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Electronic Supplementary Information for *Theoretical Insights into Non-Arrhenius Behaviors of Thermal Vacancies in Anharmonic Crystals*

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I. THE HETEROGENEITY OF DEFECTIVE FCC CRYSTALS

From the Leibfried-Ludwig theory [S1], we can encode structural information about the imperfect FCC system in

$$k_i^V = \frac{1}{2}\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\phi_{ij}}{dr_{ij}^2}\frac{r_{ij\alpha}^2}{r_{ij}^2}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\phi_{ij}}{dr_{ij}}\left(\frac{1}{r_{ij}}-\frac{r_{ij\alpha}^2}{r_{ij}^3}\right)-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\frac{r_{ij\alpha}^2}{r_{ij}^2}\right.$$
$$\left.-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(\frac{1}{r_{ij}}-\frac{r_{ij\alpha}^2}{r_{ij}^3}\right)+\frac{1}{4\rho_i^{3/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}}{r_{ij}}\right)^2\right], \tag{S1}$$

$$\gamma_{1i}^V = \frac{1}{48}\left\{\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^4\phi_{ij}}{dr_{ij}^4}\frac{r_{ij\alpha}^4}{r_{ij}^4}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^3\phi_{ij}}{dr_{ij}^3}\left(\frac{6r_{ij\alpha}^2}{r_{ij}^3}-\frac{6r_{ij\alpha}^4}{r_{ij}^5}\right)+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\phi_{ij}}{dr_{ij}^2}\left(\frac{15r_{ij\alpha}^4}{r_{ij}^6}-\frac{18r_{ij\alpha}^2}{r_{ij}^4}+\frac{3}{r_{ij}^2}\right)\right.$$
$$+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\phi_{ij}}{dr_{ij}}\left(-\frac{15r_{ij\alpha}^4}{r_{ij}^7}+\frac{18r_{ij\alpha}^2}{r_{ij}^5}-\frac{3}{r_{ij}^3}\right)-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^4\varphi_{ij}}{dr_{ij}^4}\frac{r_{ij\alpha}^4}{r_{ij}^4}-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^3\varphi_{ij}}{dr_{ij}^3}\left(\frac{6r_{ij\alpha}^2}{r_{ij}^3}-\frac{6r_{ij\alpha}^4}{r_{ij}^5}\right)$$
$$-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\left(\frac{15r_{ij\alpha}^4}{r_{ij}^6}-\frac{18r_{ij\alpha}^2}{r_{ij}^4}+\frac{3}{r_{ij}^2}\right)-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(-\frac{15r_{ij\alpha}^4}{r_{ij}^7}+\frac{18r_{ij\alpha}^2}{r_{ij}^5}-\frac{3}{r_{ij}^3}\right)$$
$$+\frac{3}{4\rho_i^{3/2}}\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\frac{r_{ij\alpha}^2}{r_{ij}^2}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(\frac{1}{r_{ij}}-\frac{r_{ij\alpha}^2}{r_{ij}^3}\right)\right]^2$$
$$+\frac{1}{\rho_i^{3/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}}{r_{ij}}\right)\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^3\varphi_{ij}}{dr_{ij}^3}\frac{r_{ij\alpha}^3}{r_{ij}^3}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\left(\frac{3r_{ij\alpha}}{r_{ij}^2}-\frac{3r_{ij\alpha}^3}{r_{ij}^4}\right)+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(-\frac{3r_{ij\alpha}}{r_{ij}^3}+\frac{3r_{ij\alpha}^3}{r_{ij}^5}\right)\right]$$
$$\left.-\frac{9}{4\rho_i^{5/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}}{r_{ij}}\right)^2\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\frac{r_{ij\alpha}^2}{r_{ij}^2}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(\frac{1}{r_{ij}}-\frac{r_{ij\alpha}^2}{r_{ij}^3}\right)\right]+\frac{15}{16\rho_i^{7/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}}{r_{ij}}\right)^4\right\}, \tag{S2}$$

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$$\gamma_{2i}^{V}=\frac{1}{8}\Bigg\{\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^4\phi_{ij}}{dr_{ij}^4}\frac{r_{ij\alpha}^2r_{ij\beta}^2}{r_{ij}^4}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^3\phi_{ij}}{dr_{ij}^3}\left(\frac{r_{ij\alpha}^2}{r_{ij}^3}+\frac{r_{ij\beta}^2}{r_{ij}^3}-\frac{6r_{ij\alpha}^2r_{ij\beta}^2}{r_{ij}^5}\right)+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\phi_{ij}}{dr_{ij}^2}\left(-\frac{3r_{ij\alpha}^2}{r_{ij}^4}-\frac{3r_{ij\beta}^2}{r_{ij}^4}+\frac{15r_{ij\alpha}^2r_{ij\beta}^2}{r_{ij}^6}+\frac{1}{r_{ij}^2}\right)$$
$$+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\phi_{ij}}{dr_{ij}}\left(\frac{3r_{ij\alpha}^2}{r_{ij}^5}+\frac{3r_{ij\beta}^2}{r_{ij}^5}-\frac{15r_{ij\alpha}^2r_{ij\beta}^2}{r_{ij}^7}-\frac{1}{r_{ij}^3}\right)-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^4\varphi_{ij}}{dr_{ij}^4}\frac{r_{ij\alpha}^2r_{ij\beta}^2}{r_{ij}^4}-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^3\varphi_{ij}}{dr_{ij}^3}\left(\frac{r_{ij\alpha}^2}{r_{ij}^3}+\frac{r_{ij\beta}^2}{r_{ij}^3}-\frac{6r_{ij\alpha}^2r_{ij\beta}^2}{r_{ij}^5}\right)$$
$$-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\left(-\frac{3r_{ij\alpha}^2}{r_{ij}^4}-\frac{3r_{ij\beta}^2}{r_{ij}^4}+\frac{15r_{ij\alpha}^2r_{ij\beta}^2}{r_{ij}^6}+\frac{1}{r_{ij}^2}\right)-\frac{1}{2\rho_i^{1/2}}\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(\frac{3r_{ij\alpha}^2}{r_{ij}^5}+\frac{3r_{ij\beta}^2}{r_{ij}^5}-\frac{15r_{ij\alpha}^2r_{ij\beta}^2}{r_{ij}^7}-\frac{1}{r_{ij}^3}\right)$$
$$+\frac{1}{4\rho_i^{3/2}}\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\frac{r_{ij\alpha}^2}{r_{ij}^2}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(\frac{1}{r_{ij}}-\frac{r_{ij\alpha}^2}{r_{ij}^3}\right)\right]\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\frac{r_{ij\beta}^2}{r_{ij}^2}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(\frac{1}{r_{ij}}-\frac{r_{ij\beta}^2}{r_{ij}^3}\right)\right]$$
$$+\frac{1}{2\rho_i^{3/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}}{r_{ij}}\right)\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^3\varphi_{ij}}{dr_{ij}^3}\frac{r_{ij\alpha}r_{ij\beta}^2}{r_{ij}^3}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\left(\frac{r_{ij\alpha}}{r_{ij}^2}-\frac{3r_{ij\alpha}r_{ij\beta}^2}{r_{ij}^4}\right)+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(-\frac{r_{ij\alpha}}{r_{ij}^3}+\frac{3r_{ij\alpha}r_{ij\beta}^2}{r_{ij}^5}\right)\right]$$
$$+\frac{1}{2\rho_i^{3/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\beta}}{r_{ij}}\right)\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^3\varphi_{ij}}{dr_{ij}^3}\frac{r_{ij\alpha}^2r_{ij\beta}}{r_{ij}^3}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\left(\frac{r_{ij\beta}}{r_{ij}^2}-\frac{3r_{ij\alpha}^2r_{ij\beta}}{r_{ij}^4}\right)+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(-\frac{r_{ij\beta}}{r_{ij}^3}+\frac{3r_{ij\alpha}^2r_{ij\beta}}{r_{ij}^5}\right)\right]$$
$$+\frac{1}{2\rho_i^{3/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\frac{r_{ij\alpha}r_{ij\beta}}{r_{ij}^2}-\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}r_{ij\beta}}{r_{ij}^3}\right)^2-\frac{3}{8\rho_i^{5/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}}{r_{ij}}\right)^2\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\frac{r_{ij\beta}^2}{r_{ij}^2}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(\frac{1}{r_{ij}}-\frac{r_{ij\beta}^2}{r_{ij}^3}\right)\right]$$
$$-\frac{3}{8\rho_i^{5/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\beta}}{r_{ij}}\right)^2\left[\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\frac{r_{ij\alpha}^2}{r_{ij}^2}+\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\left(\frac{1}{r_{ij}}-\frac{r_{ij\alpha}^2}{r_{ij}^3}\right)\right]$$
$$-\frac{3}{2\rho_i^{5/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}}{r_{ij}}\right)\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\beta}}{r_{ij}}\right)\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d^2\varphi_{ij}}{dr_{ij}^2}\frac{r_{ij\alpha}r_{ij\beta}}{r_{ij}^2}-\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}r_{ij\beta}}{r_{ij}^3}\right)$$
$$+\frac{15}{16\rho_i^{7/2}}\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\alpha}}{r_{ij}}\right)^2\left(\sum_{\substack{j\neq i\\ j\neq l}}^{N}\frac{d\varphi_{ij}}{dr_{ij}}\frac{r_{ij\beta}}{r_{ij}}\right)^2\Bigg\}, \tag{S3}$$

$$\phi_{ij}=\varepsilon\left(\frac{a}{r_{ij}}\right)^n,\quad \varphi_{ij}=4\varepsilon^2c^2\left(\frac{a}{r_{ij}}\right)^m,\quad \rho_i=\sum_{\substack{j\neq i\\ j\neq l}}^{N}\varphi_{ij}. \tag{S4}$$

Here, blue terms arise from the breakdown of FCC symmetry. It is conspicuous that k_i^V, γ_{1i}^V, and γ_{2i}^V depend on the relative position between the ith and lth lattice sites. Therefore, each atom has a different set of coupling parameters. This interesting characteristic cannot be found in perfect FCC structures.

To further clarify the heterogeneous nature, we apply Equations (S1)-(S4) to the 1st and 2nd neighbors of the point defect. As shown in Figure S1, while numerical results for 2nd neighbors are very close to ideal values, those for 1st ones are significantly lower. These discrepancies imply that the vacancy formation is dominated by the local dynamics. Our conclusion is consistent with recent DFT studies [S2,S3].

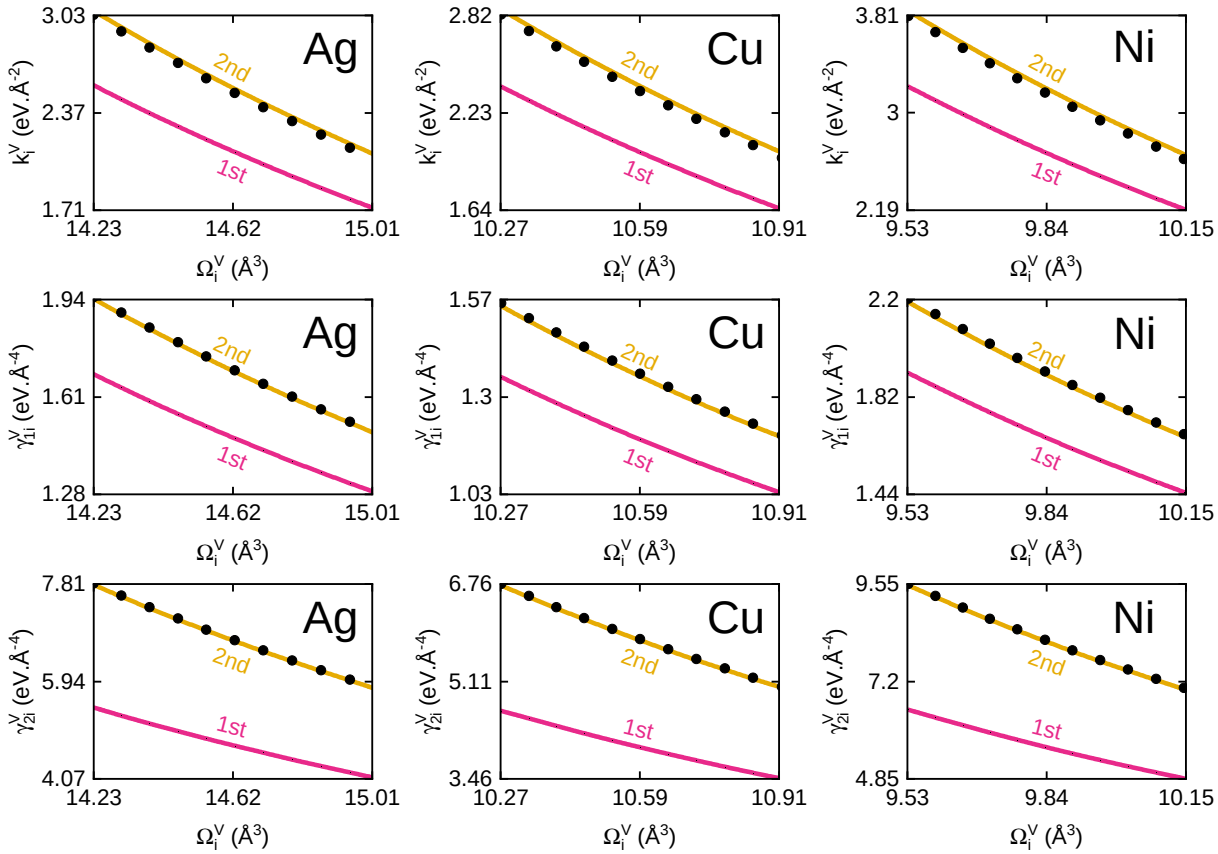

FIG. S1: (Color online) Coupling parameters versus atomic volumes in perfect (filled symbols) and imperfect (solid lines) FCC metals.

II. THE EXTENSION OF SMM ANALYSES FOR BCC SYSTEMS

According to Finnis and Sinclair [S4], the cohesion in BCC metals can be appropriately described by

$$E_i = \sum_{j\neq i}^{N} (r_{ij}-c)^2 \left(c_0 + c_1 r_{ij} + c_2 r_{ij}^2\right) - 2A\sqrt{\sum_{j\neq i}^{N}\left[(r_{ij}-d)^2 + \frac{B}{d}(r_{ij}-d)^3\right]}. \tag{S5}$$

The first part of Equation (S5) denotes pairwise interactions, whereas the second part represents many-body effects. Finnis-Sinclair parameters (c, c_0, c_1, c_2, A, d, B) were determined in Ref.[S4] via experimental data for the lattice constant, the cohesive energy, and the elastic modulus.

Based on the Finnis-Sinclair potential, we consider the thermal evolution of vacancies in two typical refractory materials, Mo and W. Remarkably, the loss of BCC symmetry leads to the emergence of a new coupling parameter, which is

$$\beta_i^V = \frac{1}{2}\left(\frac{\partial^3 E_i^V}{\partial u_{i\alpha}^V \partial u_{i\beta}^V \partial u_{i\eta}^V}\right)_{eq}, \tag{S6}$$

where $u_{i\alpha}^V$ is the atomic displacement along the α axis ($\alpha \neq \beta \neq \eta = x, y, z$). Equation (S6) enables us to add odd-order contributions to the anharmonic free energy as [S5]

$$F_i^{V(ANH)} = 3\left(\int_0^{\gamma_{1i}^V} \langle u_i^{V4}\rangle d\gamma_{1i}^V + \int_0^{\gamma_{2i}^V} \langle u_i^{V2}\rangle^2 d\gamma_{2i}^V + \int_0^{\beta_i^V} \langle u_i^{V2}\rangle\langle u_i^V\rangle d\beta_i^V\right). \tag{S7}$$

Therefore, at high temperatures $\left(x_i \coth x_i \approx x_i^V \coth x_i^V \approx 1\right)$, the Gibbs energy of vacancy formation is given by

$$G^f = \sum_{i \neq l}^{N} \left\{ \frac{1}{2}\left(E_i^V - E_i\right) + \frac{3}{2}\theta \ln\left(\frac{k_i^V}{k_i}\right) + 3\theta^2 \left[\frac{\gamma_{2i}^V - \gamma_{1i}^V}{K_i^{V2}} - \frac{\gamma_{2i} - \gamma_{1i}}{k_i^2} + \left(\frac{\gamma_i^V}{K_i^{V3}}\right)^{\frac{1}{2}} \frac{\beta_i^V}{K_i^V} \right] \right.$$
$$\left. + \; 3\theta^3 \left[\frac{4\left(\gamma_{2i}^{V2} - 3\gamma_{1i}^{V2} - 6\gamma_{1i}^V \gamma_{2i}^V\right)}{K_i^{V4}} - \frac{4\left(\gamma_{2i}^2 - 3\gamma_{1i}^2 - 6\gamma_{1i}\gamma_{2i}\right)}{k_i^4} + \left(\frac{\gamma_i^V}{K_i^{V3}}\right)^{\frac{3}{2}} \beta_i^V + \frac{2k_i^V \gamma_i^V}{K_i^{V6}} \beta_i^{V2} \right] \right\}, \qquad \text{(S8)}$$

where $\gamma_i^V = 4\left(\gamma_{1i}^V + \gamma_{2i}^V\right)$ and $K_i^V = k_i^V - \beta_i^{V2}/3\gamma_i^V$. As illustrated in Figure S2, the odd-order anharmonicity in defective BCC crystals is very large. This event naturally explains why G^f plunges nonlinearly during heating. A strong correlation among asymmetric properties, anharmonic excitations, and non-Arrhenius behaviors is highlighted. Our SMM calculations agree quantitatively well with the latest atomistic simulations [S6,S7].

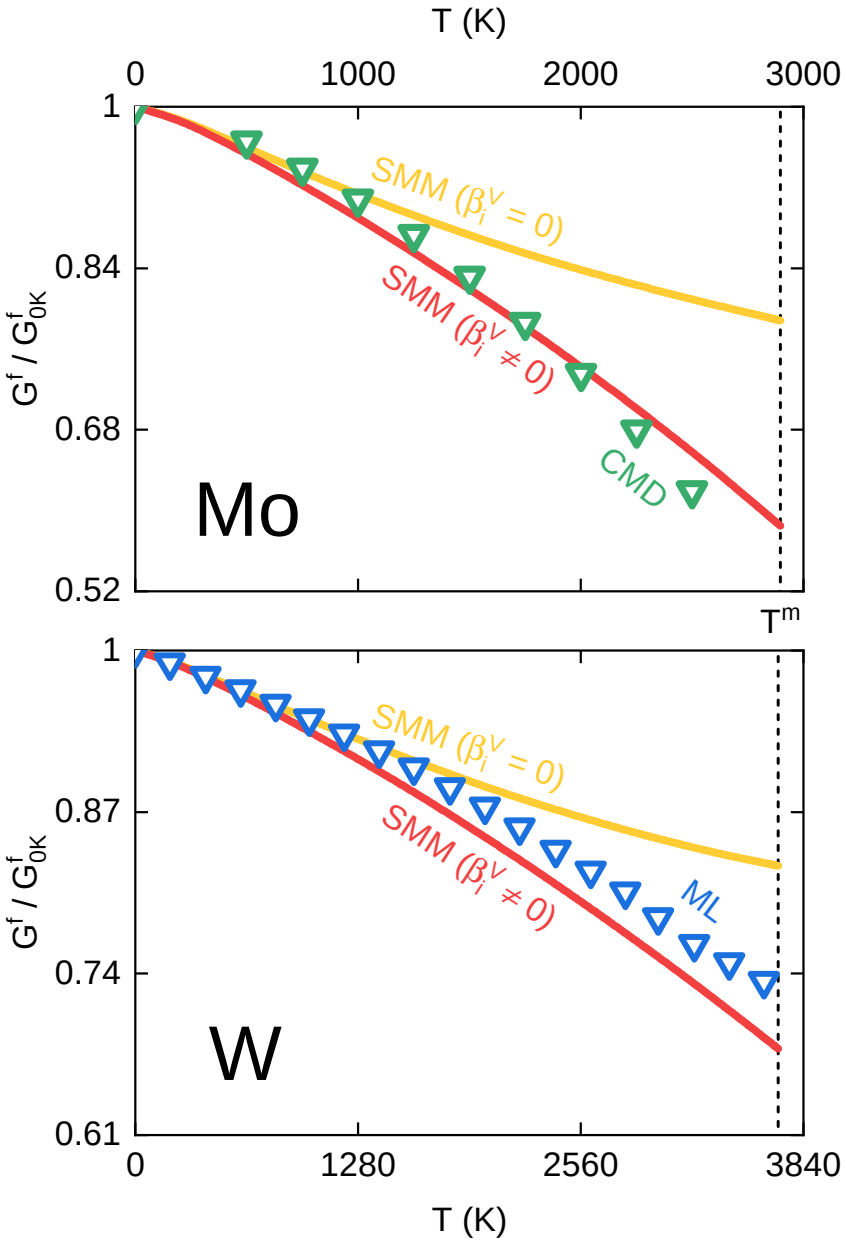

FIG. S2: (Color online) SMM analyses (solid lines) and CMD/ML computations [S6,S7] (open symbols) for the scaled Gibbs energy of vacancy formation in Mo and W.

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