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

$$|\psi_{4s}(0)|^2 = \int_0^{E_F} N_s(E)|\psi_s(0, E)|^2\, dE \tag{7}$$

where $N_s(E)$ is the number of s-states in the 3d–4s conduction band. Ingalls (1967) performed a modified tight-binding calculation of the 4s wave functions at $\Gamma_1(\mathbf{k}\equiv 0)$ for several volumes and found

$$|\psi_{\Gamma_1}(0)|^2 = 7{\cdot}1\, a_0^{-3} \quad \text{for} \quad V = 80\, a_0^{+3} \tag{8}$$

and

$$|\psi_{\Gamma_1}(0)|^2 = \text{const } V^{-\gamma} \tag{9}$$

where $\gamma \simeq 1{\cdot}25$. With the assumption that $|\psi_s(0, E)|^2$ equals $|\psi_{\Gamma_1}(0)|^2$, 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

$$|\psi_{4s}(0)|^2 = n_s|\psi_{\Gamma_1}(0)|^2 \tag{10}$$

where $n_s = 0{\cdot}53$ is the number of s-electrons per iron atom.

The 3s contribution is approximated by using the proportionality found by Watson (1959) and Clementi (1965) between the density of 3s electrons at the nucleus and $\langle nu_m^2\rangle$

$$|\psi_{3s}(0)|^2 = \beta\langle nu_m^2\rangle \tag{11}$$

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

$$\langle nu_m^2\rangle = \int_0^{E_F} N_d(E)\, u_m^2(E)\, dE \tag{12}$$

where $\beta = -5{\cdot}5\, a_0^{-2}$. The integral in eqn (12) 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 3s and 4s contributions we have

$$|\psi(0)|^2 = n_s|\psi_{\Gamma_1}(0)|^2 + \beta\langle nu_m^2\rangle. \tag{13}$$

Taking the volume derivative of eqn (12) gives

$$\frac{d|\psi(0)|^2}{d(\ln V)} = -n_s\gamma|\psi_{\Gamma_1}(0)|^2 + \beta\frac{\partial\langle nu_m^2\rangle}{\partial(\ln V)} + |\psi_{\Gamma_1}(0)|^2\frac{\partial n_s}{\partial(\ln V)} + \beta\frac{\partial\langle nu_m^2\rangle}{\partial n_d}\frac{\partial n_d}{\partial(\ln V)}. \tag{14}$$

Here one sees the expression for $d(\Delta\epsilon)_L$, due to volume scaling, and for $d(\Delta\epsilon)_B$, due to $s \leftrightarrow d$ electron transfer

$$\frac{d(\Delta\epsilon)_L}{d(\ln V)} = \alpha\left[-n_s\gamma|\psi_{\Gamma_1}(0)|^2 + \beta\frac{\partial\langle nu_m^2\rangle}{\partial(\ln V)}\right] \tag{15}$$

$$\frac{d(\Delta\epsilon)_B}{d(\ln V)} = \alpha\left[|\psi_{\Gamma_1}(0)|^2\frac{\partial n_s}{\partial(\ln V)} + \beta\frac{\partial\langle nu_m^2\rangle}{\partial n_d}\frac{\partial n_d}{\partial(\ln V)}\right]. \tag{16}$$

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

$$\frac{\partial\langle nu_m^2\rangle}{\partial(\ln V)} = 0{\cdot}03\, a_0^{-1} \qquad \frac{\partial\langle nu_m^2\rangle}{\partial n_d} = 0{\cdot}9\, a_0^{-1} \tag{17}$$

gives

$$\frac{d(\Delta\epsilon)_L}{d(\ln V)} = -4{\cdot}86 \tag{18}$$

$$\frac{d(\Delta\epsilon)_B}{d(\ln V)} = \alpha\left[7{\cdot}1\frac{\partial n_s}{\partial(\ln V)} - 4{\cdot}95\frac{\partial n_d}{\partial(\ln V)}\right] \text{mm/sec} \tag{19}$$

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

Equation (18) can be viewed as an alternative to eqn (6), which gave a rough value of $d(\Delta\epsilon)/d(\ln V)$ from volume scaling alone, and it will be used instead of eqn (6). To obtain agreement between these equations we would need $\alpha = -0{\cdot}35\, a_0^3$ mm/sec which is significantly different from the value of $\alpha = -0{\cdot}47\, a_0^3$ mm/sec found above.

By combining the theory with the experimental measurements and assuming the total number of electrons in the combined 4s–3d band is constant, we obtain:

$$\frac{d(\Delta\epsilon)}{d\ln V} = -4{\cdot}86\alpha + 12{\cdot}05\alpha X = 1{\cdot}32 \tag{20}$$

where

$$X = \frac{\partial n_s}{\partial\ln V} = -\frac{\partial n_d}{\partial\ln V}. \tag{21}$$

This relationship is plotted in Fig. 10.