Effect of Pressure on Crystal Structure and Lattice Parameters of Iron up to 300 kbar

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Lattice parameters of the bcc and hcp phases of iron have been determined as a function of pressure up to 300 kbar at 23°±5°C by means of x-ray diffraction techniques. The c/a ratio for hcp iron has been determined to be 1.603±0.001 at pressures between 80 and 300 kbar and is independent of pressure. Based upon the extrapolation of the high-pressure data using an exponential form of the Murnaghan equation of state, the volume of hcp iron at zero pressure is 6.72±0.06 cm³/mole. The volume change for the bcc–hcp transformation at 130 kbar is —0.34±0.01 cm³/mole. This value satisfies the triple point conditions for the bcc–hcp–fcc triple point when published values for the other phase transformations are used.

I. INTRODUCTION

Since the discovery of a high-pressure phase of iron at 130 kbar with shock wave techniques by Bancroft et al., a various properties of iron have been investigated as a function of pressure. For example, the effect of pressures of several hundred kilobars on the crystal structure, lattice parameters, and molar volume were investigated by Clendenen and Drickamer, b and by Takahashi and Bassett. c Electrical resistivity and phase relations were studied by Bundy d up to 900°C and 200 kbar employing static techniques. Pressure and volume relations were investigated by Bancroft et al., e Johnson et al., f and McQueen et al. g using shock wave technique up to several thousand kilobars. Below 130 kbar, iron has a bcc structure (α), and above that pressure, it has a hcp structure (ε). h

In the present study, the effect of pressure on iron was investigated by means of a high-pressure x-ray diffraction camera capable of producing high resolution patterns. The crystallographic relationship between the bcc and hcp phases has been clarified. It has been possible to further refine the measurements of the lattice parameters and volume as a function of pressure.

II. EXPERIMENTAL METHODS

A high-pressure x-ray diffraction camera using diamond anvils driven by a piston and screw assembly was employed in the present investigation. h The anvils are ½-carat, brilliant-cut, gem-quality diamonds with enlarged culet faces which serve as anvil faces. When a polycrystalline sample is compressed between the anvil faces, a maximum pressure is produced at the center of the sample area. A finely collimated beam of radiation passes through one of the anvils and impinges upon the central portion of the sample area where the maximum pressure and minimum pressure gradient exist. h Diffracted rays pass out through the other anvil to a curved film having a radius of 50 mm and a 2θ arc of 45°.

Samples were prepared by mixing powdered iron h with sodium chloride. A small x-ray beam directed at the center of the sample area produces high resolution photographs (Fig. 1) from which lattice parameters of the sodium chloride and iron can be calculated with a standard deviation of ±0.1%. From the lattice parameter of sodium chloride and the data of Decker, i the pressure exerted on the sample is determined. Based on the assumption that the accuracy for the equation of state is comparable with that of the lattice parameter measurements, the calculated pressure has an accuracy of ±2%. The experimental data are listed in Table 1.

III. EFFECT OF PRESSURE ON LATTICE PARAMETERS

The empirical equations expressing the pressure dependence of the lattice parameters of the bcc and hcp phases of iron at 23°±3°C are:

for the bcc phase of iron,

\[ a(\text{bcc}) = 2.866(1+P/275)^{-0.66}, \]

dependent on the pressure in kilobars, and \( a(\text{bcc}), a(\text{hcp}) \), and \( c \) are lattice parameters in angstroms.

The \( c/a \) ratio for hcp iron obtained in the present work is independent of pressure, and has an average value of 1.603±0.001. Clendenen and Drickamer, b on the other hand, reported that the \( c/a \) ratio at ambient room temperature decreases from 1.645 to 1.580 with increasing pressure from 150 to 400 kbar (Fig. 2). Because there is not enough information in their article

\[ c/a = 1.603±0.001, \]

CRYSTAL STRUCTURE OF IRON TO 300 KBAR

Table I. Experimental data of the pressure effect on the lattice parameters and the molar volume of iron at 23°±3°C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>a (NaCl) (Å)</th>
<th>P (kbar)</th>
<th>a (bcc) (Å)</th>
<th>a (hcp) (Å)</th>
<th>c (hcp) (Å)</th>
<th>c/a</th>
<th>V (bcc) (cm³/mole)</th>
<th>V (hcp) (cm³/mole)</th>
<th>ΔV (cm³/mole)</th>
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</thead>
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<tr>
<td>3LD 47p</td>
<td>5.365</td>
<td>34.5</td>
<td>2.839</td>
<td>2.487</td>
<td>3.995</td>
<td>1.607</td>
<td>6.79</td>
<td>6.44</td>
<td>-0.35</td>
</tr>
<tr>
<td>3LD 56f</td>
<td>5.193</td>
<td>103</td>
<td>2.802</td>
<td>2.469</td>
<td>3.958</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.33</td>
</tr>
<tr>
<td>3LD 49f</td>
<td>5.146</td>
<td>122</td>
<td>2.802</td>
<td>2.469</td>
<td>3.958</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.33</td>
</tr>
<tr>
<td>3LD 50f</td>
<td>5.128</td>
<td>131</td>
<td>2.802</td>
<td>2.469</td>
<td>3.958</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.33</td>
</tr>
<tr>
<td>3LD 51f</td>
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<td>145</td>
<td>2.796</td>
<td>2.461</td>
<td>3.952</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 52f</td>
<td>5.023</td>
<td>183</td>
<td>2.793</td>
<td>2.453</td>
<td>3.932</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 53f</td>
<td>5.008</td>
<td>202</td>
<td>2.783</td>
<td>2.453</td>
<td>3.929</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 54f</td>
<td>4.975</td>
<td>223</td>
<td>2.776</td>
<td>2.443</td>
<td>3.922</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 55f</td>
<td>4.974</td>
<td>221</td>
<td>2.774</td>
<td>2.442</td>
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<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 56f</td>
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<td>228</td>
<td>2.771</td>
<td>2.441</td>
<td>3.918</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 57f</td>
<td>4.968</td>
<td>228</td>
<td>2.771</td>
<td>2.441</td>
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<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
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<tr>
<td>3LD 58f</td>
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<td>230</td>
<td>2.769</td>
<td>2.438</td>
<td>3.914</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 59f</td>
<td>4.962</td>
<td>232</td>
<td>2.767</td>
<td>2.437</td>
<td>3.914</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
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<td>3LD 60f</td>
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<td>2.758</td>
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<td>6.65</td>
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<td>3LD 61f</td>
<td>4.938</td>
<td>249</td>
<td>2.757</td>
<td>2.435</td>
<td>3.904</td>
<td>1.602</td>
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<td>6.32</td>
<td>-0.34</td>
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<td>3LD 62f</td>
<td>4.936</td>
<td>250</td>
<td>2.756</td>
<td>2.435</td>
<td>3.904</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 63f</td>
<td>4.921</td>
<td>252</td>
<td>2.754</td>
<td>2.435</td>
<td>3.904</td>
<td>1.602</td>
<td>6.65</td>
<td>6.32</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 64f</td>
<td>4.903</td>
<td>276</td>
<td>2.746</td>
<td>2.429</td>
<td>3.895</td>
<td>1.602</td>
<td>6.65</td>
<td>5.99</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 65f</td>
<td>4.875</td>
<td>300</td>
<td>2.738</td>
<td>2.429</td>
<td>3.883</td>
<td>1.602</td>
<td>6.65</td>
<td>5.97</td>
<td>-0.34</td>
</tr>
<tr>
<td>3LD 66f</td>
<td>4.844</td>
<td>309</td>
<td>2.731</td>
<td>2.416</td>
<td>3.870</td>
<td>1.602</td>
<td>6.65</td>
<td>5.89</td>
<td>-0.34</td>
</tr>
</tbody>
</table>

* Letter p after the run numbers indicates powder sample, and f indicates foil sample.

regarding the calculation of the c/a ratio, differences between the present data and the present data cannot be explained.

IV. CRYSTALLOGRAPHY OF THE PHASE TRANSFORMATION

According to the rigid-sphere model, the hcp structure can be derived from the bcc structure by a shortening of the interatomic distances along the [001] direction of the bcc structure and by a gliding of the (110) atomic planes in the [100] or [110] directions (Fig. 3). This ideal relationship between the two structures is indicated in Table II.

Table II. Comparison between crystallographic and volume relationships for the bcc–hcp phase transformations in the rigid-sphere model and those experimentally obtained for iron. r(bcc) represents nearest-neighbor interatomic distance in bcc iron.

<table>
<thead>
<tr>
<th>Rigid-sphere model</th>
<th>Experimental value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial ratio, c/a</td>
<td>1.633</td>
</tr>
<tr>
<td>Volume difference, [V(bcc) - V(hcp)]/V(bcc)</td>
<td>8.15%</td>
</tr>
<tr>
<td>d-spacing difference, [d(110) of bcc] - [d(002) of hcp]</td>
<td>0.00</td>
</tr>
<tr>
<td>Interatomic distance in (002) plane of hcp</td>
<td>1.000Xr(bcc)</td>
</tr>
<tr>
<td>Interatomic distance between (002) layers of hcp</td>
<td>1.000Xr(bcc)</td>
</tr>
</tbody>
</table>

Diffraction patterns of coexisting bcc and hcp phases have been obtained on a single photograph. With the present instrument which possesses a maximum d-value resolution of 0.05%, it was impossible to resolve the (110) line of bcc from the (002) line of hcp. Thus as predicted for the ideal rigid-sphere model, the d values for these planes are the same within experimental uncertainty. However, iron fails to satisfy

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Fig. 1. X-ray diffraction patterns of (a) bcc iron mixed with sodium chloride, and (b) hcp iron mixed with sodium chloride. For the calculation of the lattice parameters for bcc iron and sodium chloride, three diffraction lines of each were used; for hcp iron, six were used.
other features of ideal rigid-sphere packing (Table II). The \( c/a \) ratio of hcp iron is less than that for ideal packing, and the interatomic distances in hcp iron are larger than those in the bcc iron. Thus, in this phase transformation, as in others, the increase in coordination number is accompanied by an increase in interatomic distance. The increase in interatomic distance and the low \( c/a \) ratio together can account for \( d(110) \) of bcc being equal to \( d(002) \) of hcp.

V. EFFECT OF PRESSURE ON MOLAR VOLUME

The molar volumes of bcc and hcp phases of iron calculated from lattice parameters are plotted as a function of pressure in Fig. 4. For purposes of comparison, the shock Hugoniot volume data of Loree et al.\textsuperscript{10} are also shown in this figure. The present isothermal data are consistent with their data, when the effects of thermal expansion and mixture of phases are taken into consideration at pressures above the bcc–hcp transformation.

An exponential form of the Murnaghan equation has been used to express the experimental data:

\[
V_P(\text{bcc}) = V_0(\text{bcc}) (1 + P/275)^{-0.169},
\]

\[
V_0(\text{bcc}) = 7.093 \text{ cm}^3/\text{mole};
\]

and

\[
V_P(\text{hcp}) = V_0(\text{hcp}) (1 + P/325)^{-0.196},
\]

\[
V_0(\text{hcp}) = 6.72 \pm 0.06 \text{ cm}^3/\text{mole},
\]

where \( V_0(\text{bcc}) \) and \( V_0(\text{hcp}) \) are, respectively, the molar volume of bcc and hcp iron at zero pressure, and \( P \) is the pressure in kilobars. Since the high-pressure phase cannot be quenched to \( P = 0 \), no direct determination of \( V_0(\text{hcp}) \) is possible. Extrapolation of the high-pressure data to \( P = 0 \) yields a value of \( 6.72 \pm 0.06 \text{ cm}^3/\text{mole} \).

The volume change associated with the bcc–hcp phase transformation at 130 kbar has been determined from x-ray diffraction photographs of samples in which bcc and hcp coexist. In order to obtain such photographs, iron foil,\textsuperscript{11} which permits visual observation of

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\textsuperscript{11} Supplied by Dr. Francis P. Bundy of the General Electric Research Laboratory. This is the same material used for his electrical resistivity measurements.
the phases (Fig. 5), was used. The pressure on the sample was adjusted so that both the bcc and hcp phases coexisted within the x-ray beam. Four determinations gave an average value of $-0.34 \pm 0.01$ cm$^3$/mole. This value is higher than any previously reported, which ranged from $-0.15$ to $-0.25$ cm$^3$/mole.

X-ray determinations of the volume of iron under static pressure conditions at room temperature by Clendenen and Drickamer$^2$ yielded a value of $-0.15$ cm$^3$/mole for the volume change at 130 kbar. Their volume data for bcc iron agree well with the shock data$^6,10$ and the results of the present work, whereas their data for hcp iron are consistently higher than those obtained by the shock experiments in the pressure range measured (Fig. 4). However, values obtained under shock conditions should be higher than those obtained under static conditions at room temperature because of adiabatic heating of the sample. Therefore, the hcp iron data of Clendenen and Drickamer appear to be too high and thus result in a volume change that seems to be too low.

The volume change of $-0.20$ cm$^3$/mole reported by Takahashi and Bassett$^3$ was obtained with an x-ray camera which lacked the precision of the camera used in the present investigation. Thus, the value reported in this paper should be considered superior to their value.

The volume change determinations based on shock data are probably less accurate than those based on static measurements because the volume data just above the transformation pressure (130–200 kbar) obtained by shock experiments (Fig. 4) represent a mixture of bcc and hcp phases.

VI. ISOThERMAL COMPRESSIBILITY

On the basis of ultrasonic measurements at room temperature, Voronov and Vereshchagin$^2$ obtained for the isothermal compressibility of bcc iron at zero pressure, $\beta_0 = 6.098 \times 10^{-4}$ kbar$^{-1}$ and its pressure derivative, $(\partial \beta / \partial P)_{P=0} = -1.88 \times 10^{-6}$ kbar$^{-2}$. By means of similar ultrasonic measurements up to 3.6 kbar at room temperature, Rotter and Smith$^13$ determined for bcc iron single crystals $\beta_0 = 6.098 \times 10^{-4}$ kbar$^{-1}$ and $(\partial \beta / \partial P)_{P=0} = -2.11 \times 10^{-6}$ kbar$^{-2}$. Their value for $\beta_0$ is in excellent agreement with that of Voronov and Vereshchagin. On the other hand, Bridgman$^14$ obtained the values of $5.94 \times 10^{-4}$ kbar$^{-1}$ and $-1.3 \times 10^{-4}$ kbar$^{-2}$ for $\beta_0$ and $(\partial \beta / \partial P)_{P=0}$ respectively. Since the ultrasonic method is a more reliable means of determining compressibility, Bridgman’s data are probably in error by a few percent.

The present investigation yields $\beta_0 = (6.4 \pm 0.8) \times 10^{-4}$ kbar$^{-1}$ and $-(\partial \beta / \partial P)_{P=0} = +2.3(-2.7, -1.6) \times 10^{-6}$ kbar$^{-2}$. When the ultrasonic $\beta_0$ value, $6.098 \times 10^{-4}$ kbar$^{-1}$, is accepted, a value of $+(1.6 \pm 0.4) \times 10^{-4}$ kbar$^{-2}$ can be obtained for $-(\partial \beta / \partial P)_{P=0}$. Although the compressibility and its pressure derivative obtained from the results of the present study exhibit relatively large uncertainties because of the nature of the experiments employed, the values of $\beta_0$ and $(\partial \beta / \partial P)_{P=0}$ calculated from the present data are entirely consistent with those obtained by the ultrasonic methods.

For hcp iron, the data of this work yield $\beta_0 = (6.0 \pm 1.3) \times 10^{-4}$ kbar$^{-1}$ and $(\partial \beta / \partial P)_{P=0} = +1.9(+2.1, -1.1) \times 10^{-6}$ kbar$^{-2}$. The values for hcp iron are indistinguishable from those for bcc iron within the experimental uncertainties.

VII. DISCUSSION

Error in determination of lattice parameters can be attributed to the following sources: (1) reading error, (2) change in film dimensions, (3) change in sample-to-film distance, and (4) change in x-ray wavelength due to change in monochromator orientation.

Direct determination of reading error (1) can be made by comparing repeated readings of the same line. The standard deviation found this way is 0.03%.

The lattice parameters and $c/a$ ratio in hcp iron when calculated from lines within a single photograph have a standard deviation of 0.1%. Sources (2), (3), and (4), which apply to variation from photograph to photograph,


graph, cannot be evaluated independently but together influence the scatter for the lattice parameters as a function of pressure. The standard deviations for the lattice parameter and volume data are 0.15% and 0.3%, respectively. The \( c/a \) ratio, however, is not influenced by sources (2), (3), and (4). Therefore, the standard deviation for \( c/a \) determinations as a function of pressure remains at 0.1%.

Bundy compiled published values for the change in molar volume of iron between bcc and hcp, hcp and fcc, and fcc and bcc phases. He found that no combination of those values met the thermodynamic requirements at the triple point:

\[
\sum \Delta V = 0,
\]

\[
\sum \Delta S = \sum \Delta V (dP/dT) = 0.
\]

He attempted to resolve the inconsistency by distributing the error among the volume data around the triple point. However, the volume change between bcc and hcp iron reported in this paper obviates such an adjustment. The following values now seem to be the most reliable and to satisfy the triple point conditions:

\[
\Delta V(\text{bcc-hcp}) = -0.34 \text{ cm}^3/\text{mole},
\]

\[
\Delta V(\text{hcp-fcc}) = +0.13 \text{ cm}^3/\text{mole},^15
\]

and

\[
\Delta V(\text{fcc-bcc}) = +0.21 \text{ cm}^3/\text{mole}.^15,^16
\]

**ACKNOWLEDGMENTS**

The authors wish to thank Francis P. Bundy of the General Electric Company for providing a sample of pure iron foil which was used in his resistivity experiments, and Larry Kaufman of ManLabs Inc. for critical reading of manuscript. J. Dean Barnett and Daniel L. Decker of the Brigham Young University kindly provided tabulated data of lattice parameter versus pressure for sodium chloride. This research program was supported by a National Science Foundation grant.