be considered; thus we get

$$5C = \frac{1}{2} (A_{zx}I_x + A_{zy}I_y + A_{zz}I_z) S_z,$$

$$A_{zi} = 2 \sum_{j=\xi, \eta, \zeta} \alpha_{jz}A_{jj}\alpha_{ji}.$$
 (8)

Equation (8) represents the most general hyperfineinteraction Hamiltonian, and is the same as given in Ref. (5) except for the factor $\frac{1}{2}$. The latter is again introduced in order to ensure that the parameters A_{zi} are quantitatively the same as given in the $S=\frac{1}{2}$ formalism. If $A_{zx} = A_{zy} = 0$, (8) reduces to the term that we already introduced in (4) without justification at that point.

Note added. A spin-1 formalism was independently

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proposed at the International Conference on Magnetism, Boston, 1967, by Orbach.²²

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After completion of the present study, Professor R. Lacroix informed us that in his Pisa lectures²³ he had pointed out the difficulties in using half-integral effective spins for even-electron systems. We are indebted to Dr. H. Thomas and Dr. J. Armstrong for very fruitful discussions, to Dr. F. I. B. Williams and Professor J. W. Culvahouse for comments on the manuscript.

²² R. Orbach (private communication).

²³ R. Lacroix, Lectures on Paramagnetic Resonance given in Pisa, Italy, 1964 (unpublished).

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Mössbauer-Effect Measurements in Iron at High Pressures*†

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Six-line Mössbauer spectra were obtained for Fe⁵⁷ in a natural iron-foil source over the pressure range 0 to 85 kbar, using a tetrahedral anvil press. An analysis of the data yielded the following results: The linewidth was not altered by pressure and was consistent with the Fe⁵⁷ thickness of the source and absorber. The relative line intensities changed from 2.8:2.4:1.0:1.0:2.4:2.8 at atmospheric pressure to 2.6:1.3:1.0: 1.0:1.3:2.6 at 80 kbar. This indicates that pressure polarized the iron foil so that the magnetic moments rotated out of the plane of the foil. This polarization was reversible. The isomer shift decreases linearly with pressure with a slope $(-7.46\pm0.21)\times10^{-5}$ cm sec⁻¹ kbar⁻¹. The effective magnetic field at the nucleus also decreased with pressure according to $\Delta H/H_0 = (-1.34 \pm 0.25) \times 10^{-4}P - (0.60 \pm 0.39) \times 10^{-6}P^2$, with P in kbar. A small quadrupole splitting was observed with the source under pressure, which increased as $\partial E_Q/\partial P = (0.96 \pm 0.23) \times 10^{-5}$ cm sec⁻¹ kbar⁻¹. The ratio of the splitting of the excited to the ground state was measured as $g_1/g_0 = 0.5714 \pm 0.0011$ and was independent of pressure. The absorption areas of the Mössbauer lines were measured, but attempts to calculate the f factor indicate a possible variation of f with polarization. Possible explanations are given for the polarization effect and quadrupole splitting.

I. INTRODUCTION

T high pressures Mössbauer measurements are a A most useful tool for extracting information concerning pressure effects on solid-state properties of materials. One advantage of this technique is that no electrical leads need be placed in the high-pressure cell in order to measure the effects. Another important use of this technique is that the local environment of the source nuclei can be studied and pressure effects on electron shell wave functions can be measured. The theory of the Mössbauer effect has been extensively treated in several texts and will not be enlarged upon here^{1,2}; but rather we will discuss a new technique for high-pressure Mössbauer measurements and results obtained from Fe⁵⁷ in a natural iron foil.

Three previous experiments on the Mössbauer effect in iron under pressure have been reported. Pound, Benedek, and Drever³ measured a decrease in the isomer shift with pressure to 3 kbar using a fluid-pressure system. They found a decrease in the isomer shift with pressure amounting to $(-7.98\pm0.31)\times10^{-5}$ cm sec⁻¹ kbar-1. Nicol and Jura⁴ used a Bridgman anvil apparatus to measure the Mössbauer spectrum to 140 kbar. There was a great amount of scatter in their results, but they agreed within experimental accuracy with a linear extrapolation of the isomer shift data of Pound et al. and the NMR effective magnetic field measurements of Litster and Benedek.⁵ Because of the large amount of absorbing material in Nicol and Jura's pressure cell, their counting times were very long and the

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of Mines and Technology, Rapid City, S.D. ¹ H. Frauenfelder, *The Mössbauer Effect* (W. A. Benjamin, Inc.,

New York, 1962). ² G. K. Wertheim, Mössbauer Effect: Principles and Applications

⁽Academic Press Inc., New York, 1964).

³ R. V. Pound, G. B. Benedek, and R. Drever, Phys. Rev. Letters 7, 405 (1961).

 ⁴ M. Nicol and G. Jura, Science 141, 1035 (1963).
⁵ J. D. Litster and G. B. Benedek, J. Appl. Phys. 34, 688 (1963).

background radiation excessively high. Due to these factors they could not measure the effects of pressure on the Lamb-Mössbauer factor in iron. Pipkorn *et al.*,⁶ using a supported flat anvil press and LiH windows to transmit the γ rays, measured the Mössbauer spectrum to 240 kbar. They reported a somewhat larger isomer shift than Pound *et al.* and agreed with Litster and Benedek as to the change in the effective field at the nucleus. Pipkorn *et al.* were also unsuccessful in measuring the pressure dependence of the recoilless fraction in iron. They were most interested in observing the phase change in iron above 100 kbar and made only one measurement below 100 kbar (at 70 kbar).

We have referred to the measurement of the effective magnetic field at the iron nucleus in iron by Litster and Benedek.⁵ This they accomplished by detecting the zero-field NMR frequency changes for an iron specimen under pressure. The measurement was made to about 60 kbar and the above Mössbauer experiments were compared with a linear extrapolation of these results up to 140 kbar. Litster and Benedek found $\partial(H/H_0)/\partial P = -(1.69\pm0.05) \times 10^{-4}$ kbar⁻¹.

The purpose of this research was to develop a new method for making Mössbauer measurements at high pressures and to accurately measure the γ -ray spectrum of Fe⁵⁷ in a natural iron matrix.

II. EXPERIMENTAL TECHNIQUES

The sources and absorbers used in this study were prepared by the New England Nuclear Corp. Two sources were prepared by electroplating Co^{57} onto a 0.0025-cm rolled natural iron foil and diffusing in a hydrogen atmosphere at 925°C. One source consisted of 10 mCi of Co^{57} on a 6-mm-diam active area and the other of 27 mCi on a 3-mm-diam active area. The absorber was Na₄Fe(CN)₆·10H₂O enriched to 91.2% Fe⁵⁷, and had a thickness of 1 mg/cm² of Fe⁵⁷. This is a single-line absorber, allowing the six-line spectrum of the source to be displayed.

The velocity spectrometer consisted of a pair of coupled loudspeakers driven to give a linear sawtooth function of velocity with time. Similar systems have been described in the literature.⁷ The speakers were purchased from the Jensen Manufacturing Co. Their voice coils were coupled via a thin-wall, 2.54-cm-diam Al tube through which the γ rays passed on their way to the detector. The absorber was mounted on one end of this tube. A Hewlett-Packard Model 202A lowfrequency function generator provided the reference triangular wave form which was compared to the signal from one of the voice coils after amplification by a Dymec Model 2460A operational amplifier. The error voltage fed a Hewlett-Packard 476A power amplifier, which drove the speaker system. The electronics in-



FIG. 1. Boron plastic tetrahedron containing iron-foil Mössbauer source. The tetrahedron measured 1.9 cm along an edge.

cluded a filter network to remove a 4200-Hz resonance which appeared at large loop gain. The speakers were driven between 11 and 12 Hz. The drive was linear to within 0.5% of the maximum signal as measured by the atmospheric-pressure Mössbauer spectrum.

In 5 of the 6 runs the γ rays were detected with a Reuter-Stokes proportional counter filled with 95% Xe and 5% N. In one run a 2.2-cm-diam, 1-mm-thick NaI detector was used. The efficiency of this detector was near 100% at 14.4 keV, but its resolution was too poor to separate the 14.4-keV line from the 6.4-keV x rays. In the press, however, the x rays were almost completely absorbed and were of no consequence. The background radiation in the 14.4-keV gate was more than twice as large with this system as with the former.

The data was collected with a RIDL Model 24-2 400channel analyzer operating in the time scale mode and synchronized with the velocity drive. The amount of background radiation in the 14.4-keV gate was measured by observing the pulse-height energy spectrum near the 14.4-keV line in both the gated condition and with the gate opened, to include background on either side. In the final two runs this quantity was measured by counting the radiation in the 14.4-keV gate with and without a 0.0125-cm brass absorber in front of the detector. This absorber essentially removes all 14.4-keV radiation and passes 96% of the 122-keV γ rays, the primary source of the background in the 14.4-keV gate. These two techniques give the same background correction.

For the measurements at high pressure the iron-foil source was placed between 0.025-cm-thick disks of BN and embedded in a tetrahedron, 1.9 cm on an edge, formed from a 50-50 mixture by weight of boron and Durez plastic, as shown in Fig. 1. For two of the runs the source was placed in the plastic tetrahedron without BN. This plastic, developed by Barnett and Hall,⁸ has good high-pressure properties as well as an absorption length of 1.3 cm at 14.4 keV. Unfortunately the purest amorphous boron contains a small amount of iron as an impurity. The effect of this impurity on the measured absorption areas was determined experimentally. The pressures were obtained in a tetrahedral

⁶ D. N. Pipkorn, C. K. Edge, P. Debrunner, G. DePasquali, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. **135**, A1604 (1964). ⁷ Mössbauer Effect Methodology, edited by I. J. Gruverman (Plenum Press, Inc., New York, 1965), Vol. 1.

⁸ J. D. Barnett and H. T. Hall, Rev. Sci. Instr. 35, 175 (1964).

200 000

100 000

110 000

40 000

40 000

100

100

100

400

400

TABLE I. Comparison of the high-pressure runs.

anvil press developed by Hall.⁹ Four tungsten carbide anvils are simultaneously driven against the faces of the plastic tetrahedron. The radiation emerges from the press through gaskets formed between the anvils and the Mössbauer spectrum is measured using the radiation passing out through the apex of the tetrahedron. This radiation is emitted normal to the surface of the iron-foil source. The distance between the source and the detector is 28.5 cm, and the absorber is 8.5 cm from the source.

34

5 6

27

 $\overline{27}$

RSG-30A

RSG-30A

RSG-30A

NaI(Tl)

RSG-61

In each of the six runs a zero-pressure spectrum was obtained with the sample in the press, followed by several spectra at higher pressures. Some pertinent information about the several runs is given in Table I. We add here a few comments pertaining to the individual runs and other statements of procedure common to all runs. The RSG-30A proportional counter deteriorated in run 4, making the background correction unreliable. This run was terminated with a "blowout" of the high-pressure cell at about 97 kbar. The blowout distorted the shape of the 27-mCi source. In all runs the amount of gasket material along the γ -ray path increased with pressure, and the gasket thickness decreased, requiring longer counting times. In particular, for run 3 the counting times increased from 2.7 h at zero pressure to 15 h at 86 kbar, while in run 5 the corresponding times were 4.5 h at atmospheric pressure and 32 h at 78 kbar.

In order to determine the pressure at the iron foil, the sample chamber was calibrated using the phase changes on increasing pressure, of Bi and Ba, as detected by electrical resistance measurements. These transitions were assigned the values Bi I-II 26 kbar. Ba I-II 57 kbar, and Bi III-V 78 kbar.¹⁰ Run 5 included a Bi wire behind the iron foil as an internal calibrant and two of the spectra were taken at the pressures of the lower and upper Bi transitions.

III. ANALYSIS OF THE DATA

Each six-line Mössbauer spectrum was fit by a leastsquares analysis to six Lorentzian lines using an IBM 7040 computer. The program utilized the variable metric-minimization method.¹¹ This process returned values for the line depths, widths, and positions, as well as the background count when well off-resonance. In addition, a mean-square deviation was calculated for each parameter.

none

PHA

PHA

PHA

brass absorber

brass absorber

From the calculated line positions the program then calculated the ratio of the Zeeman splitting in the excited to that in the ground state g_1/g_0 , the isomer shift E_s , the quadrupole splitting $E_Q = \frac{1}{4}e^2qQ$, the quantity $g_0\mu_n H$, where g_0 is the gyromagnetic ratio of the ground state, μ_n the nuclear magneton, and H the effective magnetic field at the nucleus, and the area in the absorption dips. The best value for each of these parameters consistent with the positions of all six lines was used along with an estimated mean deviation for each parameter.¹² E_s and E_Q were converted to velocity by using the zero-pressure spectrum and assigning the value 10.657 mm/sec to the separation between lines 6 and 1.13

The fraction of 14.4-keV γ rays emitted without an exchange of energy with the lattice is the Lamb-Mössbauer f factor. This fraction is directly proportional to the area above the dips in the transmission curve normalized to unity far off-resonance and corrected for background in the 14.4-keV gate.¹⁴ For a thin single-line absorber having a Lorentzian line of width Γ , this area is given by Preston *et al.*¹³ as

$$A = \frac{1}{2}\pi n_a f_a f_s \sigma_0 \Gamma G(n_a f_a \sigma_0), \qquad (1)$$

which is independent of the shape of the emission radiation. f_s and f_a denote the f factor for source and absorber, respectively, n_a the absorber thickness in nuclei per cm² and σ_0 the resonant cross section. All the factors in (1) are functions of the absorber only excepting f_s . Thus it would appear that, with the absorber outside the press, the ratio of this area with the source at pressure P to that with the source at atmospheric pressure

⁹ H. T. Hall, Rev. Sci. Instr. 29, 267 (1958). ¹⁰ R. N. Jeffery, J. D. Barnett, H. B. Vanfleet, and H. T. Hall, J. Appl. Phys. 37, 3172 (1966). We chose the Ba and upper Bi point higher than given in this reference because of recent private correspondence with G. C. Kennedy and H. B. Vanfleet.

¹¹ W. C. Davidon, Argonne National Laboratory Report No. ANL 5900 (Rev.), 1959 (unpublished).

¹² W. H. Southwell, dissertation, Brigham Young University, 1966 (unpublished) ¹³ R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. 128,

^{2207 (1962)} 14 D. A. Shirley, M. Kaplan, and P. Axel, Phys. Rev. 123, 816

^{(1961).}

would give the relative f factor of the source as a function of pressure.

In addition to the background correction one must also correct the measured absorption areas for resonant self-absorption in the source,¹⁵ and absorption from the small iron impurity in the boron-plastic pressure cell. These will be discussed later along with a more serious problem concerning effects of polarization on the validity of Eq. (1) and these corrections.

In considering the line intensity results, the intensity was taken as the product of linewidth and line depth. Average intensities for lines 1 and 6, lines 2 and 5, and lines 3 and 4 were calculated for each spectrum.

IV. RESULTS

For all runs the χ^2 values for the fit to a set of Lorentzian lines were typically within the statistically ex-



FIG. 2. Mössbauer spectra of iron at various pressures and room temperature.

pected value. An attempted fit with Gaussians gave twice the expected χ^2 . To within experimental accuracy, the linewidth was independent of pressure, and its value for the outer lines of 0.43 mm/sec for the first four runs is nearly that to be expected when considering broadening due to the thickness of the source and absorber.¹⁶ After the blowout which greatly distorted the iron foil, the linewidth for these outer lines was 0.56 mm/sec for the final two runs, but was again independent of pressure. The intensity ratios for lines 1:3 also decreased in the final two runs, indicating more absorption in the source after this distortion.



FIG. 3. Ratio of line intensities of line 2 to line 1 versus pressure. \Box , \bigcirc , \triangle , and \bigtriangledown correspond to runs 1, 2, 3, and 4 respectively. Run 1 was on the 5-mCi source and the others in the 27-mCi source before it was mechanically distorted by a high-pressure blowout.

Some of the spectra from run 3 are shown in Fig. 2. The figure clearly shows a variation of relative line intensities with pressure, indicating a changing polarization. This same effect was observed in every run; thus the line intensities were computed and the results graphed in Fig. 3. The general trend appears quite reproducible.

The effect of pressure on the effective magnetic field at the nucleus is graphed in Fig. 4. The data have been normalized to unity at atmospheric pressure. Results of Pipkorn *et al.*⁶ are also shown in this graph and the NMR measurements of Litster and Benedek⁵ are represented by the solid line. The dashed line is an extrapolation of their data above 65 kbar. Our results tend to curve slightly and are best represented by a leastsquares fit to the parabola

$$\Delta H/H_0 = (-1.34 \pm 0.25) \times 10^{-4} P - (0.60 \pm 0.39) \times 10^{-6} P^2, \quad (2)$$

with P in kbar.

The effect of pressure on the isomer shift is graphed in Fig. 5. Again the measurements by Pipkorn *et al.*⁶ are included for reference, with the dashed line repre-



FIG. 4. Fractional change in the effective magnetic field at the iron nucleus versus pressure. The solid point is a measurement of Pipkorn *et al.* (Ref. 6). The line follows the NMR results of Litster and Benedek (Ref. 5).

¹⁵ R. M. Housley, Nucl. Instr. Methods **35**, 77 (1965).

¹⁶ D. W. Hafemeister and E. B. Shera, Nucl. Instr. Methods 41, 133 (1966).

senting the interpolation of their results¹⁷; the solid line is a linear extrapolation of the results of Pound *et al.*³ In contrast to Pipkorn *et al.* we find the isomer shift varies linearly with pressure over the entire range, with a slope of $(-7.46\pm0.21) \times 10^{-5}$ cm sec⁻¹ kbar⁻¹.

A quadrupole splitting was observed at high pressure, which increased slightly with pressure according to

$$\partial E_Q / \partial P = (0.96 \pm 0.23) \times 10^{-5} \text{ cm sec}^{-1} \text{ kbar}^{-1}.$$
 (3)

Nicol and Jura⁴ indicate a possible increase in the quadrupole shift at the highest pressure and this result is not inconsistent with Pipkorn *et al.*,⁶ who state that the quadrupole splitting was less than 7×10^{-4} cm/sec. These measurements are shown in Fig. 6.

The ratio of the splittings of the nuclear levels was determined to be independent of pressure to within



FIG. 5. Isomer shift of iron versus pressure. The solid points are from measurements of Pipkorn *et al.* (Ref. 6). The solid line is an extrapolation of the 3-kbar measurements of Pound, Benedek, and Drever (Ref. 3) and the dashed line is the fit to Pipkorn's measurements given by Ingals *et al.* (Ref. 17).

experimental accuracy. The average value from these experiments is $g_1/g_0=0.5714\pm0.0011$. This is in excellent agreement with the average value of 0.5717 ± 0.0013 reported by Preston, Hanna, and Heberle¹³ over the temperature range from 4 to 913°K at atmospheric pressure and the value of 0.5707 ± 0.0005 reported by Perlow *et al.*¹⁸

Figure 7 shows the results for the pressure dependence of the relative absorption areas under the curve after correcting for background. This data is not corrected for resonance absorption in the source and the gasket material. The agreement in results from the several runs, when considering the different methods of making the background correction as well as the large differences in the magnitude of the correction, indi-



FIG. 6. Quadrupole splitting versus pressure for iron.

cates that the background can be successfully determined. With the source at atmospheric pressure (but still in the press), 12 to 33% of the radiation at the 14-keV line was background in the different runs. At 80 kbar 26 to 50% of the radiation was background. The error bars on the data in Fig. 7 include statistical errors in the measurement and the estimated error from the uncertainties in the background correction. A leastsquares linear fit to the experimental data gives the result $\partial (A/A_0)/\partial P = 0.0017$ kbar⁻¹.

V. DISCUSSION AND SUMMARY

This method is capable of giving Mössbauer patterns at high pressure with as much precision as at atmospheric pressure. The large volume allows one to design the system so as to reduce scattered radiation from the tungsten carbide anvils,¹⁹ and the background from higher-energy radiation, scattered into the 14-keV gate, can be made small enough and can be measured with enough precision to allow a meaningful measurement



FIG. 7. Relative absorption areas of iron versus pressure. The \bigtriangledown were measured in the last run and show more scatter than in the earlier runs, possibly from distortion of the source because of the blowout in an earlier run.

¹⁹ R. Ingals, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum Press, Inc., New York, 1965), Vol. 1, p. 185.

 ¹⁷ R. Ingalls, H. G. Drickamer, and G. DePasquali, Phys. Rev.
155, 165 (1967).
¹⁸ G. J. Perlow, C. E. Johnson, and W. Marshall, Phys. Rev.

¹⁸ G. J. Perlow, C. E. Johnson, and W. Marshall, Phys. Rev. **140**, A875 (1965).

of absorption areas. Other pressure effects, previously unobserved, are also reported here.

No pressure broadening of the Mössbauer lines was observed, which is a strong indication that the applied pressure is nearly hydrostatic. The broader lines in the last two runs, after the blowout distorted the shape of the foil, also indicate that stresses due to pressure gradients, if such existed, could be expected to give some line broadening. The evidence is not conclusive in that it is possible to imagine a uniaxial stress pattern that would not broaden the lines, but it is hard to imagine that one would get this same stress pattern for different types of sample geometry and environment. We mention this because a uniaxial stress could cause polarization and a quadrupole splitting as observed at high pressure. However, the pressure at the sample in a large volume system, as used here, is much more likely to be nearly hydrostatic than in a thin wafer compressed between two anvils, as in the measurements of Pipkorn et al.⁶ These authors make no mention of observing any polarization effects with pressure, but such would probably have been obscured by the large angle subtended by their detector. Their linewidths are much larger than ours, but it is not evident whether that is due to pressure gradients or other sources of broadening.

Polarization and Quadrupole Splitting

We have not been able to satisfactorily explain the polarization effects and the pressure variation of the quadrupole splitting, but we give some possible causes. Both effects may arise from changes in the anisotropy and magnetostriction constants with pressure. The electric field gradients at a point of cubic symmetry should be zero to first order; however, the slight distortion of cubic symmetry due to magnetostriction and the fields of the unfilled d shells may give rise to small electric field gradients. An increase in the anisotropy energy with pressure would enhance the spin alignment along the easy axes. Also, a change in the magnetostriction constants would alter the magnetoelastic distortion and affect the electric field gradients. We note that there is an anisotropic change in the magnetostriction constants of iron with pressure.²⁰ There are, however, three mutually perpendicular easy axes for magnetization and for our argument one must become preferred over the others. This must be related to the domain structure in the iron foil, and for our specimen must be affected by the texture of the foil.

The polarization effects under pressure are probably related to a nonrandom distribution of crystallite orientations in a rolled metal foil. The rolling process in the production of the foil and the annealing in its preparation as a source produce many grains with the

Goss, or cube-on-edge, texture.²¹ X-ray analysis of the 27-mCi source revealed a large amount of such orientation, but we were unsuccessful in obtaining any quantitative estimate of the texture. It is difficult to make an unpolarized iron foil; and because of the relatively large demagnetization energy density of a foil, the magnetization will initially favor a direction in the plane of the foil. If pressure increases the anisotropy and magnetoelastic energy densities, then high pressures may cause the magnetic moments of the iron foil to favor the easy direction of magnetization at 45° with respect to the plane of the foil. If all the moments were at 45° with respect to the direction of the γ rays entering the detector, the line intensities as emitted would be in the ratio¹³ 3: $\frac{4}{3}$:1:1: $\frac{4}{3}$:3, making $I_2/I_1 = 4/9$, which is near the limiting ratio approached at high pressures as seen in Fig. 3. The problem of finding the magnetization direction which minimizes the energy is complicated by the presence of many easy directions of magnetization, i.e., along each (100) axis, and apparently has not been completely investigated. Another evidence favoring the above arguments as the source of the observed polarization, rather than pressure gradients, is the reversibility and repeatability of the effect. It has been observed with two different sources and repeated five times on the second source using two different sample geometries and different materials in contact with the source. The ratio I_2/I_1 does not decrease as rapidly with pressure in the final two runs after distorting the foil with a blowout. This might be due to an alteration in the texture of the foil caused by the blowout.

Isomer Shift and Zeeman Splitting

The isomer shift is linear with pressure within the accuracy of the measurement and agrees with a linear extension of the measurements of Pound *et al.*,³ but with a slightly less negative slope. In a recent article by Ingalls *et al.*¹⁷ the isomer-shift pressure data of Pipkorn *et al.*⁶ for iron is shown to curve with pressure. If we consider curvature in our results we obtain for the initial slope, in units of 10^{-5} cm sec⁻¹ kbar⁻¹, -7.9 ± 0.8 compared to -8.3 for the Illinois group, and at 50 kbar -7.2 ± 0.6 compared to -6.4.

In both the isomer shift with pressure and the change of internal magnetic fields with pressure, we observe a different curvature than Pipkorn *et al.*⁶ This difference is partly due to the difference in pressure calibrations; they used 87 kbar and we used 78 kbar as the pressure at the Bi III-V transition in a solid medium. Most of the difference, however, is due to the fact that they made only one measurement below 100 kbar with the sample in the pure α phase while in their next higher pressure run the sample was in a mixed α and ϵ phase. Flat anvil devices have large pressure variations over

²⁰ J. J. M. Franse, R. Winkel, R. J. Veen, and G. deVries, Physica **33**, 475 (1967).

²¹ R. H. Pry, J. Appl. Phys. 30, 189S (1959).

the pressure cell, and in such a mixture the α -phase material will be at the lowest pressure regions of the source. Extrapolations of both our measurements of internal fields and isomer shifts to high pressure indicate that the α -iron in the higher pressure point of Pipkorn et al. was below 120 kbar rather than 145 kbar. Because of the large number of measurements this work gives a more reliable variation of H and E_s with pressure over the range of pressures measured.

Lamb-Mössbauer Factor

Hanks²² and Mahesh²³ have calculated the pressure dependence of f in the range $T \ll \Theta$. This range is not appropriate for this work, but it is a simple matter to extend the theory to higher temperatures. We take

$$f = \exp\left\{-\frac{6R}{k\Theta}\left[\frac{1}{4} + (T/\Theta)^2 \int_0^{\Theta/T} \frac{xdx}{e^x - 1}\right]\right\},\qquad(4)$$

where R is the recoil energy and Θ a characteristic temperature.

Letting $T = 300^{\circ}$ K; $\Theta = \Theta_0 (V/V_0)^{-\gamma}$, where $\Theta_0 =$ 400°K and the Grüneisen constant $\gamma = 1.6$ (Ref. 24); and using recent measurements of volume versus pressure^{25–27} for iron, one can calculate Θ versus pressure, and from (4) a theoretical value for f versus pressure. This calculation neglects any volume dependence of γ . At room temperature the calculation indicates that θ should increase from 400°K at zero pressure to 430°K at 80 kbar and that the initial slope should be $\partial f/\partial P = 0.38 \times 10^{-3}$ kbar⁻¹. Assuming the absorption areas to be proportional to f_s [Eq. (1)] and then correcting for self-absorption in the source²⁸ and in the pressure-transmitting medium, we arrive at an f factor which increases with pressure more than twice as rapidly as the theoretical estimate. This discrepancy is probably due to the polarization of the iron with pressure. The proportionality of f_s with area in Eq. (1), which was derived¹³ for the case of unpolarized γ rays, may not be valid for partially polarized radiation, particularly if the f factor is dependent upon polarization. The correction for self-absorption in the source is also a function of polarization. As discussed by Hanna and Preston,²⁹ the absorption integrals are altered for a polarized absorber and this is also true for partially polarized resonantly absorbing nuclei in the source. Nussbaum and Housley³⁰ claim a polarized absorber has less opacity than an unpolarized absorber. It was not possible, however, to determine exactly the distribution of the magnetic moments in the source nor has a theory for resonant absorption of partially polarized radiation been completely worked out. Thus in the calculation mentioned above²⁸ we attempted to include polarization effects by calculating emission probabilities using an iterative technique which would yield the experimental line intensities when considering self-absorption in the source. There is some evidence that the *f* factor of iron is a function of polarization. This can be inferred from the fact that Hanna and Preston found a great deal of scatter in measuring $f\sigma_0$ for nonpolarized iron foils because of the difficulty in completely depolarizing the foils,13,29 while this scatter was not present in their measurements on completely polarized iron foils. Because of the problems involved and the fact that it was not possible to completely polarize the foils in our experiment, the variation of f with pressure cannot as yet be measured with certainty for iron.

ACKNOWLEDGMENTS

We are grateful to the Argonne National Laboratory for supplying a copy of the computer program and to H. T. Hall for the use of a high-pressure press.

 ²² R. V. Hanks, Phys. Rev. **124**, 1319 (1961).
²³ K. Mahesh, Indian J. Pure Appl. Phys. **4**, 480 (1966).
²⁴ C. Kittel, *Introduction to Solid State Physics* (John Wiley &

Sons, Inc., New York, 1956), p. 155. ²⁵ C. A. Rotter and C. S. Smith, J. Phys. Chem. Solids **27**, 267 (1966).

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