Appendix

In this appendix we apply the Clausius-Clapeyron relation three times and use the slope of the solid-solid phase transition determined here to find this useful expression for the change in slope of the melting curve at 30 Gpa:

$$\frac{\left.\frac{dT}{dP}\right|_{+}}{\left.\frac{dT}{dP}\right|_{-}} \geq \left(1 + \frac{\left(V_\varepsilon - V_{B2}\right)/\left.V_\varepsilon\right|_{30GPa}}{\left(V_l - V_\varepsilon\right)/\left.V_\varepsilon\right|_{0GPa}}\right)\bigg/1.06 \qquad (1)$$

Next, we apply the Clausius-Clapeyron equation once again to find the volume change upon melting at 0 GPa: we take the product of the Clapeyron slope from Lord et al. (2010), 50 K/GPa, the entropy of fusion from Zaitsev et al. (1991), 18 J/mol K, and the density, 0.08 mol/cm^3, to find $\left(V_l - V_\varepsilon\right)/\left.V_\varepsilon\right|_{0GPa} = \Delta V\big/V_\varepsilon = \Delta S\frac{dT}{dP}\rho_\varepsilon = 0.07$. Since our data confirms the volume change of the crystal-crystal phase transition to be 5%, expression (1) is $(1 + 0.05/0.07)/1.06 = 1.6$, meaning we expect the slope of the melting curve of Lord et al. (2010) to change by at least 60% at the ε-B2-liquid triple point, a change well within the precision of the published melting curve, which shows no such kink.

Now we derive equation (1). Applying the Clapeyron relation to the slopes of the melting curve just above and just below the triple point, we find the ratio of slopes is

$$\frac{\left.\frac{dT}{dP}\right|_{+}}{\left.\frac{dT}{dP}\right|_{-}} = \frac{\Delta V_{l/B2}}{\Delta S_{l/B2}}\bigg/\frac{\Delta V_{l/\varepsilon}}{\Delta S_{l/\varepsilon}} = \frac{V_l - V_{B2}}{V_l - V_\varepsilon}\bigg/\frac{S_l - S_{B2}}{S_l - S_\varepsilon}$$

$$= \frac{V_l - V_\varepsilon + V_\varepsilon - V_{B2}}{V_l - V_\varepsilon}\bigg/\frac{S_l - S_\varepsilon + S_\varepsilon - S_{B2}}{S_l - S_\varepsilon}$$

$$= \left(1 + \frac{V_\varepsilon - V_{B2}}{V_l - V_\varepsilon}\right)\bigg/\left(1 + \frac{S_\varepsilon - S_{B2}}{S_l - S_\varepsilon}\right) \qquad (2)$$

Whereas this equation is exact at the triple point, we make two approximations to allow use of data at ambient pressure. Since liquids are typically more compressible than solids, the fractional change in volume upon melting at 30 GPa is less than the change at 0 GPa, meaning the numerator of expression (2) is at least $\left(1+\frac{\left(V_\varepsilon - V_{B2}\right)/\left.V_\varepsilon\right|_{30GPa}}{\left(V_l - V_\varepsilon\right)/\left.V_\varepsilon\right|_{0GPa}}\right)$ The denominator of (2) is approximately 1, because the boundary between ε and B2 phases is nearly vertical. Assuming the shallowest slope our data allow, 1200 K over 2 GPa (Fig. 1), a third use of the

Clausius- Clapeyron relation yields a change in entropy of 1.1 J/mol K, which is ~6% of the entropy of fusion reported by Zaitsev et al. (1991) at ambient pressure, making the denominator of expression (2) at most ~1.06. Substitution of both numerator and denominator yields equation (1).