**Mössbauer Effect in Iron under Very High Pressure**

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(Received 3 April 1964)

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 $H_s$ at the nucleus decreases linearly with volume; $\partial (H/\delta V)/\partial V = 0.34 \pm 0.01$, where $H_s$ and $V$ 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, $-8.3 \times 10^{-4}$ 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 $0\pm 3$ kbar. 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 need 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, $\alpha$ iron). It is ferromagnetic up to the Curie temperature 770°C. At 910°C it transforms to a face-centered-cubic phase (fcc, $\gamma$ iron). The $\alpha$-$\gamma$ 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 transition.

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The experimental arrangement is sketched in Fig. 1. The experimental arrangement was applied to the Mössbauer source in the source cell by the hydraulic press. The 14.4-keV Fe$^{57}$ ray from the source were detected by a spinner-filled proportional counter with a wide beryllium window. A stainless-steel absorber containing Fe$^{57}$ moved relative to the source by a mechanical device utilizing a constant velocity cam and a wide speed drive. This motion introduces a Doppler effect on the emission spectrum and the single 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 shifts, splittings, and intensities of the lines of the gamma ray spectrum gave information about the effect of pressure properties of the iron.

**II. EXPERIMENTAL APPARATUS AND PROCEDURE**

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

The sample was pressed between Carboly 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 Carboly (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 materials. 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

![DIAGRAM]
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.
III. RESULTS

Figure 4 shows the Mössbauer spectrum of iron at atmospheric pressure. The statistical errors of the data are indicated. As the pressure increases the splitting decreases and the center of gravity shifts in negative direction corresponding to increasing 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 at pressure is very slight.

Figures 7 and 9 show results for the center of gravity 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 $\epsilon$ and $\delta$ 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. have made an accurate measurement of the pressure shift up to 20 kbar. In their experiments a fluid pressure transmitter was used, and the pressures were truly hydrostatic and could be measured accurately. Their result is $\epsilon(P) = (-7.98 \pm 0.31) \times 10^{-4} \text{ cm sec}^{-1} \text{ kbar}^{-1}$. (1)

Linear extrapolation of this to higher pressures is shown in Fig. 7. Converting Eq. (1) to volume using the compressibility of iron at low pressure ($\Delta V/V_0 \Delta P = 3.95 \times 10^{-4} \text{ kbar}^{-1}$) one obtains

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

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

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

Fig. 8. Center of gravity of Mössbauer spectrum versus volume change. The broken line is an extrapolation of the data of Ref. 13.
Nicol and Jura\textsuperscript{14} have measured the Mössbauer spectrum of iron up to 140 kbar using Bridgman anvils. Their results for the shift and splitting in the \( \alpha \) 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 \((-0.0127\pm0.0064)\text{ cm/sec}\) which agrees with our value within experimental error.

Litster and Benedek\textsuperscript{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 silver chloride. This may produce more nearly hydrostatic pressures than those in our experiments. Their results for the shift and splitting in the \( \alpha \) 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 \((-0.0127\pm0.0064)\text{ cm/sec}\) which agrees with our value within experimental error.

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

In the hcp phase the isomer shift shows only very small pressure dependence. The volume change over pressure range 150 to 240 kbar is about 4% and Eq. (5) would imply a shift of $-0.0056$ cm/sec. Thus the 4s wave function alone will not explain the observed shift. The 4s wave functions are not sensitive to 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 change in the $c$ axis with only small decreases in the $a$ and $b$ axes.

The shift in the hcp phase relative to the $\alpha$ phase is 567 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 contribution of the 3d electrons by using the data of Booker et al. for the configuration $3d^8-4s^0$. The added shift corresponds to a change from 1 to 1.06.

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

The shift may also arise as a result of the core polarization from a ferromagnetic phase to a paramagnetic one. Preston et al. observed a shift of $-0.001$ cm/sec for the Fe-Curie temperature in Fe. They found that this shift, in addition to a shift of $-0.003$ cm/sec at the $\alpha$-Fe transition. A decrease at this transition is 1% so Eq. (5) would predict a shift of $-0.0014$ cm/sec. Results not in agreement with these have been obtained by Esch et al. in Fe, S. S., and Eberly, J. H., Phys. Rev. 123, 1000 (1961). They found a difference of $(-0.0027 \pm 0.0030)$ cm/sec between the center of gravity of the parent atom and $\alpha$ Fe. A difference of about $(-0.002 \pm 0.002)$ cm/sec observed between the paramagnetic phase above Curie temperature and the antiferromagnetic phase.

Comparison can also be made with the data of W. Marshall 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. These electrons contribute positively

B. Internal Magnetic Field

Mössbauer experiments 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 and Watson and Freeman. 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. The main contribution is the field due to the spin density arising partly from core polarization of the 4s electrons.

The 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.
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 $\sigma$. This can be written

$$H = a\sigma$$

or

$$\nu = A\sigma,$$

where $\nu$ is the nuclear magnetic resonance frequency. $\sigma$ depends both on $\sigma_0$, the value of $\sigma$ at $0^\circ K$, 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 $\sigma$ is small.

The temperature and pressure dependences of $\nu$ have been measured by Benedek$^{30}$ and compared with similar measurements on $\sigma$. $A$ 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 $\left(\partial \ln \nu / \partial P\right)_T$ is nearly independent of temperature between $0^\circ K$ and $300^\circ K$.

$$\frac{\partial \ln \nu}{\partial P} = \frac{\partial \ln A}{\partial P} + \frac{\partial \ln \sigma}{\partial P},$$

where $A_0$ and $\sigma_0$ are the values at $0^\circ K$. Using the result of Kouvel and Wilson$^{31}$

$$\frac{\partial \ln \nu}{\partial P} = (-2.83 \pm 0.25) \times 10^{-4} \text{ kbar}^{-1},$$

and of Benedek

$$\frac{\partial \ln \nu}{\partial P} = (-1.67 \pm 0.01) \times 10^{-4} \text{ kbar}^{-1},$$

the pressure dependence of $A$ is

$$\frac{\partial \ln A_0}{\partial P} = (1.16 \pm 0.25) \times 10^{-4} \text{ kbar}^{-1}.$$

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 is in good agreement with the resonance measurement. This shows that the temperature dependences of $\sigma$ 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 $\sigma$ 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

$$\frac{\partial \ln (|\psi_1(0)|^2 - |\psi_4(0)|^2)}{\partial \ln V} = -0.19,$$  

where $\psi_1(0)$ and $\psi_4(0)$ are the wave functions at the nucleus for electrons whose spins are parallel and antiparallel to $\sigma$. From the magnitude and direction of the internal field the spin density is

$$|\psi_1(0)|^2 - |\psi_4(0)|^2 = 0.63 \text{ a.u.}^{-3},$$

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

$$\frac{\partial (|\psi_1(0)|^2 - |\psi_4(0)|^2)}{\partial \ln V} = -0.12 \text{ a.u.}^{-3}.$$

From the isomer shift data the total charge density is

$$\frac{\partial \ln V}{\partial \ln V} = \frac{\partial (|\psi_1(0)|^2 + |\psi_4(0)|^2)}{\partial \ln V} = (-2.7 \pm 0.4) \text{ a.u.}^{-3}.$$

Therefore the effect of changing the volume (at constant


The Mössbauer effect in Fe under very high pressure

The Mössbauer effect in Fe under very high pressure 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 \( g \) to 150 kbar is substantially linear, and the main effects up to this pressure must be essentially the same 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 of the properties of iron in a fcc lattice.

Fcc iron can be obtained by coherent precipitation in copper. These \( \gamma \)-iron precipitates were shown to be antiferromagnetic by neutron diffraction. Mössbauer measurements have shown that the internal field is about 24 kG and the Néel temperature \( T_N \) about 60°K. Iron in a fcc lattice can also be studied by alloying. The example is the Fe-Ni-Cr stainless steel which is derived to be antiferromagnetic with \( H = 21 \) kG and \( T_N = 38°K \). Other examples are the Fe-Ni and Fe-Mn alloys discussed in IV-A.

The fcc Fe-Mn alloys are known to be antiferromagnetic. The internal fields and Néel temperatures were measured for fcc alloys near 50% Mn and 17% Mn up alloy. The Néel temperatures were compared with those for fcc alloys in the intermediate composition range stabilized by addition of carbon. Since these data on a smooth curve, it appears that the 17% Mn up 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 those of the \( \gamma \) precipitate in Cu and stainless steel.

An explanation of the properties of \( \gamma \) iron and fcc iron is given in terms of two electronic states. A 35% Mn and 17% Mn up 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 those of the \( \gamma \) precipitate in Cu and stainless steel.

An explanation of the properties of \( \gamma \) iron and fcc iron in terms of two electronic states has been given by Tauer and Weiss. 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.

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 \( \alpha \) 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 \( \alpha \) 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. for the apparent width \( \Gamma_A \) of an unresolved spectrum

\[
\Gamma_A = 1 + \left( \frac{\Delta \gamma}{\Gamma_1} \right) \left( 1 + \left( \frac{\Delta \gamma}{\Gamma_1} \right)^2 \right),
\]

where \( \Gamma_1 \) is the width of the lines if the hyperfine field could be turned off and \( \Delta \) is the splitting of the outer lines. \( \Gamma_1 \) is 0.070 cm/sec; \( \Gamma_A \) 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 \( H = (0 \pm 3) \) 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. 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.

**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 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 not only to investigate the electron distribution in solids, but also to examine the applicability of the experimental method. Some of the first such experiments made use of imperfect single crystals for which it was necessary, however, to make corrections for extinction. 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. 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, 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 crystals. 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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**ACKNOWLEDGMENTS**

We acknowledge helpful suggestions from R. L. Ingalls, R. L. Mössbauer, C. P. Slichter, and F. Schütz. We thank A. H. Muir and C. Kimball for isomer shift data, R. Morrison and D. Hafemeister for computer programs, and M. Atac for constructing parts of the apparatus.