] on iron rich alloys with Mn and Ni. In the vicinity of 30% Ni there is a two-phase region consisting of a bcc ferromagnetic phase and a fcc phase paramagnetic at room temperature. The relative amounts of each phase depend on the treatment of the alloy. They observe a shift of the fcc line with respect to the bcc line of -0.012 cm/sec. Mn dissolves in α Fe up to 4% and metastable bcc solutions up to 15% exist. These alloys are ferromagnetic. For higher Mn content the alloys are fcc and not ferromagnetic. The shift of the fcc line with respect to the bcc line is -0.01 cm/sec. In both of these systems about half of the observed shift may be explained by scaling the $4s$ wave function with volume.

In the Fe-Mn system with 17% Mn a hcp phase can be formed. The shift of this phase has been measured by Kimball.[23] With respect to α Fe the shift is (-0.0121 ± 0.0002) cm/sec.

B. Internal Magnetic Field

Mössbauer experiments[6] have shown that the magnetic field at the nucleus in iron is large and opposite in direction to the magnetization. The origin of this field is discussed by Marshall[24] and Watson and Freeman.[25] There are the following contributions to the internal field: (1) the local field composed of the external, demagnetizing, and Lorentz fields; (2) the dipolar field of the spin moment of the $3d$ electrons on the parent atom; (3) the field produced by unquenched orbital angular momentum of the $3d$ electrons on the parent atom; (4) the field proportional to the spin density at the nucleus. This field is a result of the Fermi contact interaction.

The first of these is a negligible part of the total field (-330 kG at room temperature). The second is zero for cubic lattices. The orbital contribution has been estimated at $+70$ kG in Fe.[26] The main contribution is the field due to the spin density arising partly from core polarization of the $4s$ electrons.

The large negative part of this field is due to core polarization. This results from the differing exchange interactions of the 1, 2, and $3s$ electrons of parallel and antiparallel spin with the aligned $3d$ electrons. Slightly different radial distributions are produced for the two spin states. Since the s wave functions for the inner electrons are large at the nucleus a slight difference can produce a large field. Watson and Freeman have determined the core polarization by unrestricted Hartree-Fock calculation (i.e., different radial distributions allowed for the two spin states) and obtained a value of about -330 kG. The core polarization was found to be quite sensitive to the size and shape of the $3d$ electron distribution.

The spin density due to the $4s$ electrons is not well understood.[25,27] These electrons contribute positively

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[20] U. Gonser, C. J. Meechan, A. H. Muir, and H. Wiedersich, J. Appl. Phys. **34**, 2373 (1963).
[21] A. H. Muir (private communication).
[22] C. E. Johnson, M. S. Ridout, and T. E. Cranshaw, Proc. Phys. Soc. (London) **81**, 1079 (1963).
[23] C. Kimball (private communication).
[24] W. Marshall, Phys. Rev. **110**, 1280 (1958).
[25] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).
[26] W. Marshall and C. E. Johnson, J. Phys. Radium **23**, 733 (1962).
[27] H. Brooks, *Electronic Structure and Alloy Chemistry of the Transition Elements*, edited by P. A. Beck (Interscience Publishers, Inc., New York, 1963), p. 3.

to the internal field via polarization by the $3d$ electrons and admixing into the $3d$ band and negatively by covalent mixing with the $3d$ wave functions. The net contribution of the $4s$ electrons is probably small and may be negative.

Recent neutron diffraction measurements[28] find -0.2 Bohr magnetons for the $4s$ contribution to the magnetization. This result would increase the calculated value for the core polarization and strengthen the conclusion that the internal field due to the $4s$ electrons is small.

The important contributions to the field are proportional to the mean spin per atom and therefore to the saturation magnetization σ. This can be written

$$H = a\sigma \tag{6}$$

or

$$\nu = A\sigma, \tag{7}$$

where ν is the nuclear magnetic resonance frequency. σ depends both on σ_0, the value of σ at 0°K, and on the Curie temperature. Changes of volume can affect both of these; however, for Fe the measurements of Patrick[29] and Kaufman[7] show that the pressure dependence of the Curie temperature is small.

The temperature and pressure dependences of ν have been measured by Benedek[30] and compared with similar measurements on σ. A is found to be temperature-dependent. This is attributed to the temperature dependence of the occupation of the $3d$ states and the variation of the coupling constants for states in the $3d$ band due to the varying spatial dependence of these states.

The explicit pressure dependence of A is found by differentiating Eq. (7) with respect to pressure and using the fact that $(\partial \ln\nu/\partial P)_T$ is nearly independent of temperature between[30] 0 and 300°K

$$\frac{\partial \ln\nu}{\partial P} = \frac{\partial \ln A_0}{\partial P} + \frac{\partial \ln\sigma_0}{\partial P}, \tag{8}$$

where A_0 and σ_0 are the values at 0°K. Using the result of Kouvel and Wilson[31]

$$\partial \ln\sigma_0/\partial P = (-2.83\pm0.25)\times10^{-4}\ \text{kbar}^{-1},$$

and of Benedek

$$\partial\, ln\nu/\partial P = (-1.67\pm0.01)\times10^{-4}\ \text{kbar}^{-1},$$

the pressure dependence of A is

$$\partial \ln A_0/\partial P = (1.16\pm0.25)\times10^{-4}\ \text{kbar}^{-1}. \tag{9}$$

Part of the pressure dependence of A must result from changes in the core polarization due to changes in size or shape of the $3d$ wave functions. The remainder must be due to the $4s$ electrons which are most sensitive to changes in lattice spacing. The explicit pressure dependence of A cannot be determined for pressures above 11 kbar since the magnetization has been measured only to this pressure.[32]

The magnetic resonance signal arises mainly from nuclei in domain walls.[33] The Mössbauer effect does not distinguish between nuclei in domain walls and those within the domains, and therefore measures mainly the field at nuclei within the domains. The Mössbauer measurement of the temperature dependence of the internal field[6] is in good agreement with the resonance measurement. This shows that the temperature dependences of a in Eq. (6) and A in Eq. (7) are the same. Similarly the data of the present experiment on the pressure dependence are in good agreement with the resonance measurement. Thus the pressure dependences of A and a are also the same.

An interpretation in terms of the spin density has been given by Benedek.[34] Dividing Eq. (9) by the compressibility he obtains

$$\partial \ln A/\partial \ln V = -0.19,$$

and in terms of spin density this is

$$\frac{\partial \ln(|\psi_\uparrow(0)|^2 - |\psi_\downarrow(0)|^2)}{\partial \ln V} = -0.19, \tag{10}$$

where $\psi_\uparrow(0)$ and $\psi_\downarrow(0)$ are the wave functions at the nucleus for electrons whose spins are parallel and antiparallel to σ. From the magnitude and direction of the internal field the spin density is

$$|\psi_\uparrow(0)|^2 - |\psi_\downarrow(0)|^2 = 0.63\ \text{a.u.}^{-3}, \tag{11}$$

where a.u. = atomic unit = 0.529×10^{-8} cm. The product of Eqs. (10) and (11) is

$$\frac{\partial(|\psi_\uparrow(0)|^2 - |\psi_\downarrow(0)|^2)}{\partial \ln V} = -0.12\ \text{a.u.}^{-3}.$$

From the isomer shift data the total charge density is

$$\frac{\partial|\psi(0)|^2}{\partial \ln V} = \frac{\partial(|\psi_\uparrow(0)|^2 + |\psi_\downarrow(0)|^2)}{\partial \ln V} = (-2.7\pm0.4)\ \text{a.u.}^{-3}.$$

Therefore the effect of changing the volume (at constant

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magnetization) is to change the spin parallel and spin antiparallel charge densities by approximately the same amount with the spin parallel density changing slightly more. If the volume is changed without holding the magnetization constant, the antiparallel density changes more.

The data show that the variation of the internal field up to 150 kbar is substantially linear, and the main effects up to this pressure must be essentially the same as in the low-pressure range. While the dependence of the internal field on volume is linear, the isomer shift changes less rapidly at higher pressures. Thus, the factors controlling these phenomena are not identical, at least in their relative importance.

Ferromagnetism is apparently absent in the hcp phase. If we assume that the magnetic properties depend more on the interatomic spacing than on the symmetry of the lattice, then a comparison can be made to the properties of iron in a fcc lattice.

Fcc iron can be obtained by coherent precipitation in copper. These γ-iron precipitates were shown to be antiferromagnetic by neutron diffraction.[35] Mössbauer measurements have shown that the internal field is about 24 kG and the Néel temperature T_n about 60°K.[20]

Iron in a fcc lattice can also be studied by alloying. One example is the Fe-Ni-Cr stainless steel which is observed to be antiferromagnetic with $H=21$ kG and $T_n=38$°K.[20,36] Other examples are the Fe-Ni and Fe-Mn alloys discussed in IV-A.

The fcc Fe-Mn alloys are known to be antiferromagnetic.[37] The internal fields and Néel temperatures were measured for fcc alloys near 50% Mn and 17% Mn hcp alloy.[38] The Néel temperatures were compared with those for fcc alloys in the intermediate composition range stabilized by addition of carbon. Since these data fall on a smooth curve, it appears that the 17% Mn hcp alloy is antiferromagnetic with $H=22$ kG and $T_n=240$°K, and that the magnetic properties of Fe in fcc and hcp environments are similar. Extrapolating these curves to pure iron cannot be done very accurately but would seem to give H and T_n roughly like those of the γ precipitate in Cu and stainless steel.

An explanation of the properties of γ iron and fcc alloys in terms of two electronic states has been given by Tauer and Weiss.[7,39] They assume that iron atoms in fcc lattices are mixtures of two states; one with high volume, high spin, and ferromagnetic coupling; the other with low spin, low volume, and antiferromagnetic coupling. This point of view may also be applicable to hcp iron, and under pressure, the latter state would tend to be stabilized.

The Bethe-Slater curve would also imply that fcc and hcp iron would be antiferromagnetic.[40]

In the present experiment we made no provision for varying the temperature of the source under pressure. It would be possible by modifying the design of the press to cool the cell to liquid-nitrogen temperature but rather difficult to go to lower temperatures which may be necessary to observe antiferromagnetism in the hcp iron.

C. Electric Field Gradient, Linewidth and Recoilless Fraction

The spectra of the α phase showed no significant quadrupole splitting (less than 0.0007 cm/sec). The linewidths were similar to those at atmospheric pressure.

In the hcp phase the linewidth due to the source can be estimated by correcting the observed width for the absorber width and thickness. A correction must also be made for the self-absorption in the source because it is natural iron. Under pressure the pistons are about half as far apart as the initial spacing causing changes in the source geometry that can only be estimated. The linewidth increases slightly between the region where most of the iron is still in the cubic phase and that where most is transformed to the hcp phase in agreement with the estimated self-absorption.

A limit can be put on the possible internal field using the formula of Kimball *et al.*[38] for the apparent width Γ_a of an unresolved spectrum

$$\frac{\Gamma_a}{\Gamma_1}=1+\left(\frac{\Delta}{\Gamma_1}\right)\left\{1+\left[\left(\frac{\Delta}{\Gamma_1}\right)^4+\frac{3}{2}\right]^{-1}\right\},$$

where Γ_1 is the width of the lines if the hyperfine field could be turned off and Δ is the splitting of the outer lines. Γ_a is 0.070 cm/sec; Γ_1 is 0.052 to 0.070 cm/sec depending on the amount of self-absorption in the source. Using $\Gamma_1=0.060$ cm/sec we obtain $\Delta=0.006$ cm/sec equivalent to 1.9 kG. We conclude that $H=(0\pm3)$ kG in the hcp phase. There probably is a small broadening arising from electric quadrupole interactions in the hexagonal lattice.

Using the Debye model to describe the lattice vibrations with Debye temperatures of 400°K at

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atmospheric pressure and 450°K at 150 kbar (estimated from Lindemann or Grüneisen relations) the recoilless fraction increases from 0.77 to 0.81 over this pressure range.[16] Under the experimental conditions of high background and uncertain self-absorption in the source it is difficult to determine f precisely enough to measure a change of this size.

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Measurement of the Scattering Factor of Copper in a Perfect Crystal

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Several studies of the scattering factors of metal powders have shown that the charge distribution is more spread out than that calculated by the Hartree-Fock (HF) method for free atoms. On the other hand, measurements on gases have yielded agreement with the HF calculations. In order to distinguish whether the disagreement in the case of the metals arises from the powder measurement technique or from solid-state effects, we have measured the scattering factor of copper in a nearly perfect crystal and compared the result with that obtained previously on copper powder; we find agreement within experimental error. The inference from this result is that the previous powder measurements on aluminum, which yielded a scattering factor even lower than that calculated for the core electrons by the HF method, are also reliable.

INTRODUCTION

One of the most direct ways of studying the accuracy of approximate wave functions in solids or atoms is to determine the electron density through a study of the x-ray scattering. Several considerations have, however, limited the extensive use of the x-ray technique. For example, it is not at present possible to obtain the higher order Fourier components of the charge density, given through the scattering factor, because of wavelength limitations and increasingly serious uncertainties in the Debye-Waller factor. As a result, it is not possible to completely synthesize the charge distribution from the experimental results. Instead, one may compare the observed values for the low-order components with those given on the basis of various theories. Unfortunately, many recent theoretical discussions[1] do not include values for the scattering factor, or even for the charge density, although such information is available within the framework of the theory. Furthermore, because of difficulties in technique and in interpretation, it is not always clear that the scattering factor may be derived from the measured results to the accuracies which at first sight seem possible.

To elucidate this latter point, there have recently been a number of projects whose purpose has been not only to investigate the electron distribution in solids, but also to examine the applicability of the experimental method.[2] Some of the first such experiments made use of imperfect single crystals for which it was necessary, however, to make corrections for extinction.[3] Since such corrections are most in doubt for the lowest reflections, which are the very ones which most distinguish the solid from the free atom, much recent work has been done on powders.[4–9] In this case, it is easier to prepare an extinction free sample, but one must avoid porosity and preferred orientation effects. Nevertheless, a number of experiments on powders have given scattering factors within an accuracy of the order of 1%. Since some of these results, notably those for Al,[4,5] were somewhat surprising, it has seemed desirable to us to check these results with a different experimental technique. Such a check has recently been made possible by the production of nearly-perfect copper cyrstals.[10] We have measured the scattering factor of the (111), (222), and (333) reflections from nearly perfect copper single crystals kindly supplied to us by Dr. F. W. Young, and

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