Isomer Shift of Fe^{57} in Iron*

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The contributions to the Fe^{57} isomer shift in bcc iron are calculated. Both the direct density at the nucleus due to 4s-like conduction electrons and the modification of the 3s density at the nucleus through 3d shielding are considered. Wave functions for the solid are calculated using Stern's modified tight-binding (MTB) method. These are coupled with a decomposition of the total density of states, obtained by Wood and by Cornwell and Wohlfarth, into separate components associated with s-, p-, and d-like character of the conduction-band wave functions. Special attention is given the variation of the isomer shift with atomic volume, and the amount of s and d character on the iron atom. One is able to account qualitatively for the measured volume dependence of the isomer shift, as well as the anomalies at the Curie-point, bcc-fcc, and bcc-hcp transitions. However, the constant of proportionality between isomer shift and density at the nucleus cannot be determined here with much accuracy.

I. INTRODUCTION

SINCE its discovery by Kistner and Sunyar,[1] and subsequent interpretation,[2,3] the Fe^{57} isomer shift as measured in Mössbauer experiments has provided a wealth of data. By means of the expression

$$\epsilon = \alpha \psi^2(0) + \text{const}, \qquad (1)$$

the isomer shift ϵ (the displacement of a Mössbauer absorption spectrum from zero velocity for a given source-absorber combination), is related to $\psi^2(0)$, the total s-electron density at the Fe^{57} nucleus in the host under consideration. The constant of proportionality α depends upon the change in charge distribution within the nucleus during the nuclear transition. In particular, when relativistic corrections are neglected, and one assumes a uniformly charged nucleus,

$$\alpha \cong (c/E)(2\pi/5)Ze^2(R_1^2 - R_0^2), \qquad (2)$$

where E is the nuclear γ transition energy ($E = 14.4$ keV for Fe^{57}), and R_1 and R_0 are the charge radii of the first-excited and ground states of Fe^{57}, respectively.

Originally the isomer shift in Fe^{57} was calibrated[2,3] using the isomer-shift difference between ferrous and ferric absorbers relative to a common source and calculating the electron densities at the nucleus, using Watson's free-ion wave functions.[4] In particular, using[2-4]

$$\epsilon(\text{Fe}^{2+}) - \epsilon(\text{Fe}^{3+}) \cong 0.90 + 0.03 \text{ cm/sec}$$
and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3)$
$$\psi_{2+}^2(0) - \psi_{3+}^2(0) \cong -(1.9 \pm 0.2)a_0^{-3},$$

together with Eq. (1), one obtained

$$\alpha \cong -(0.47 \pm 0.05)a_0^3 \text{ mm/sec}. \qquad (4)$$

The smaller density for the ferrous ion was almost entirely due to shielding of the 3s wave function by the additional 3d electron.

Using such a calibration and the measurement of the difference

$$\epsilon(\text{Fe}^{2+}) - \epsilon(\text{Fe metal}) \cong (1.28 \pm 0.03) \text{ mm/sec}, \qquad (5)$$

one then obtained a value of approximately 2.7 a_0^{-3} for the increase in density in going from the free ferrous ion to the metal. This difference was shown to be consistent with an assignment of $3d^74s^1$ for an iron atom in the metal, in two ways (assuming free-atom wave functions to be adequate): (a) It lay midway[2] between values obtained for the configurations $3d^8$ and $3d^64s^2$ for atomic iron and (b) it was also obtained by calculating, by means of the Fermi-Segré-Goudsmit (FSG) formula, the additional density gained in adding a single 4s electron to the free $3d^7(\text{Fe}^{1+})$ core,[3] i.e.,

$$\psi_{2+}^2(0) - \psi_{1+}^2(0) \cong 0.5a_0^{-3}$$
and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad (6)$
$$\psi_{4s}^2(0) \cong 3.0a_0^{-3}.$$

There has been much theoretical work done relevant to iron. In addition to Watson's excellent set of free-ion wave functions[4] used in the original calibration, another comprehensive set has subsequently been published.[5] Moreover, the band structure of iron has been determined in some detail.[6-9]

It is the purpose of this paper to tie such work together in an attempt to calculate the behavior of

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[1] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters 4, 412 (1960).
[2] S. De Benedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters 6, 60 (1961).
[3] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters 4, 98 (1961).
[4] R. E. Watson, Technical Report No. 12, Solid State and Molecular Theory Group, MIT (unpublished); Phys. Rev. 119, 1934 (1960).

[5] E. Clementi, IBM J. Res. Develop., Suppl. 9, 2 (1965).
[6] F. Stern, Phys. Rev. 116, 1399 (1959).
[7] J. H. Wood, Phys. Rev. 126, 517 (1962).
[8] J. F. Cornwell and E. P. Wohlfarth, J. Phys. Soc. Japan 17, Suppl. B-1, 32 (1962); E. P. Wohlfarth and J. F. Cornwell, Phys. Rev. Letters 7, 342 (1961).
[9] J. F. Cornwell, thesis, Imperial College, London, England, Chap. 11 (unpublished).

TABLE I. Iron-57 isomer-shift data considered in this work. Numerical subscripts are pressure in kbar. Negative changes in the isomer shift ϵ indicate increasing density at the nucleus.

Quantity	Value (mm/sec)	T(°K)	Reference
$\epsilon(Fe^{2+}) - \epsilon(Fe^{3+})$	(0.90 ± 0.03)	295	a
$\epsilon(Fe^{2+}) - \epsilon(bcc)_0$	(1.28 ± 0.03)	295	a
$\epsilon(bcc)_{para} - \epsilon(bcc)_{ferro}$	~-0.01	~1040	b
$\epsilon(fcc) - \epsilon(bcc)$	~-0.03	~1200	b
$\epsilon(hcp)_{130} - \epsilon(bcc)_0$	~-0.23	295	c
$\left[\Omega\dfrac{\partial\epsilon(bcc)}{\partial\Omega}\right]_0$	(1.34 ± 0.05)	295	d
$\left[\Omega\dfrac{\partial\epsilon(hcp)}{\partial\Omega}\right]_{130}$	~0.8	295	c

a See Refs. 2 and 3.   c See Ref. 11.
b See Ref. 10.   d See Ref. 12.

$\psi^2(0)$ associated with the isomer-shift data[10–12] on the various forms of metallic iron given in Table I. In the present case the atomic volume also plays an important role (see Table II), not only for the purpose of understanding the isomer shift in iron but also in order to obtain some semiquantitative results that may be useful in interpreting isomer-shift studies of Fe^{57} in other transition metals under pressure.[13,14]

II. METHOD OF CALCULATION

A. Assumptions

In studying the behavior of the wave functions[4,5] for the various configurations of atomic iron and its ions, one observes that the density at the nucleus from the $1s$, $2s$, and $3s$ electrons is relatively insensitive to the amount of $4s$ electron density present. The $1s$ and $2s$ densities at the nucleus are also insensitive to modification of the $3d$ density, whereas the $3s$ density in fact *is* sensitive to such modification. On the other hand, placing an iron atom in the metal has very little direct effect on the core electrons inside the $3d$-$4s$ shell. We thus assume our tasks separate into (a) a calculation of the direct density $\psi_{4s}^2(0)$ from $4s$-like electrons in the $3d$-$4s$ conduction band in the solid and (b) a calculation of the shielding effect on the $3s$ density $\psi_{3s}^2(0)$ by the modified $3d$-like band electrons.

The $4s$ contribution involves a sum over the s-like part of the band

$$\psi_{4s}^2(0) = \int^{E_F} N_s(E)\psi_s^2(0,E)\,dE, \qquad (7)$$

where $N_s(E)$ is the s-like density of states per atom (Sec. II C) and $\psi_s^2(0,E)$ is the density at the origin from an s-like conduction electron of energy E with wave function $\psi_s(\mathbf{r},E)$ normalized to the unit cell, or rather, to the atomic sphere in this work.

A rigorous calculation of the effect of the $3d$-like electrons upon $\psi_{3s}^2(0)$ is not attempted here, since not only is it hopelessly difficult, but it is only of secondary importance. Instead one may draw upon the very useful correlation to be found between the $3s$ density $\psi_{3s}^2(0)$ and total maxima, nu_{max}^2, of the squared $3d$ radial wave functions for the free iron ions $3d^n$ as calculated by Watson[4] and Clementi,[5] Fig. 1. The quantity u_{max}^2 is the maximum of the squared radial wave function for a single $3d$ electron having total wave function $\psi_d(\mathbf{r}) = Y_{lm}(\theta,\phi)ru(r)$. Although the absolute value of $\psi_{3s}^2(0)$ differs between the two sets of wave functions the relationship is quite linear for small values of n with a slope

$$\beta \simeq -(5.5\pm0.5). \qquad (8)$$

For higher values of n (our region of interest) the linear relationship is somewhat worse but still sufficiently useful. For comparison we also show similar curves for Mn and Co. There seems to be no obvious trend away from linearity at the highest values of n. We then assume a similar relation holds for the solid; that is,

$$\psi_{3s}^2(0) \simeq \beta\langle nu_{max}^2\rangle_{av} + const,$$

where   (9)

$$\langle nu_{max}^2\rangle_{av} \equiv \int^{E_F} N_d(E)u_{max}^2(E)\,dE,$$

where $N_d(E)$ is the d-like density of states per atom (Sec. II C) and $u_{max}^2(E)$ is the maximum of the squared d-band radial wave function of energy E normalized to the atomic sphere.

B. Wave Functions in the Solid

In this section we follow Stern's modified tight-binding (MTB) method[6] of calculating the wave functions for bcc metallic iron (and also for the fcc structure here) starting from the free-atom wave functions for the configuration $3d^74s^1$, which, as Stern

[10] R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. 128, 2207 (1962).

[11] D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De Pasquali, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. 135, A1604 (1964).

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

[13] C. K. Edge, R. Ingalls, P. Debrunner, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. 138, A729 (1965).

[14] R. Ingalls, H. G. Drickamer, and G. De Pasquali, Phys. Rev. 154, 166 (1967), following paper.

TABLE II. Atomic volumes of the forms of iron considered in this work relative to ferromagnetic bcc iron at standard temperature and pressure, $\Omega_0 \simeq 80a_0^3$.

Form of iron	P(kbar)	T(°K)	Ω/Ω_0	Reference
bcc	0	295	1	
bcc	130	295	0.94	a
bcc	0	1189	1.04	b
fcc	0	1196	1.03	b
hcp	130	295	0.92	a

a R. L. Clendenen and H. G. Drickamer, J. Phys. Chem. Solids 25, 865 (1964).
b Z. S. Basinski, W. Hume-Rothery, and A. L. Sutton, Proc. Roy. Soc. (London) A229, 459 (1955).

has shown, is known to give reliable results for iron. Since analytic Hartree-Fock wave functions such as those of Watson and Clementi have not been published for this configuration, such wave functions were interpolated from Clementi's wave functions for $Fe^{1+}(3d^7)$, and $Fe^{1-}(3d^7 4s^2)$ for the $3d$ wave functions, and both interpolated and extrapolated from those for $Fe^{1-}(3d^7 4s^2)$, $Cu(3d^{10} 4s^1)$, $Cu^{1-}(3d^{10} 4s^2)$, $K(4s^1)$, and $K^{1-}(4s^2)$ for the $4s$ wave function. Since the $3d$ wave functions were almost identical in going from $Fe^{1+}(3d^7)$ to $Fe^{1-}(3d^7 4s^2)$, the interpolation was quite straightforward.[15] The $4s$ function obtained was carefully orthogonalized to the core s electrons. It turns out to be virtually identical to the numerical $4s$ Hartree wave function used by Stern.[16] For the present function, $\psi_{4s}^2(0) = 1.8 a_0^{-3}$ compared with $1.7 a_0^{-3}$ for Stern's wave function and $\simeq 3.0 a_0^{-3}$ for the FSG value used in the original calibration of the isomer shift.[3] With these wave functions the MTB calculations were carried out for wave vectors along the Δ axis $[\mathbf{k} \lesssim 2\pi/a(1,0,0)]$ shown in Fig. 2. The calculation was essentially the same as Stern's and will not be described here, except that it was also performed for the fcc as well as bcc structure for atomic volumes, Ω, between $50 a_0^3$ and $500 a_0^3$.

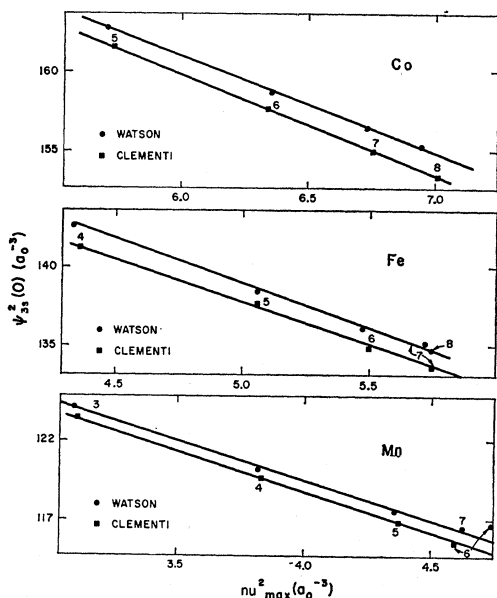As we shall see, the main contribution from s-like electrons occurs near the bottom of the band where

FIG. 2. Energy versus wave vector along the $[1,0,0]$ axis for bcc iron, taken from Ref. 9.

FIG. 1. The $3s$ electron density at the nucleus as a function of the total maximum of the squared $3d$ radial wave functions for the configurations $3d^n$ for the ions of Co, Fe, and Mn. Numbers in the figures are the number of d electrons, n. Results of both Watson (Ref. 4) and Clementi (Ref. 5) are shown.

[15] The $3d$ wave function agrees closely with that of Watson's calculation for $3d^7$ (Ref. 4), but is somewhat more contracted than one used by Stern (Ref. 16).
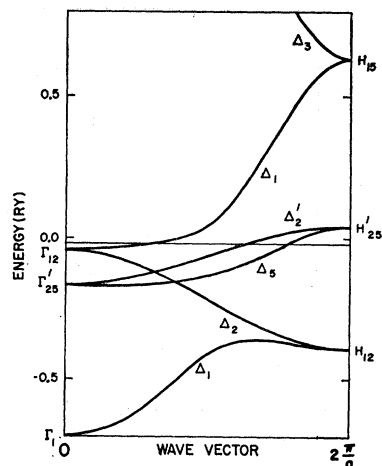
[16] F. Stern, Phys. Rev. 104, 684 (1956).

(for the $4s$ band) Stern's method is the most reliable. (His method is reliable for all of the more localized $3d$ band.) In Fig. 3 are shown the squared radial wave functions for the point Γ_1, namely at $\mathbf{k} = \pi/a(0,0,0)$ for bcc iron at atmospheric pressure and room temperature, where $\Omega \simeq 80 a_0^3$. In Fig. 4 we show the volume dependence of $\psi_{4s}^2(0)$ corresponding to two directions in $\mathbf{k}$ space for the bcc lattice. For comparison we have also calculated $\psi_{4s}^2(0)$ at Γ_1 using the orthogonalized plane wave[17] (OPW):

$$\psi_{\Gamma_1}(r) = N^{-1}\Big[1 - \sum_{n=1}^{3} \mu_n \psi_{ns}(r)\Big], \qquad (10)$$

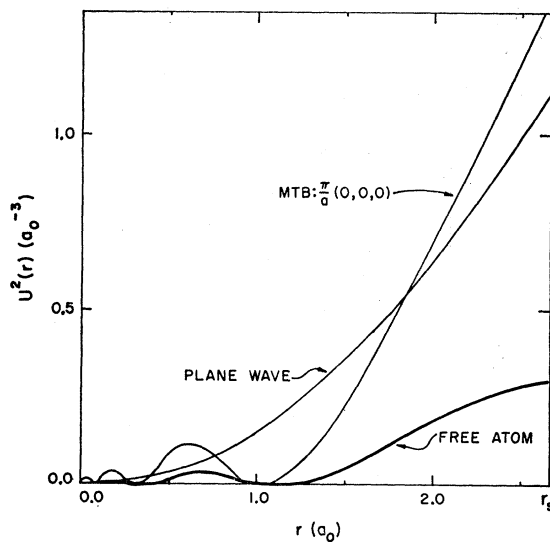where $\psi_{ns}(r)$ is a core wave function $\mu_n = \int \psi_{ns}(r) d\tau$

FIG. 3. The squared $4s$ radial wave functions for the band bottom, Γ_1, for bcc iron at atmospheric pressure as calculated by MTB method, compared with a plane wave and also the function for the free atom in the $3d^7 4s^1$ configuration.

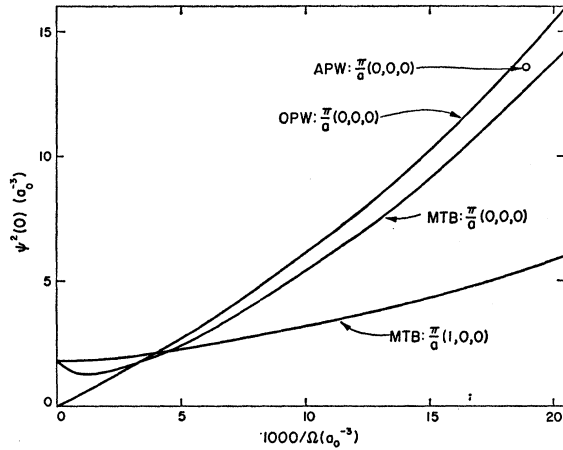[17] C. Herring, Phys. Rev. 57, 1169 (1940).

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FIG. 4. Electron density at the nucleus as a function of atomic volume calculated by the MTB method for two wave vectors compared with an OPW calculation and an APW result of Ref. 18.

and the normalization constant is

$$N = (\Omega - \sum_{n=1}^{3} \mu_n{}^2)^{1/2}.$$

The agreement is quite satisfactory for volumes appropriate to the solid. We also show in Fig. 4 the good agreement with a value of $\psi_{\Gamma_1}{}^2(0)$ from the augmented plane wave (APW) of Yamashita and Wakoh[18] for a somewhat contracted volume of iron. It is noted that the $4s$ density at the nucleus for a given wave function is generally greater in the solid than in the free atom, but that it is almost completely determined by normalization and orthogonalization requirements. We find that for either OPW or MTB calculations $\psi_{\Gamma_1}{}^2(0)$ varies as

$$\psi_{\Gamma_1}{}^2(0) = \text{const} \times \Omega^{-\gamma} \quad \text{with} \quad \gamma = 1.25 \pm 0.05. \quad (11)$$
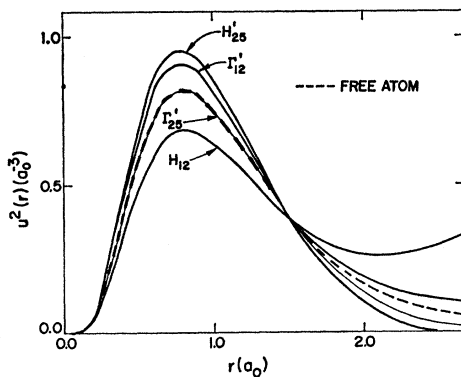

FIG. 5. The squared $3d$ radial wave functions for several wave vectors along the [1,0,0] axis for bcc iron at atmospheric pressure as calculated by the MTB method compared with the function for the free atom.

[18] J. Yamashita and S. Wakoh (unpublished). See T. Muto, S. Kobayasi, and H. Hayakawa, J. Phys. Soc. Japan 20, 395 (1965).

The decrease observed at the higher wave vectors is essentially an admixture effect, since the p and d admixture increases as one moves away from Γ_1, as will be discussed in more detail in the next section.

The squared radial wave functions for the d-like electrons at several points in $\mathbf{k}$ space are shown in Fig. 5. They have the general feature described by Stern[6] and Wood,[19] namely, those at the lower portion of the band are more extended and those at the higher portion more contracted. Of course this is the principal feature of interest here since we have assumed the $3s$ density $\psi_{3s}{}^2(0)$ to be linear in squared $3d$ amplitude. Figure 6 shows $u_{\text{max}}{}^2$ versus energy, for a series of points along the Δ_2 and $\Delta_2{}'$ branches of $\mathbf{k}$ space, and also for bcc iron at $\Omega = 80a_0{}^3$. The relation between $u_{\text{max}}{}^2$ and energy is essentially linear. We will therefore assume it to be a straight line passing through points corresponding to
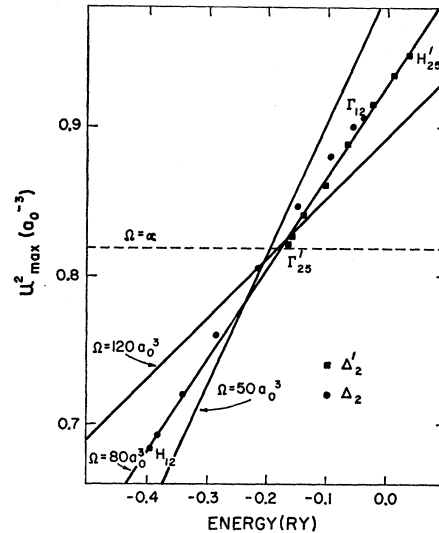

FIG. 6. Maxima $u_{\text{max}}{}^2$ of the squared radial wave functions at a series of points along the Δ_2 and $\Delta_2{}'$ branches (see Fig. 2) for bcc iron at atmospheric pressure ($\Omega = 80a_0{}^3$). The behavior at other volumes is also indicated.

H_{12} and $H_{25}{}'$, which are near the bottom and top of the d-like portion of the band, respectively. Similar lines are also drawn for other volumes where it is noted that the difference in $u_{\text{max}}{}^2$ for the top and bottom of the band increases as the volume decreases. (We neglect, for the present, the possible change in energy with volume.) Detailed calculations at other points in $\mathbf{k}$ space with some s or p character in the waves have not been performed, since we are assuming a linear relationship and rely upon the density of d-like states $N_d(E)$ to properly correct for such admixtures.

C. Densities of States for s-, p-, and d-like Electrons

It is a well-known fact that an electron at a given energy in the band has a wave function which trans-

[19] J. H. Wood, Phys. Rev. 117, 714 (1960).

forms in accordance with the group of the wave vector associated with that particular energy.[20] For instance, along the line Δ_1 (Fig. 2) the wave functions have pure s character at Γ_1, have s, p, and d character at a somewhat higher point, and pure d character at H_{12}. As previously mentioned, the wave functions along Δ_2 and Δ_2' are completely d like (neglecting small g-like terms). At intermediate points in the zone there are both p- and d-like states associated with the Δ_5 branch. Similar behavior may be found along other directions in $\mathbf{k}$ space. Thus one expects the central portion of the band to be mainly d like with some s and p character, while at the bottom and top it is expected to be mainly s like with a small amount of p character and somewhat less d character.

Such qualitative features are borne out in a detailed analysis[8,9] of the bcc-iron band structure based upon an interpolation of the original APW calculations by Wood.[7] In addition to obtaining a total density of states per atom $N(E)$ in Refs. 8 and 9 the wave functions are also broken up into their s-, p-, and d-like components in a manner which may be written

$$\psi(\mathbf{r},E) = a_s(E)\psi_s(\mathbf{r},E) + a_p(E)\psi_p(\mathbf{r},E)$$
$$+ a_d(E)\psi_d(\mathbf{r},E), \quad (12)$$

with

$$a_s{}^2 + a_p{}^2 + a_d{}^2 = 1.$$

By multiplying the total density of states $N(E)$ by each of the functions $a_s{}^2(E)$, $a_p{}^2(E)$, and $a_d{}^2(E)$, one thus obtains the desired component densities of s-, p-, and d-like states per atom $N_s(E)$, $N_p(E)$, and $N_d(E)$ shown in Fig. 7.

In using the above results to calculate the direct density at the nucleus from s-like electrons, we shall assume that the function $a_s(E)$ completely accounts for the reduced density at the nucleus due to p and d admixture. This is supported by the result that $\psi^2(0)$ at $\pi/a(1,0,0)$ on the Δ_1 branch (see Figs. 2 and 4) is about $0.5 \psi_{\Gamma_1}{}^2(0)$, while $a_s{}^2$ corresponding to the same point is also about 0.5, etc. Of course hybridization with the Δ_2 branch was not considered in obtaining our result and the MTB method is not as accurate at this point as at Γ_1. The $4s$ contribution at the nucleus [Eq. (7)] may then be written

$$\psi_{4s}{}^2(0) \simeq \psi_{\Gamma_1}{}^2(0) \int^{E_F} N_s(E)dE \equiv n_s\psi_{\Gamma_1}{}^2(0), \quad (13)$$

where n_s is the effective number of s-like states per atom in the occupied portion of the $3d$-$4s$ band.

D. Numbers of Electrons

In working with the densities of states discussed in the last section, we find for paramagnetic iron, with

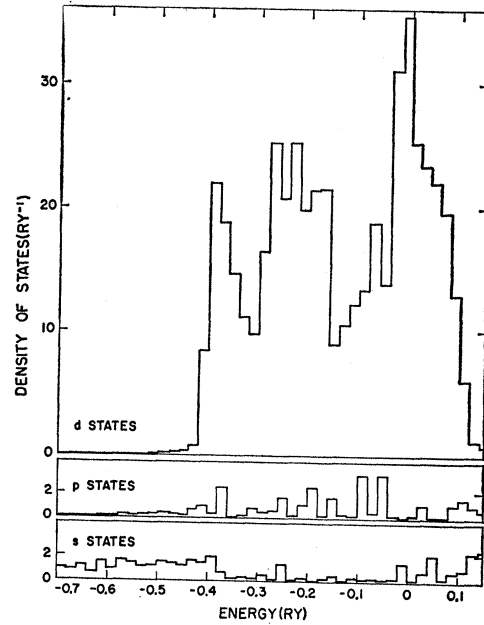[20] J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964), Chap. 1, Sec. 1.6.

FIG. 7. Density of states for bcc iron (from Ref. 9), decomposed into component histograms associated with s-, p-, and d-like character of the wave function.

$E_F \simeq -0.02 \pm 0.01$ Ry, corresponding to a total of 8 electrons per atom, the number of s-like states per atom is

$$n_s = \int^{E_F} N_s(E)dE = 0.50 \pm 0.04. \quad (14)$$

The stated error estimate is based upon uncertainties in locating the exact Fermi level E_F, in deriving $N_s(E)$ from $a_s(E)$ and $N(E)$, and in using the histogram method. In a similar manner one obtains

$$n_p = \int^{E_F} N_p(E)dE = 0.48 \pm 0.04$$

and

$$n_d = \int^{E_F} N_d(E)dE = 7.02 \pm 0.04.$$

For the ferromagnetic state, if the complete density-of-states curve for ↑ electrons is lowered with respect to the ↓ electrons such that $n{\uparrow} - n{\downarrow} = 2.2$ and $n{\uparrow} + n{\downarrow} = 8.0$ (i.e., $E_{F\downarrow} \simeq -0.13$ and $E_{F\uparrow} \simeq +0.06$ Ry), one obtains

$$n_s = n_{s\uparrow} + n_{s\downarrow} = 0.28 + 0.25 = 0.53 \pm 0.04,$$
$$n_p = n_{p\uparrow} + n_{p\downarrow} = 0.25 + 0.19 = 0.44 \pm 0.04, \quad (15)$$
$$n_d = n_{d\uparrow} + n_{d\downarrow} = 4.57 + 2.46 = 7.03 \pm 0.04.$$

Thus, although one starts from a free-atom configuration of $3d^7 4s^1$, from a density of states consideration the configuration can be taken as roughly $3d^7 4s^{0.5} 4p^{0.5}$.

III. RESULTS

A. Ferromagnetic, bcc Iron

At atmospheric pressure the atomic volume for ferromagnetic iron is[6] $\sim 80a_0^3$. At this volume the present MTB calculation yields

$$\psi_{\Gamma_1}^2(0) \simeq (7.1 \pm 0.3)a_0^{-3}. \tag{16}$$

From Eqs. (13) and (15) one has

$$\psi_{4s}^2(0) \simeq (3.8 \pm 0.4)a_0^{-3}. \tag{17}$$

Using the linear approximation for $u_{max}^2(E)$ at this volume (Fig. 6) and summing over each half of the band up to its respective Fermi level as given in the last section, one obtains [Eq. (9)]

$$\langle nu_{max}^2 \rangle_{av} \simeq 5.64 \pm 0.04a_0^{-3}. \tag{18}$$

In order to compare these numbers with the calibration described in Sec. I, we take the difference $\psi_{2+}^2(0) - \psi_{Fe}^2(0)$ using the average of the two values for nu_{max}^2, derived from the ferrous $3d$ wave functions of Watson and Clementi:

$$(nu_{max}^2)_{2+} = 5.49 \pm 0.01a_0^{-3}. \tag{19}$$

Using Eqs. (8), (9), and (17)-(19), we obtain

$$\psi_{2+}^2(0) - \psi_{Fe}^2(0)$$
$$= \beta[(nu_{max}^2)_{2+} - \langle nu_{max}^2 \rangle_{av}] - \psi_{4s}^2(0) \tag{20}$$
$$= -(3.0 \pm 0.5)a_0^{-3}.$$

Using the calibration constant from Sec. I, Eq. (4), $\alpha = -0.47 \pm 0.05a_0^3$ mm/sec, one calculates

$$\epsilon(Fe^{2+}) - \epsilon(Fe\ metal) = 1.4 \pm 0.2\ mm/sec, \tag{21}$$

which agrees with the experimental result [Eq. (5)] of 1.28 ± 0.03 mm/sec. However, for purposes of later discussion, it should be noted that good agreement with experiment is also obtained with $\alpha = -0.37a_0^3$ mm/sec, in which case one calculates the experimental isomershift difference to be 1.1 ± 0.2 mm/sec.

B. Volume Dependence of the Isomer Shift

As stated in Sec. II, the MTB or OPW results [Eq. (11)] revealed $\psi_{\Gamma_1}^2(0)$ to vary as $\Omega^{-\gamma}$ with $\gamma = 1.25$. Therefore for n_s constant

$$\left[\Omega \frac{\partial \psi_{4s}^2(0)}{\partial \Omega}\right]_0 \simeq -n_s\gamma[\psi_{4s}^2(0)]_0, \tag{22}$$

where both sides of the equation are evaluated at some reference volume, such as that for atmospheric pressure, $p = 0$.

In calculating the volume dependence of the function $\langle nu_{max}^2 \rangle_{av}$ for the d contribution it must suffice here to assume that the shape of $N_d(E)$ is independent of volume. Therefore, with n_d held constant, to calculate $\langle nu_{max}^2 \rangle_{av}$ versus Ω, one may use the appropriate curve

for $u_{max}^2(E)$ (Fig. 6) for each particular volume, together with $N_d(E)$ for $\Omega \simeq 80a_0^3$ (Fig. 7). That is, any shifting, broadening, or narrowing of the band with volume change has no effect as long as n_d remains fixed.

In Fig. 8 we show curves of $\langle nu_{max}^2 \rangle_{av}$ versus atomic volume, for bcc, paramagnetic iron for several values of n_d corresponding to different values of E_F. Several qualitative features are observed. At large volumes $\langle nu_{max}^2 \rangle_{av}$ decreases with decreasing volume so that $\psi_{3s}^2(0)$ would be expected to increase, whereas at small volumes the reverse would be true. The slopes of the linear portion of the curves (for $\Omega > 80a_0^3$) also decrease as n_d increases because more of the contracted type-d wave functions become occupied. In fact one finds that for very small values of $n_d (< 5)$ the slope remains positive down to very small volumes and at large values of $n_d (> 9)$ it remains negative out to large volumes.

We also give the results of $\langle nu_{max}^2 \rangle_{av}$ versus Ω for ferromagnetic bcc iron in Fig. 8 for $n_d = 7.03$ as given in Eq. (15). Qualitatively, this curve is similar to the curves for the paramagnetic state, except that the slope is very small at $\Omega \simeq 80a_0^3$. One may now calculate the volume dependence of $\psi^2(0)$ in ferromagnetic, bcc iron [Eqs. (9), (11), and (13)]:

$$\psi^2(0) = n_s\psi_{\Gamma_1}^2(0) + \beta\langle nu_{max}^2 \rangle_{av} + const,$$

$$\left[\Omega \frac{\partial \psi^2(0)}{\partial \Omega}\right]_0 = -[n_s\gamma\psi_{\Gamma_1}^2(0)]_0 + \beta\left[\Omega \frac{\partial \langle nu_{max}^2 \rangle_{av}}{\partial \Omega}\right]_0$$
$$+ \left[\psi_{\Gamma_1}^2(0)\Omega \frac{\partial n_s}{\partial \Omega}\right]_0$$
$$+ \beta\left[\Omega \frac{\partial n_d}{\partial \Omega} \frac{\partial \langle nu_{max}^2 \rangle_{av}}{\partial n_d}\right]_0. \tag{23}$$

Again with $\Omega = 80a_0^3$, first assuming n_s, n_d to be independent of Ω, and using Eqs. (8), (11), and (16), and $[\Omega(\partial\langle nu_{max}^2 \rangle_{av}/\partial\Omega)]_0 = (0.03 \pm 0.03)a_0^{-3}$ (Fig. 8), one obtains

$$[\Omega\partial\psi^2(0)/\partial\Omega]_0 \simeq -(4.9 \pm 0.5)a_0^{-3}, \tag{24}$$

where roughly 3% of this result is seen to come from the second term on the right-hand side of Eq. (23). Using this value together with $\alpha = -0.47 \pm 0.05a_0^3$ mm/sec, one obtains $[\Omega(\partial\epsilon/\partial\Omega)]_0 = 2.3 \pm 0.2$ mm/sec compared with the experimental value (Table I) of 1.34 ± 0.05 mm/sec. With $\alpha = -0.37a_0^3$ mm/sec one obtains $[\Omega(\partial\epsilon/\partial\Omega)]_0 = 1.8 \pm 0.2$ mm/sec which is not yet in agreement with experiment.

In Stern's work,[21] several volumes are also considered with the qualitative feature that all bandwidths increase in an absolute sense as the volume decreases. However it appears that the ratio

$$[E(H_{12}) - E(\Gamma_1)]/[E(H_{25}') - E(\Gamma_1)]$$

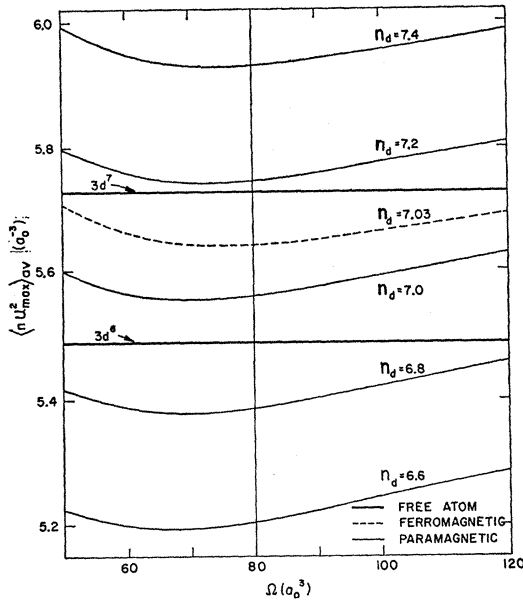[21] F. Stern, thesis, Princeton University, 1955 (unpublished).

FIG. 8. Integrated maxima per atom of the squared radial wave functions for bcc iron as a function of volume and number of occupied states in the portion of the band having d-like character.

decreases as the volume decreases, suggesting a lowering of $N_d(E)$ with respect to $N_s(E)$ and thus a transfer of electrons from the s band to the d band. If one estimates from Stern's work a small decrease in n_s with decreasing volume and an equal increase in n_d such that

$$[\Omega(\partial n_s/\partial \Omega)]_0 = -[\Omega(\partial n_d/\partial \Omega)]_0 \simeq 0.1 \qquad (25)$$

and, using the calculated value (Fig. 8),

$$[(\partial \langle nu_{max}^2 \rangle_{av}/\partial n_d)]_0 \simeq 0.9, \qquad (26)$$

one obtains from Eqs. (8), (16), and (23)–(26)

$$[\Omega(\partial \psi^2(0)/\partial \Omega)]_0 \simeq -3.7. \qquad (27)$$

It is significant that in this case agreement with experiment can be obtained with $\alpha = -0.37 a_0^3$ mm/sec which yields

$$[\Omega(\partial \epsilon/\partial \Omega)]_0 = 1.37 \text{ mm/sec}. \qquad (28)$$

However, while there is undoubtedly some s-to-d transfer with volume decrease, it is difficult to make a more precise calculation. It is also noted that a calibration of, say, $\alpha = -0.42 \pm 0.05 a_0^3$ mm/sec would still yield agreement between the rough estimate in Eq. (27) and experiment. At the same time such a value is compatible with the results of Sec. I, Eqs. (3), as well as the results of the previous calculation in Sec. III A.

C. The Curie-Point Anomaly

As shown in Table I, a slight isomer-shift anomaly is measured as bcc iron is carried upward through the Curie temperature, indicating an increase in $\psi^2(0)$. At

this temperature $\Omega \simeq 83 a_0^3$, so that

$$\psi_{\Gamma_1}^2(0) \simeq 6.8 a_0^{-3} \qquad (29)$$

and

$$\langle nu_{max}^2 \rangle_{av} \simeq 5.85 a_0^{-3} \qquad (30)$$

for the paramagnetic state. In comparing these values with those for the ferromagnetic state, one obtains, using Eqs. (8), (9), (13)–(15), (29), and (30),

$$[\psi_{4s}^2(0)]_{para} - [\psi_{4s}^2(0)]_{ferro} \simeq -0.20 a_0^{-3},$$

$$\beta[\langle nu_{max}^2 \rangle_{av\ para} - \langle nu_{max}^2 \rangle_{av\ ferro}] \simeq +0.33 a_0^{-3}, \qquad (31)$$

so that

$$[\psi^2(0)]_{para} - [\psi^2(0)]_{ferro} \simeq 0.13 a_0^{-3}. \qquad (32)$$

Thus we calculate an increase in going from ferromagnetic iron at room temperature to paramagnetic iron immediately above the Curie point. A similar increase has been calculated by Alexander and Treves.[22] However, in the present result the increase comes about by transferring some d electrons from contracted orbitals above the paramagnetic Fermi level to more extended ones below it. The term $\psi_{4s}^2(0)$ appears to decrease slightly since $N_s(E)$ increases above this level. Such behavior is in disagreement with that deduced by Alexander and Treves who take $N_s(E)$ as constant in this region of the band. Thus they conclude that $\psi_{4s}^2(0)$ increases in the paramagnetic state with more s-like states occupied (since $E_F - E_{F\downarrow} > E_{F\uparrow} - E_F$).

Following Alexander and Treves, we assume that approximately $\frac{1}{3}$ of the total increase in $\psi^2(0)$ (and corresponding decrease in ϵ) takes place within the interval immediately below the Curie point. Using $\alpha \sim -0.4 a_0^3$ mm/sec, we then calculate, from Eqs. (1) and (32), an isomer-shift anomaly of ~ -0.02 mm/sec. Although this agrees favorably with the experimental result (Table I) of ~ -0.01 mm/sec, the error can be appreciable because we have taken differences in small differences to get the result.[23]

It should be mentioned here that in the above calculation the complete $\uparrow$ band was shifted with respect to the $\downarrow$ band in the ferromagnetic case. There is reason to treat the problem somewhat differently by shifting the d band by a different amount than the s band.[24] If one did so in a way such that there would be 2.2 unpaired electrons of d character rather than 2.1 [Eq. (15)], then the calculated anomaly could be reduced by about 50%.

D. The bcc-fcc Transition

From the change in isomer shift (Table I) the quantity $\psi^2(0)$ is also observed to increase during the bcc-fcc transition at 1200°K. From Table II the volume

[22] S. Alexander and D. Treves, Phys. Letters **20**, 134 (1966).

[23] *Note added in proof.* R. S. Preston (private communication and to be published) has kindly informed us that a new measurement shows a sharp anomaly of ~ -0.025 mm/sec occurring within ~ 0.3°K of T_c.

[24] N. F. Mott, Advan. Phys. **13**, 325 (1964); **13**, 330 (1964).

decrease at this transition is approximately 1%. The results of our MTB calculation show $\psi_{\Gamma_1}^2(0)$ to be $\sim 1.3\%$ larger in the fcc lattice. Combining these facts, one calculates a change for n_s constant [see Eqs. (11) and (22)]:

$$[\psi_{4s}^2(0)]_{fcc} - [\psi_{4s}^2(0)]_{bcc} \simeq 0.09 a_0^{-3}. \quad (33)$$

Using $\alpha \simeq -0.4 a_0^3$ mm/sec, one obtains $\epsilon(\text{fcc}) - \epsilon(\text{bcc}) \simeq -0.04$ mm/sec, which is to be compared with the experimental value of -0.03 mm/sec. Certainly, although volume arguments seem favorable, one should not attach much quantitative significance to this result, since the details of the density of states are not known in enough detail for fcc iron.

In order to make a very crude estimate of the behavior of $\langle nu_{max}^2 \rangle_{av}$ for the fcc case, we may let $N_d(E)$ take the form of a Gaussian. Such a shape may bear some resemblance to reality since there is some evidence that the density of states for this structure does not possess the deep minimum characteristic of bcc structures.[25] According to Wood's APW calculation the bandwidth in fcc iron is roughly 15% narrower than in the bcc case. We therefore assume $N_d(E)$ to contain ten electrons when full, and have a width 15% narrower than $N_d(E)$ for the bcc case. Our curves of $u_{max}^2(E)$ versus E (not shown) which result from the MTB calculation of d-like wave functions along the Δ direction for the fcc case show no significant difference in slope when compared with the bcc results. Following the trend suggested for the positions of E_F in Ni and Co,[26] we thus place the curves $u_{max}^2(E)$ so that the point for Γ_{12} lies at E_F for $n_d = 7$. The behavior of $\langle nu_{max}^2 \rangle_{av}$ versus volume was examined for this rather simplified model. Around volumes appropriate to iron, the values of $\langle nu_{max}^2 \rangle_{av}$ are not significantly different than in the bcc case (Fig. 8). The chief difference is that such curves are displaced toward higher volume so that the slope is negative up to perhaps $\Omega \simeq 120 a_0^3$ rather than $\Omega \simeq 70 a_0^3$, as in the bcc case. Thus for a form of iron having a Gaussian-like density of states, one might expect, from this model, that the isomer shift would show weaker volume dependence than in the bcc case considered above. This possibility will be considered again in the following section and in discussing the pressure results for Fe^{57} in other transition metals.[14]

E. The hcp Form of Iron

Ferromagnetic bcc iron transforms to hcp iron at approximately 130 kbar with a large isomer-shift anomaly[16] (Table I). In Sec. III C the ferromagnetic-paramagnetic transition was shown [Eq. (32)] to give an increase in $\psi^2(0)$ of $\sim 0.1 a_0^{-3}$. Keeping n_s fixed and considering only the volume, one sees (Table II) that the atomic volume is approximately 8% less than for bcc iron at $p=0$. Thus we obtain, again using Eqs.

(11) and (22),

$$[\psi_{4s}^2(0)]_{hcp} - [\psi_{4s}^2(0)]_{bcc} \simeq 0.5 a_0^3, \quad (34)$$

which, when combined with $\alpha \simeq -0.4 a_0^3$ mm/sec, yields $\epsilon(\text{hcp})_{130} - \epsilon(\text{bcc})_0 \simeq -0.2$ mm/sec. This is to be compared with the net measured change of -0.23 mm/sec. Therefore, arguments based upon volume and magnetic structure certainly can account for the major portion of the anomaly. Again, as with fcc iron, one can make no definite statement concerning $\langle nu_{max}^2 \rangle_{av}$. It is to be noted, however, that the volume dependence of the isomer shift is rather small for the hcp phase. As shown in the previous section, a density of states more similar to a Gaussian than in bcc iron could possibly account for such behavior. Another possibility of course would be a lowering, with pressure, of the d-like part of the band with respect to the s-like part, with a transfer of s to d character as considered in Sec. III B.

IV. DISCUSSION AND SUMMARY

We have attempted to gain an understanding of the isomer shift in iron using calculated wave functions for the solid, together with previous results on the band structure and density of states. From these results we have then been able to break the total density of states into its s-, p-, and d-like components and gain an understanding of the relative importance of the direct $4s$ contribution and indirect $3d$ contributions to $\psi^2(0)$. To do so, however, many simplifying approximations were made. No attempts at any form of self-consistency were made; neither were correlation nor exchange considered. Shielding effects by $4s$ electrons on core electrons were neglected as were shielding effects by $3d$ on all electrons other than $3s$. In addition, the effect of $3d$ shielding of $3s$ electrons was approximated as a function of the squared $3d$ amplitude, a practice that suffices for the free ion but which could be of less value in performing solid-state calculations.[27] The above approximations appear to be somewhat justified in view of the qualitative agreement with a variety of experimental isomer-shift results.

Quantitatively, we have had somewhat less success, especially in view of the smaller values of the calibration constant α inferred from pressure work versus the larger values obtained in other ways. A transfer of electrons from the s band to the d band with pressure helps reduce this difference. However, it should be noted that others,[28,29] using chemical or molecular orbital arguments, have succeeded in getting even

[25] Reference 24, p. 334.
[26] L. F. Mattheiss, Phys. Rev. 134, A970 (1964).

[27] Preliminary results of perturbation calculations of this effect for the solid by R. W. Vaughan, of this laboratory, support the present results.
[28] V. I. Gol'danskii, in Proceedings of the Dubna Conference on the Mössbauer Effect (Consultants Bureau Enterprises, Inc., New York, 1963), p. 17–19.
[29] J. Danon, in Applications of the Mössbauer Effect in Chemistry and Solid-State Physics, Technical Report Series No. 50 (International Atomic Energy Agency, Vienna, Austria, 1966), p. 89.

smaller values of α ($-0.2a_0^3$ mm/sec or less). If such a low value were correct, our qualitative agreement with experiments other than that of bcc iron under pressure would perhaps be worsened. However, here we have found it quite reasonable to adopt a value of $\alpha \sim -0.4a_0^3$ mm/sec. This value is also used in discussing the experimental shifts of Fe⁵⁷ in other metals.[14]

In this work we have again met the interesting question concerning how many $3d$ and $4s$ electrons are in iron. Although the free-atom configuration $3d^7 4s^1$ gives excellent band-structure results, from a density-of-states point of view, one has $3d^7 4s^{0.5} 4p^{0.5}$. From a Mössbauer-effect standpoint, that is, in terms of $\psi^2(0)$

relative to some free-atom configuration, the effective result is closer perhaps to $3d^{6.5} 4s^{1.5}$.

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Isomer Shift of Fe⁵⁷ in Transition Metals under Pressure*

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Isomer shifts of Fe⁵⁷ in several transition metals have been measured as a function of pressure up to nearly 300 kbar. The host metals studied were Cr, Co, Ni, Nb, Mo, Pd, Ta, W, Pt, and Au. The data are discussed in terms of the volume dependence of (1) the density at the nucleus from $4s$-like conduction electrons and (2) the density at the nucleus from $3s$ core electrons which are shielded by the $3d$-like conduction electrons. Results of the previous paper regarding amount of $4s$ character, n_s, and amount of $3d$ character, n_d, on the iron impurity atom, are used. The data are shown to be consistent with (1) n_s decreasing or n_d increasing, or both, as one goes through each transition-metal series toward more d electrons of the host, and (2) n_s decreasing or n_d increasing, or both, as pressure is applied to the host metal. The degree of the effect (2) is shown to be related to the calibration constant of the isomer shift.

I. INTRODUCTION

THE work reported here represents a continuation of Mössbauer studies of Fe⁵⁷ in transition metals under very high pressure which began with work on iron by Pipkorn et al.[1] and continued on titanium, vanadium, and copper by Edge et al.[2] The host metals studied here are Cr, Co, Ni, Cu, Nb, Mo, Pd, Ta, W, Pt, and Au. In the present report we are solely concerned with the isomer shifts of Fe⁵⁷ in these hosts. Data for the pressure dependence of the Fe⁵⁷ internal magnetic field in cobalt and nickel, as well as the electric field gradient in cobalt, has been reported earlier[3] together with some preliminary isomer-shift results.

As with Fe, Cu, Ti, and V, our results show that the isomer shift ϵ decreases with increasing pressure corresponding to increasing electron density at the nucleus, $\Psi^2(0)$. Pound et al.,[4] in interpreting their original pressure experiment on Fe⁵⁷ in Fe, used a calibration based on free-ion wave functions to show this increase to be consistent with simple scaling of the $4s$ density $\Psi_{4s}^2(0)$ with inverse volume. Although the behavior in bcc vanadium roughly supported this interpretation, the results on hcp Fe, Ti, and fcc Cu showed a much smaller change in $\Psi^2(0)$ with volume[1,2] indicating a possible role of crystal symmetry and host band structure as well as possible complications due to effects of d electron shielding on the $3s$ electron. Indeed, large increases in $\Psi^2(0)$ with pressure have recently been observed in several ionic compounds of Fe in which very little $4s$ density is expected to be present.[5]

[1] D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De Pasquali, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. **135**, A1604 (1964).

[2] C. K. Edge, R. Ingalls, P. Debrunner, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. **138**, A729 (1965).

[3] H. G. Drickamer, R. L. Ingalls, and C. J. Coston, in *Physics of*

Solids at High Pressures, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York, 1965), p. 313.

[4] R. V. Pound, G. B. Benedek, and R. Drever, Phys. Rev. Letters **7**, 405 (1961).

[5] R. Ingalls, C. J. Coston, G. De Pasquali, H. G. Drickamer, and J. J. Pinajian, J. Chem. Phys. **45**, 1057 (1966); A. R. Champion and R. W. Vaughan (private communication).