Rose universal curve of energy vs volume for first-principles calculation

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In the paper "Relativistic effects on ground state properties of 4d and 5d transition metals" by C. Elsässer, N Takeuchi, K M Ho, C T Chan, P Braun, M Fähnle. J. Phys.: Condens. Matter (1990) vol. 2 pp. 4371-4394, they showed "Rose universal equation for energy vs volume curve" that was reported in "Universal Binding Energy Curves for Metals and Bimetallic Interfaces" by J H Rose, J Ferrante, J R Smith, Phys. Rev. Lett. (1981) vol. 47 pp. 675-678. In the Christian's paper the equation was mis-typed (V_0^3 should be V_0^2).

The equation have three parameters that are used to fit the energy E vs volume V relation calculated by first-principles calculations. E is defined by -(cohesive energy) and < 0. Cohesive energy is defined by the energy required to form separated neutral atoms in the ground electronic state from the solid at 0 K 1 atm. The cohesive energies of Li and Si are 1.63 and 4.63 eV / atom, respectively.

$$E(V) = E_0(1+\sigma)e^{-\sigma}, \qquad \sigma = \frac{s-s_0}{\lambda}, \qquad \lambda = \frac{1}{(36\pi V_0^2)^{1/3}}\sqrt{\frac{-E_0V_0}{B_0}} \tag{1}$$

$$V = \frac{4\pi}{3}s^3, \quad V_0 = \frac{4\pi}{3}s_0^3, \quad s = \left(\frac{3V}{4\pi}\right)^{1/3}, \; s_0 = \left(\frac{3V_0}{4\pi}\right)^{1/3} \tag{2}$$

$$B_0 = V_0 \left.\frac{dE^2}{dV^2}\right|_{V_0} \tag{3}$$

Here V_0 is the volume where the energy E has minimum $E_0 < 0$, and the B_0 is the bulk modulus. If we calculate the first and second derivative,

$$\frac{dE}{dV} = \frac{dE}{d\sigma}\frac{d\sigma}{dV} = E_0[e^{-\sigma} - (1+\sigma)e^{-\sigma}]\frac{d\sigma}{dV} = -E_0\sigma e^{-\sigma}\frac{d\sigma}{dV} \tag{4}$$

$$\sigma(V_0) = 0, \quad \left.\frac{dE}{dV}\right|_{V_0} = 0 \tag{5}$$

$$\frac{d\sigma}{dV} = \frac{d\sigma}{ds}\frac{ds}{dV} = \frac{1}{\lambda}\frac{1}{3}\left(\frac{3V}{4\pi}\right)^{-2/3}\frac{3}{4\pi} = \frac{1}{4\pi\lambda}\left(\frac{3V}{4\pi}\right)^{-2/3} \tag{6}$$

$$\begin{aligned}\frac{dE^2}{dV^2} &= \frac{dE'}{dV} = \frac{d}{dV}[-E_0\sigma e^{-\sigma}\frac{1}{4\pi\lambda}\left(\frac{3V}{4\pi}\right)^{-2/3}] = \frac{-E_0}{4\pi\lambda}\frac{d}{dV}[\sigma e^{-\sigma}\left(\frac{3V}{4\pi}\right)^{-2/3}] \\ &= \frac{-E_0}{4\pi\lambda}[\frac{d\sigma}{dV}e^{-\sigma}\left(\frac{3V}{4\pi}\right)^{-2/3} - \sigma e^{-\sigma}\frac{d\sigma}{dV}\left(\frac{3V}{4\pi}\right)^{-2/3} + \sigma e^{-\sigma}\frac{-2}{3}\left(\frac{3V}{4\pi}\right)^{-5/3}\frac{3}{4\pi}]\end{aligned} \tag{7}$$

$$\begin{aligned}\left.\frac{dE^2}{dV^2}\right|_{V_0} &= \frac{-E_0}{4\pi\lambda}\frac{1}{4\pi\lambda}\left(\frac{3V_0}{4\pi}\right)^{-2/3}e^0\left(\frac{3V}{4\pi}\right)^{-2/3} = \frac{-E_0}{(4\pi)^2}(36\pi V_0^2)^{2/3}\frac{B_0}{-E_0V_0}\left(\frac{3V_0}{4\pi}\right)^{-4/3} \\ &= \frac{4^{2/3}3^{4/3}\pi^{2/3}V_0^{4/3}}{4^2\pi^2}\frac{B_0}{V_0}\frac{4^{4/3}\pi^{4/3}}{3^{4/3}V_0^{4/3}} = \frac{B_0}{V_0}\end{aligned} \tag{8}$$

For practical use, we can write

$$
\begin{aligned}
E(V) &= E_0 \left[1 + \frac{\left(\frac{3V}{4\pi}\right)^{1/3} - \left(\frac{3V_0}{4\pi}\right)^{1/3}}{\frac{1}{(36\pi V_0^2)^{1/3}} \sqrt{\frac{-E_0 V_0}{B_0}}} \right] \exp\left[- \frac{\left(\frac{3V}{4\pi}\right)^{1/3} - \left(\frac{3V_0}{4\pi}\right)^{1/3}}{\frac{1}{(36\pi V_0^2)^{1/3}} \sqrt{\frac{-E_0 V_0}{B_0}}} \right] \quad (9) \\
&= E_0 \left[1 + 3V_0^{2/3} \sqrt{B_0} \frac{V^{1/3} - V_0^{1/3}}{\sqrt{-E_0 V_0}} \right] \exp\left[-3V_0^{2/3} \sqrt{B_0} \frac{V^{1/3} - V_0^{1/3}}{\sqrt{-E_0 V_0}} \right] \quad (10)
\end{aligned}
$$

where we assume $E_0 < 0$. If we use eV for E and Å^3 for V, the unit for B_0 is given by

$$
\begin{aligned}
\text{Å}^3 \frac{\text{eV}}{\text{Å}^6} &= \frac{\text{eV}}{\text{Å}^3} = \frac{1.60217487 \times 10^{-19}\ \text{J}}{10^{-30}\ \text{m}^3} = 1.60217487 \times 10^{11} \frac{\text{J}}{\text{m}^3} = 160.317487\text{G}\frac{\text{Nm}}{\text{m}^3} \\
&= 160.317487\ \text{GPa} \quad (11)
\end{aligned}
$$

For the use of Igor fitting, $E_0 \to a, V_0 \to v, B_0 \to b, V \to x$, you can copy&paste the following text for the fit-function.

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f(x) = a*(1.0e0+3.0e0*v^(2.0e0/3.0e0)*b^0.5e0*(x^(1.0e0/3.0e0)-v^(1.0e0/3.0e0))/(-a*v)^0.5e0)*
exp(-3.0e0*v^(2.0e0/3.0e0)*b^0.5e0*(x^(1.0e0/3.0e0)-v^(1.0e0/3.0e0))/(-a*v)^0.5e0)
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The lattice constants of Li(bcc, 78 K) and Si(diamond) are 3.491 and 5.430 Å, respectively. Then, V_0(Li) = 21.3 Å^3 and V_0(Si) = 20.0 Å^3 The room-temperature bulk modulii B_0 of Li and Si are 0.116 $\times 10^{11}$ and 0.988 $\times 10^{11}$ Pa, respectively. (11.6 GPa and 98.8 GPa)