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Effect of Pressure on the Isomer Shift of Fe^{57} in the bcc Phase*

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The effect of pressure to 130 kbar has been measured on the isomer shift of bcc iron, using the inner two lines of the magnetically split six-line iron spectrum. The isomer shift is nearly linear in pressure to about 60 kbar; at higher pressures the rate of shift to higher electron density is less. The data are not linear with volume in the higher-pressure region either. The results are interpreted in terms of Ingalls's discussion of the transfer of electrons from the 4*s* to the 3*d* bands and the value of the proportionality constant between the isomer shift and the square of the wave function. The change in magnetic field with pressure is discussed very briefly.

INTRODUCTION

THE Mössbauer spectrum of Fe^{57} has been measured as a function of pressure in the bcc phase and through the transition at 130 kbar to the hcp phase. Previous studies include measurements by Pound *et al.*[1] to 3 kbar, the pioneering exploratory high-pressure measurements of Nicol and Jura[2] to the 130-kbar transition, and the studies of Pipkorn *et al.*[3] to several hundred kbar. These last measurements included only three points in the bcc phase, concentrating on the transition and the high-pressure phase. All of the above studies were run at relatively high amplitudes of velocity (e.g., $V_{\max}=\pm 7$–8 mm/sec) to take in the entire six-line spectrum.

The work presented here differs in several ways. The work is concentrated on the low-pressure (bcc) phase and the initial transition region. Bridgman anvils were used to ensure more accurate calibration in the low-pressure region. Relatively low amplitudes of velocity were used such that only the two inner lines of the magnetically split iron spectrum were obtained. This gave maximum accuracy in determining the change in isomer shift with pressure, which is the main point of this paper. The techniques were otherwise as previously described.[4] The appearance of the paramagnetic peak at the 130-kbar transition gave an internal check on the calibration by x-ray diffraction studies on various markers, as discussed in Ref. 4. The preparation of samples was the same as in Ref. 3.

THEORY

The energy shift of the nuclear levels due to the finite size of the nucleus can be written[5,6]

$$\Delta\epsilon=\alpha\,|\,\psi(0)\,|^2, \tag{1}$$

where $|\,\psi(0)\,|^2$ is the total *s* electron density at the nucleus and α is a scaling parameter containing electronic and nuclear parameters. Experimentally, it is the difference in $\Delta\epsilon$ between materials that is measured, and comparison between isomer shifts must always be made with respect to a common material.

As shown by Walker *et al.*[7] a determination of α can be made by comparing the isomer shifts of ferric and ferrous salts and the ionic wave functions computed by Watson.[8] Experimentally,

$$\Delta\epsilon(Fe^{2+})-\Delta\epsilon(Fe^{3+})\simeq 0.90 \text{ mm/sec}. \tag{2}$$

Using the free-ion wave functions of Watson,[8] who obtained

$$|\,\Psi_{2+}(0)\,|^2-|\,\Psi_{3+}(0)\,|^2\simeq -1.9a_0^{-3}, \tag{3}$$

gives

$$\alpha\simeq -0.47a_0^3 \text{ mm/sec}. \tag{4}$$

This procedure has been criticized by Simanek and Sroubek,[9] who argue that the large increases in $|\,\psi(0)\,|^2$ on going from the ferrous to the ferric salts can be explained by an increase in the amount of 4*s* bonding and that overlap distortion is a more important contribution to $|\,\psi(0)\,|^2$ than is the 3*d* shielding that gives Watson's result for free ions.

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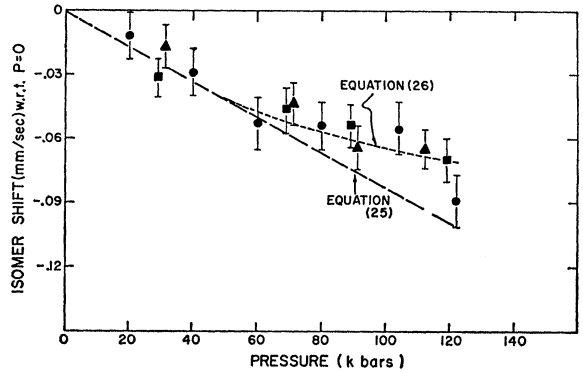

FIG. 1. Isomer shift versus pressure, Fe^{57} (with respect to zero pressure).

Since this treatment has not been applied to metallic iron, we shall use the value of α in Eq. (4) to get an approximate idea of the electronic configuration of iron. Various investigators (e.g., De Benedetti *et al.*[10]) have found

$$\Delta\epsilon(\mathrm{Fe}^{2+})-\Delta\epsilon(\mathrm{Fe}_{\mathrm{metal}})\simeq 1.3\ \mathrm{mm/sec}, \tag{5}$$

which, using Eq. (4), gives

$$|\Psi_{\mathrm{Fe}_{\mathrm{metal}}}(0)|^2-|\Psi_{\mathrm{Fe}^{2+}}(0)|^2\simeq 2.7a_0^{-3}. \tag{6}$$

This value of $\Delta|\psi(0)|^2$ indicates that metallic iron has a $3d^74s$ configuration. This can be shown in two ways. First, De Benedetti *et al.*[10] have found that the experimental isomer shift for metallic iron lies midway between the theoretical values derived for the $3d^64s^2$ and $3d^8$ configurations. Second, Walker *et al.*[7] have used the Fermi-Segré-Goudsmit[11,12] (FSG) formalism to obtain a plot of $\Delta\epsilon$ versus the amount of s-electron character in various $3d^n$ configurations. The experimental isomer shift of iron gives agreement with the $3d^74s^x$ line on this plot at $x=1.0$. Considering the effect of pressure (or volume), the change in $\Delta\epsilon$ can be written

$$d(\Delta\epsilon)=d(\Delta\epsilon)_L+d(\Delta\epsilon)_B, \tag{7}$$

$d(\Delta\epsilon)_L$ representing simple volume scaling where $|\psi(0)|^2$ increases because of compression of the s-electron wave functions without change of shape, while $d(\Delta\epsilon)_B$ represents the transfer of electrons into or out of the s-like states in the s-d conduction band.

A value of $d(\Delta\epsilon)_L$ can be obtained quite simply from the calculations of Walker *et al.*[7] Addition of a $4s$ electron to the $3d^7$ configuration at constant volume decreases the isomer shift by 1.4 mm/sec. Reversing the argument, holding $3d^74s$ constant, and changing the volume gives

$$d(\Delta\epsilon)_L/d(\ln V)=1.4\ \mathrm{mm/sec}. \tag{8}$$

Explicit expressions for $d(\Delta\epsilon)_L$ and $d(\Delta\epsilon)_B$ due to Ingalls[13] are discussed below, and any parameters quoted without reference may be found in that paper. In outline, his treatment is as follows.

Since we are interested in the pressure dependence of $|\psi(0)|^2$, only the $4s$- and $3s$-electron contributions are considered. The $4s$ electrons are affected in a direct way since they are itinerant and thus can be expected to scale with volume. The $1s$, $2s$, and $3s$ electrons are not directly affected by small volume changes, but the $3s$ electrons are indirectly affected by the changes in $3d$-electron wave functions.

The $4s$ contribution can be written

$$|\Psi_{4s}(0)|^2=\int^{E_F}N_s(E)\,|\Psi_s(0,E)|^2dE, \tag{9}$$

where $N_s(E)$ is the number of s states in the $3d$–$4s$ conduction band. Ingalls performed a modified tight-binding calculation of the $4s$ wave functions at Γ_1 ($\mathbf{k}\equiv 0$) for several volumes and found

$$|\Psi_{\Gamma_1}(0)|^2=7.1a_0^{-3}\quad\text{for}\quad V=80a_0^{+3} \tag{10}$$

and

$$|\Psi_{\Gamma_1}(0)|^2=\mathrm{const}\times V^{-\gamma}, \tag{11}$$

where $\gamma\simeq 1.25$. With the assumption that $|\psi_s(0,E)|^2=|\psi_{\Gamma_1}(0)|^2$, the decrease in the s-like nature of the conduction band being completely represented by the decrease in $N_s(E)$ as $\mathbf{k}$ increases, Ingalls obtained

$$|\Psi_{4s}(0)|^2=n_s\,|\Psi_{\Gamma_1}(0)|^2, \tag{12}$$

where $n_s=0.53$ is the number of s electrons per iron atom.

The $3s$ contribution is approximated by using the proportionality found by Watson[8] and Clementi[14] between the density of $3s$ electrons at the nucleus and $\langle nu_m{}^2\rangle$:

$$|\Psi_{3s}(0)|^2=\beta\langle nu_m{}^2\rangle, \tag{13}$$

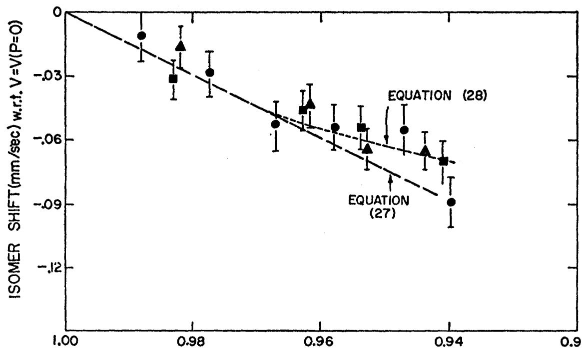

FIG. 2. Isomer shift versus V/V_0, Fe^{57} (with respect to volume at $P=0$).

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where u_m is the maximum of the radial wave function in the wave function

$$\Psi_d(\mathbf{r})=Y_{lm}(\theta,\phi)[u(r)]/r, \tag{14}$$

and

$$\langle nu_m^2\rangle=\int^{E_F} N_d(E)u_m^2(E)dE, \tag{15}$$

with $\beta=-5.5a_0^{-2}$. The integral in Eq. (15) is performed up to the respective Fermi energy in each half of the band (spin up and spin down), using the linear relationship between $u_m^2(E)$ and E discussed by Ingalls.

Thus, for the 3*s* and 4*s* contributions we have

$$|\Psi(0)|^2=n_s|\Psi_{\Gamma_1}(0)|^2+\beta\langle nu_m^2\rangle. \tag{16}$$

Taking the volume derivative of Eq. (15) gives

$$\frac{d|\Psi(0)|^2}{d(\ln V)}=-n_s\gamma|\Psi_{\Gamma_1}(0)|^2+\beta\frac{\partial\langle nu_m^2\rangle}{\partial(\ln V)} +|\Psi_{\Gamma_1}(0)|^2\frac{\partial n_s}{\partial(\ln V)}+\beta\frac{\partial\langle nu_m^2\rangle}{\partial n_d}\frac{\partial n_d}{\partial(\ln V)}. \tag{17}$$

Here we see the expressions for $d(\Delta\epsilon)_L$, due to volume scaling, and $d(\Delta\epsilon)_B$, due to $s\leftrightarrow d$ electron transfer, mentioned in the Introduction:

$$\frac{d(\Delta\epsilon)_L}{d(\ln V)}=\alpha\left(-n_s\gamma|\Psi_{\Gamma_1}(0)|^2+\beta\frac{\partial\langle nu_m^2\rangle}{\partial(\ln V)}\right), \tag{18}$$

$$\frac{d(\Delta\epsilon)_B}{d(\ln V)}=\alpha\left(|\Psi_{\Gamma_1}(0)|^2\frac{\partial n_s}{\partial(\ln V)}+\beta\frac{\partial\langle nu_m^2\rangle}{\partial n_d}\frac{\partial n_d}{\partial(\ln V)}\right). \tag{19}$$

Using the values of $|\psi_{\Gamma_1}(0)|^2$, n_s, γ, and β mentioned above and

$$\partial\langle nu_m^2\rangle/\partial(\ln V)=0.03a_0^{-1}, \tag{20}$$

$$\partial\langle nu_m^2\rangle/\partial n_d=0.9a_0^{-1}, \tag{21}$$

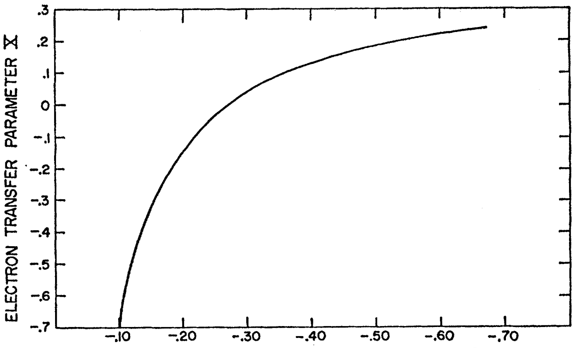

FIG. 3. α versus X.

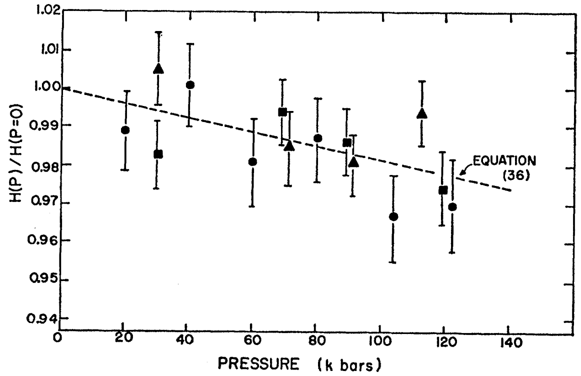

FIG. 4. H/H_0 versus pressure, Fe^{57}.

we obtain

$$d(\Delta\epsilon)_L/d(\ln V)=-4.86\alpha \text{ mm/sec}, \tag{22}$$

$$\frac{d(\Delta\epsilon)_B}{d(\ln V)}=\alpha\left(7.1\frac{\partial n_s}{\partial(\ln V)}-4.95\frac{\partial n_d}{\partial(\ln V)}\right)\text{ mm/sec}, \tag{23}$$

where $\alpha\equiv[a_0^3 \text{ mm/sec}]$.

Equation (22) can be viewed as an alternative to Eq. (8), which gave a rough value of $d(\Delta\epsilon)/d(\ln V)$ from volume scaling alone, and will be used instead of Eq. (8). To obtain agreement between these equations, we would need $\alpha=-0.35a_0^3$ mm/sec, which is significantly different from the value of $\alpha=-0.47a_0^3$ mm/sec found above. This is not important, since we shall treat α as a variable.

EXPERIMENTAL RESULTS

The experimental results for the isomer shift are plotted in Fig. 1 versus pressure and in Fig. 2 versus volume. *P–V* data for iron have been reported by Ho-Kwang Mao *et al.*,[15] who found

$$V_P/V_0=(1+P/275)^{-0.169} \tag{24}$$

for the bcc phase of iron.

It can be seen from Figs. 1 and 2 that for pressures above 60 kbar there exists a region where the change of the isomer shift with pressure becomes nonlinear, and it has been necessary to fit the data with a quadratic function in pressure and volume. Below 60 kbar there is no obvious departure from linearity.

Below 60 kbar a least-squares fit of the data to a linear dependence on pressure and volume gives

$$\Delta(\Delta\epsilon)=(-8.26\pm0.92)\times10^{-4}P \text{ mm/sec}, \tag{25}$$

where P is in kbar, and

$$\Delta(\Delta\epsilon)=(1.47\pm0.17)\Delta V/V \text{ mm/sec}. \tag{26}$$

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[15] H. K. Mao, W. A. Bassett, and T. Takahashi, J. Appl. Phys. **38**, 272 (1967).

The quadratic fit of all the data below the bcc→hcp transition at 130 kbar gives essentially the same results. Thus

$$\Delta(\Delta\epsilon)=(-8.10\pm1.10)\times10^{-4}P+(1.65\pm1.10)\times10^{-6}P^2\text{ mm/sec}\quad(27)$$

and

$$\Delta(\Delta\epsilon)=(1.38\pm0.22)\Delta V/V+(2.69\pm4.53)(\Delta V/V)^2\text{ mm/sec.}\quad(28)$$

These results are in excellent agreement with the results of Pound *et al.*[1] and Pipkorn *et al.*,[3] and there is no need to discuss the analysis of these two previous experiments separately.

Each pressure run with iron was self-calibrating; the calibration was made by obtaining the bcc→hcp transition at 130 kbar. The transition is sluggish, but a paramagnetic single peak is clearly present for pressures above 130 kbar.

From the three pressure runs we obtain

$$\Delta\epsilon\ (\text{hcp},\ P=146\text{ kbar})-\Delta\epsilon\ (\text{bcc},\ P=0)=-0.244\pm0.014\text{ mm/sec,}\quad(29)$$

which agrees with the value of about -0.25 mm/sec obtained by Pipkorn *et al.*[3]

DISCUSSION

If we assume that the number of electrons in the $3d$-$4s$ conduction band of iron is a constant, we can combine Eqs. (21) and (22) and get

$$d(\Delta\epsilon)/d(\ln V)=-4.86\alpha+12.05\alpha X,\quad(30)$$

where

$$X=\partial n_s/\partial(\ln V)=-\partial n_d/\partial(\ln V).\quad(31)$$

Equation (30), together with the experimental value of the change of the isomer shift with volume, gives a relation between the isomer-shift parameter α and the s-to-d electron transfer.

Experimentally, we have obtained

$$d(\Delta\epsilon)/d(\ln V)\,|_{V=V_0}=1.38\pm0.22\text{ mm/sec.}\quad(32)$$

The correction for the second-order Doppler shift gives

$$d(v_{\text{second order}})/d(\ln V)=6\times10^{-2}\text{ mm/sec.}\quad(33)$$

Thus, for the isomer shift alone we have

$$d(\Delta\epsilon)/d(\ln V)=1.32\pm0.22\text{ mm/sec.}\quad(34)$$

Combining Eqs. (30) and (34) gives

$$-4.86\alpha+12.05\alpha X=1.32,\quad(35)$$

where $\alpha\equiv[a_0{}^3\text{ mm/sec}]$. If $\alpha=-0.47a_0{}^3$ mm/sec, we have $X=+0.17$ and thus a transfer of electrons from the s to the d part of the conduction band. Qualitatively, Stern[16] has found that as the volume decreases, the d band drops in energy with respect to the s band, making an s-to-d electron transfer energetically favorable and justifying the sign of X.

However, no quantitative estimate can be drawn from this argument, and thus Eq. (35) has been used to make the α-versus-X plot shown in Fig. 3. An independent α and/or X determination would thus give α and X directly. From Stern's work one expects $X>0$, so that this portion of Fig. 3 would be the physically meaningful region.

It can be seen that for $X=0$, when no s-to-d electron transfer occurs, $\alpha\simeq-0.28a_0{}^3$ mm/sec. This value is certainly not outside the range of possible α values. In fact, some authors[17,18] have obtained values of $\alpha=-0.2a_0{}^3$ mm/sec or less, using chemical or molecular-orbital arguments. Here we have obtained a relationship between the isomer-shift parameter α and the s-to-d electron-transfer parameter X that any independent measurements of α or X must satisfy.

MAGNETIC FIELD

In the course of measuring the isomer shift from the inner two peaks of the spectrum, it is possible also to measure the change of the magnetic field with pressure, although the accuracy is not great. Figure 4 is a plot of H/H_0 versus pressure. The least-squares linear fit gives

$$d(\ln H)/dP=(-1.80\pm0.28)\times10^{-4}/\text{kbar},\quad(36)$$

and a similar fit to the volume data gives

$$d(\ln H)/d(\ln V)=0.36\pm0.05.\quad(37)$$

Litster and Benedek,[19] using zero-field nuclear magnetic resonance to 65 kbar, obtain

$$d(\ln H)/dP=(-1.69\pm0.05)\times10^{-4}\text{ kbar.}\quad(38)$$

The data of Pipkorn *et al.*[3] agree with this result. Since, within our accuracy, our result is consistent with the earlier ones, and since the pressure dependence of the magnetic field is considered in detail in the two references above, further discussion will not be presented here.

ACKNOWLEDGMENT

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