The following appendices from:

Molecular Crystal Global Phase Diagrams:

I. Method of Construction

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have been placed in the supplemental information repository to save space in the printed version of the journal.

Appendix A.
Spherical Tensor Coupling

Equation (13) in Sec. 2.3. uses slightly different basis functions, couplings, and normalizations than our references so a full derivation is presented here. To couple $\{D^{\ell_i}_{m_i n_i}, C^{\ell}_m, D^{\ell_j}_{m_j n_j}\}$ where (Varshalovich et $al.$, 1988)

$$D^{\ell}_{mn}(\boldsymbol{\omega}_i) = \exp\left(-im\alpha_i\right) d^{\ell}_{mn}(\beta_i) \exp\left(-in\gamma_i\right) \tag{60}$$

$$d^{\ell}_{mn}(\beta_i) = \sum_{k=\max(0,m-n)}^{\min(\ell+m,\ell-n)} (-1)^k$$

$$\times \frac{\left[(\ell+m)!\,(\ell-m)!\,(\ell+n)!\,(\ell-n)!\right]^{1/2}}{k!\,(\ell+m-k)!\,(\ell-n-k)!\,(n-m+k)!}$$

$$\times \left[\cos(\beta_i/2)\right]^{2\ell+m-n-2k} \left[\sin(\beta_i/2)\right]^{2k-m+n} \tag{61}$$

$$C^{\ell}_m(\boldsymbol{\Omega}_{ij}) = \sqrt{\frac{4\pi}{2\ell+1}} Y^{\ell}_m(\boldsymbol{\Omega}_{ij}), \tag{62}$$

we first couple angular basis functions of molecules i and j

$$A^{\ell_{(ij)}}_{m_{(ij)}} = \sum_{m_i m_j} C^{\ell_{(ij)}m_{(ij)}}_{\ell_i m_i,\ell_j m_j} D^{\ell_i}_{m_i n_i} D^{\ell_j}_{m_j n_j} \tag{63}$$

where $C^{\ell_{(ij)}m_{(ij)}}_{\ell_i m_i,\ell_j m_j}$ is a Clebsch-Gordan coefficient (Varshalovich et $al.$, 1988). Coupling $A^{\ell_{(ij)}}_{m_{(ij)}}$ to the $C^{\ell}_m(\boldsymbol{\Omega}_{ij})$ and requiring the overall state to be a scalar W we obtain

$$W^{n_i n_j}_{\ell_i \ell \ell_j} = \sum_{m m_{(ij)}} C^{00}_{\ell m,\ell_{(ij)}m_{(ij)}} A^{\ell_{(ij)}}_{m_{(ij)}} C^{\ell}_m \tag{64}$$

By definition the Clebsch-Gordan coefficient $C^{\ell m}_{\ell_1 m_1, \ell_2 m_2}$ is zero unless $m_1 + m_2 = m$ so that $m_2 = -m_1$ if $m = 0$. It is also zero unless $|\ell_1 - \ell_2| \leq \ell \leq \ell_1 + \ell_2$, and since $m_{1,2} \in \{\ell_{1,2} ... - \ell_{1,2}\}$ this implies that $\ell_1 = \ell_2$. Thus $C^{00}_{\ell m, \ell_{(ij)} m_{(ij)}}$ in Eq. (64) simplifies to $C^{00}_{\ell m, \ell \overline{m}}$. With the identity (Varshalovich *et al.*, 1988)

$$C^{00}_{\ell m, \ell \overline{m}} = \frac{(-1)^{\ell + m}}{\sqrt{2\ell + 1}} \tag{65}$$

we have

$$W^{n_i n_j}_{\ell_i \ell \ell_j} = \sum_{m_i m m_j} C^{\ell \overline{m}}_{\ell_i m_i, \ell_j m_j} \frac{(-1)^{\ell + m}}{\sqrt{2\ell + 1}} D^{\ell_i}_{m_i n_i} C^{\ell}_m D^{\ell_j}_{m_j n_j} \tag{66}$$

Likewise using the identity (Varshalovich *et al.*, 1988)

$$C^{\ell \overline{m}}_{\ell_i m_i, \ell_j m_j} = (-1)^{\ell_i - \ell_j - m} \sqrt{2\ell + 1} \begin{pmatrix} \ell_i & \ell_j & \ell \\ m_i & m_j & m \end{pmatrix} \tag{67}$$

gives

$$W^{n_i n_j}_{\ell_i \ell \ell_j} = \sum_{m_i m m_j} (-1)^{\ell_i - \ell_j + \ell} \begin{pmatrix} \ell_i & \ell_j & \ell \\ m_i & m_j & m \end{pmatrix} D^{\ell_i}_{m_i n_i} C^{\ell}_m D^{\ell_j}_{m_j n_j}. \tag{68}$$

To remove the phase factor one may exploit the mirror symmetry of the 3jm symbol

$$\begin{pmatrix} \ell_i & \ell_j & \ell \\ m_i & m_j & m \end{pmatrix} = (-1)^{\ell_i + \ell_j + \ell} \begin{pmatrix} \ell_i & \ell & \ell_j \\ m_i & m & m_j \end{pmatrix} \tag{69}$$

leaving

$$W^{n_i n_j}_{\ell_i \ell \ell_j} = \sum_{m_i m m_j} \begin{pmatrix} \ell_i & \ell & \ell_j \\ m_i & m & m_j \end{pmatrix} D^{\ell_i}_{m_i n_i} C^{\ell}_m D^{\ell_j}_{m_j n_j}. \tag{70}$$

Equation (70) gives basis functions W without any symmetry adaptation. They are the starting point for construction of symmetry-adapted basis functions in Sec. 2.3..

Appendix B.
Projection Operators

Symmetries of the molecule and Wyckoff point of the crystal exist within $D^{\ell_i}_{m_i, n_i}$ simultaneously and can be obtained by applying projection operators (Bradley &

Cracknell, 1972; Fassler & Stiefel, 1992; Fernando *et al.*, 1994; Schmidt & Zdanska, 2000)

$$P_{n_\tau n_\tau}^\tau = \sqrt{d_\tau/|G|} \sum_{g \in G} D_{n_\tau n_\tau}^{\tau*}(g) \, g \tag{71}$$

where d_τ is the dimension of the IR τ belonging to the group G of order $|G|$, $\boldsymbol{D}^\tau$ is the matrix onto which the IR maps g, and subsequent orthonormalization is occasionally required. We have used a slightly different normalization which decreases the computation in this orthonormalization. Acting upon the elements D_{mn}^ℓ gives

$$P_{n_\tau n_\tau}^\tau \circ D_{mn}^\ell = \sum_n D_{mn}^\ell S_{nn_\tau}^\ell \tag{72}$$

producing a linear combination with the symmetry of τ. The coefficients $S_{nn_\tau}^\ell$ form a sparse unitary matrix.

Appendix C.
Variational Mean Field Theory

To obtain the form of the fields $\boldsymbol{h}_i$ that gives the optimum approximation to the Helmholtz free energy, we use a variational approach and the Gibbs-Bogoliubov inequality (Girardeau & Mazo, 1974),

$$A \le A^{\mathrm{mf}} + \left\langle V - V^{\mathrm{mf}} \right\rangle , \tag{73}$$

where $\langle \cdots \rangle$ denotes the thermodynamic average over the mean field–weighted system configurations. Re-expressing Eq. (73) in terms of the partition function via Eq. (2) yields

$$Z \ge Z^{\mathrm{mf}} \exp \left(- \left\langle V - V^{\mathrm{mf}} \right\rangle / kT \right) . \tag{74}$$

To make this bound as tight as possible, we choose $\boldsymbol{h}_i$ such that the right-hand side of Eq. (74) is maximized with respect to each component of $\boldsymbol{h}_i$. This gives a set of simultaneous equations for the fields with the one non–trivial solution

$$\boldsymbol{h}_i = \sum_j \boldsymbol{K}_{ij} \cdot \langle \boldsymbol{U}_j \rangle . \tag{75}$$

Thus the associated mean field potential in Eq. (21) is given by

$$V^{\mathrm{mf}}/kT = \sum_{ij} \boldsymbol{U}_i \cdot \boldsymbol{K}_{ij} \cdot \langle \boldsymbol{U}_j \rangle \ . \tag{76}$$

Upon substitution of Eq. (21) into Eq. (10), Z_{or} is separable, so that

$$Z_{\mathrm{or}} \approx Z_{\mathrm{or}}^{\mathrm{mf}} = z_{\mathrm{rot}}^N \prod_i z_i \ . \tag{77}$$

Substituting Eqs. (20) and (22) into the Gibbs-Bogoliubov relation [Eq. (73)], the variational Helmholtz free energy as

$$A_{\mathrm{or}} \le A_{\mathrm{or}}^{\mathrm{var}} = -kT \ln Z_{\mathrm{or}}^{\mathrm{mf}} - \frac{kT}{2} \sum_{ij} \langle \boldsymbol{U}_i \rangle \cdot \boldsymbol{K}_{ij} \cdot \langle \boldsymbol{U}_j \rangle \tag{78}$$

as given in Section 2.4..

Appendix D.
Space Group Irreducible Representations

In the thermodynamic limit $N \to \infty$ a space group G consists of an infinite number of Wigner-Seitz elements $\{\phi|\boldsymbol{t}\}$ where ϕ is a rotation followed by a translation $\boldsymbol{t}$. Each space group possesses an invariant Abelian subgroup $\mathcal{T}$, the group of primitive translations $t_i = \{\epsilon|\boldsymbol{t}_i\}$ where ϵ is the identity rotation. The representations of its IR's are $e^{i\boldsymbol{k}\cdot\boldsymbol{t}_i}$ where $\boldsymbol{k}$ is a reciprocal space lattice vector which indexes all inequivalent IR's in the first Brillouin zone (Miller & Love, 1967; Zak *et al.*, 1969; Bradley & Cracknell, 1972; Kovalev *et al.*, 1993; Tolédano & Dmitriev, 1996).

The set of rotations ϕ forms a group called the point group of the crystal $\hat{G}$. Applying the operations of $\hat{G}$ to a given $\boldsymbol{k}_1$ transforms it to $\boldsymbol{k}_2, \dots \boldsymbol{k}_n$ mod a reciprocal lattice vector where n is the order of $\hat{G}$. Some rotations in $\hat{G}$ leave $\boldsymbol{k}_1$ invariant and so form $\hat{G}(\boldsymbol{k}_1)$, the *point group of $\boldsymbol{k}_1$*. The set of elements $\{\phi|\boldsymbol{t}\}$ associated with rotations in $\hat{G}(\boldsymbol{k}_1)$ forms $G(\boldsymbol{k}_1)$, the *space group of $\boldsymbol{k}_1$*. The set of *inequivalent* vectors in $\{\boldsymbol{k}_1, \boldsymbol{k}_2, \dots, \boldsymbol{k}_n\}$ generated by the application of $\hat{G}$ forms the *star* of $\boldsymbol{k}_1$ which we

denote $\boldsymbol{s}$. Each $\boldsymbol{k}_i$ in $\boldsymbol{s}$ is an arm of the star. If a vector $\boldsymbol{k}_1$ terminates at a point such that other vectors $\boldsymbol{k}_2$ terminating in the neighborhood of that point have point groups $\hat{G}(\boldsymbol{k}_2) \subset \hat{G}(\boldsymbol{k}_1)$ the point of termination of $\boldsymbol{k}_1$ is a high-symmetry point in the Brillouin zone. Analogous definitions follow for high-symmetry lines/planes.

High-symmetry point IR's (and occasionally those of lines) play a pivotal role in phase transitions so we discuss their construction in some detail. The IR's of $G(\boldsymbol{k}_1)$ map elements $g \in G(\boldsymbol{k})$ to matrices $\boldsymbol{D}^{\boldsymbol{k}_1}$ indexed by a k-vector and IR's of G to matrices $\boldsymbol{D}^{\boldsymbol{s}}$ indexed by a star. Although $G(\boldsymbol{k}_1)$ is a space group like G, its IR's are simpler and finite in number because they leave $\boldsymbol{k}_1$ invariant mod a reciprocal lattice vector. The $\boldsymbol{D}^{\boldsymbol{s}}$ can be constructed from the $\boldsymbol{D}^{\boldsymbol{k}_1}$ in two cases: (1) $\boldsymbol{k}_1$ is any vector *inside* the Brillouin zone or is any vector of the Brillouin zone and G is symmorphic. In this case

$$\boldsymbol{D}^{\boldsymbol{k}_1}(\{\phi|\boldsymbol{t}\}) = \boldsymbol{\pi}(\phi)\, e^{-i\boldsymbol{k}_1 \cdot \boldsymbol{t}} \tag{79}$$

where $\boldsymbol{\pi}(\phi)$ is an IR of $\hat{G}(\boldsymbol{k}_1)$. (2) $\boldsymbol{k}_1$ is any vector on the *surface* of the Brillouin zone and G is nonsymmorphic. In this case the $\boldsymbol{D}^{\boldsymbol{k}_1}(\{\phi|\boldsymbol{t}\})$ are finite in number and have been tabulated for all space groups and relevant $\boldsymbol{k}_1$ (Miller & Love, 1967; Kovalev *et al.*, 1993).

Full group IR's are $s \times s$ matrices of blocks containing $G(\boldsymbol{k})$ IR's. To construct these we decompose G with respect to its subgroup $G(\boldsymbol{k})$

$$G = G(\boldsymbol{k}) + \{\phi_2|\boldsymbol{t}_2\}G(\boldsymbol{k}) + \ldots + \{\phi_\sigma|\boldsymbol{t}_\sigma\}G(\boldsymbol{k}) + \ldots \tag{80}$$

and define the notational device

$$\dot{\boldsymbol{D}}^{\boldsymbol{k}}(\{\phi_p|\boldsymbol{t}_p\}) = \begin{cases} \boldsymbol{0} & \text{if } \{\phi_p|\boldsymbol{t}_p\} \text{ is not in } G(\boldsymbol{k}) \\ \boldsymbol{D}^{\boldsymbol{k}}(\{\phi_p|\boldsymbol{t}_p\}) & \text{if } \{\phi_p|\boldsymbol{t}_p\} \text{ is in } G(\boldsymbol{k}). \end{cases} \tag{81}$$

Thus if $\{\phi_p|\boldsymbol{t}_p\}$ is an arbitrary element of G, $\{\phi_\sigma|\boldsymbol{t}_\sigma\}$ and $\{\phi_\tau|\boldsymbol{t}_\tau\}$ are elements of $G/G(\boldsymbol{k})$, and $\{\phi_c|\boldsymbol{t}_c\}$ is and element of $G(\boldsymbol{k})$, we let $\{\phi_p|\boldsymbol{t}_p\} \circ \{\phi_\tau|\boldsymbol{t}_\tau\}$ be in the coset

$\{\phi_\sigma|\boldsymbol{t}_\sigma\}G(\boldsymbol{k})$ so that

$$\{\phi_p|\boldsymbol{t}_p\} \circ \{\phi_\tau|\boldsymbol{t}_\tau\} = \{\phi_\sigma|\boldsymbol{t}_\sigma\} \circ \{\phi_c|\boldsymbol{t}_c\} \tag{82}$$

$$\{\phi_\sigma|\boldsymbol{t}_\sigma\}^{-1} \circ \{\phi_p|\boldsymbol{t}_p\} \circ \{\phi_\tau|\boldsymbol{t}_\tau\} = \{\phi_c|\boldsymbol{t}_c\} \tag{83}$$

where the right hand side of the second equality is any element in $G(\boldsymbol{k})$. Using Eq. (81) we have an expression for the blocks of $\boldsymbol{D^s}$

$$\boldsymbol{D}^{\boldsymbol{s}}_{\sigma\tau}(\{\phi_c|\boldsymbol{t}_c\}) = \dot{\boldsymbol{D}}^{\boldsymbol{k}}(\{\phi_\sigma|\boldsymbol{t}_\sigma\}^{-1} \circ \{\phi_p|\boldsymbol{t}_p\} \circ \{\phi_\tau|\boldsymbol{t}_\tau\}) \tag{84}$$

so that the only nonzero block along the σ-th row and τ-th column occurs if $\phi_p \circ \phi_\tau \circ \boldsymbol{k} = \phi_\sigma \circ \boldsymbol{k}$.

We now show the $\boldsymbol{Q^s}$ transform like space group IR's (Birman, 1984). Upon Fourier transforming the potential in Eq. (26) the action of $\mathcal{T}$ on $\boldsymbol{U^k}$ induces a 1×1 matrix representation:

$$t_i \circ \boldsymbol{U^k} = \boldsymbol{U^k} e^{i\boldsymbol{k}\cdot\boldsymbol{t}_i}. \tag{85}$$

Diagonalizing $\boldsymbol{K^k}$ gives basis functions which transform like IR's of $G(\boldsymbol{k})$

$$g \circ Q^{\boldsymbol{k}}_{p_\tau} = \sum_{r_\tau} Q^{\boldsymbol{k}}_{r_\tau} D^{\boldsymbol{k}}_{r_\tau p_\tau}(g) \ \ \forall \ g \in G(\boldsymbol{k}). \tag{86}$$

As the full group IR's are constructed in blocks from those of $G(\boldsymbol{k})$ which rotate among themselves, and the action of $\{\phi_\sigma|\boldsymbol{t}_\sigma\}$

$$\{\phi_\sigma|\boldsymbol{t}_\sigma\} \circ Q^{\boldsymbol{k}}_{p_\tau} = Q^{\phi_\sigma \circ \boldsymbol{k}}_{p_\tau} \tag{87}$$

also rotates the basis functions in the same way as $\boldsymbol{D^s}$, Eqs. (84)-(87) combine to show the action of G on $\boldsymbol{Q^s}$ induces a matrix representation

$$g \circ Q^{\boldsymbol{s}}_{p_\tau} = \sum_{r_\tau} Q^{\boldsymbol{s}}_{r_\tau} D^{\boldsymbol{s}}_{r_\tau p_\tau}(g) \tag{88}$$

so that the $\boldsymbol{Q^s}$ are basis functions of a crystallographic IR space.

Appendix E.
Space-Time Symmetry

Space group IR's are of three types (Maradudin & Vosko, 1968; Bradley & Cracknell, 1972; Birman, 1984; Cornwell, 1984). Type 1, or potentially real, IR's can be brought to real form by a similarity transformation. Type 2, or pseudoreal, IR's cannot be brought to real form but can be brought to their complex conjugates. Their characters are real. Type 3, or complex, IR's cannot be brought to real form or their complex conjugates. Their characters are complex. However, as a complex space-group IR can always be made real we take the direct sum of the IR with its complex conjugate and bring the resulting representation into real form with a similarity transformation (Stokes *et al.*, 1991). Thus for a type 1 IR τ we form the physically irreducible representation by simply taking a similarity transform to make the representation real

$$\mathbf{S}^{-1} \cdot \boldsymbol{D}^{\tau}_{phys} \cdot \mathbf{S} = \boldsymbol{D}^{\tau}. \tag{89}$$

For a type 2 IR τ which is equivalent to its complex conjugate we use

$$\mathbf{S}^{-1} \cdot \boldsymbol{D}^{\tau\oplus\tau}_{phys} \cdot \mathbf{S} = \begin{pmatrix} \boldsymbol{D}^{\tau} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{D}^{\tau} \end{pmatrix}. \tag{90}$$

For type 3 IR's κ and σ which are not equivalent to their complex conjugates we have

$$\mathbf{S}^{-1} \cdot \boldsymbol{D}^{\kappa\oplus\sigma}_{phys} \cdot \mathbf{S} = \begin{pmatrix} \boldsymbol{D}^{\kappa} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{D}^{\sigma*} \end{pmatrix}. \tag{91}$$

These transformations often involve linear combinations of the $e^{i\boldsymbol{k}\cdot\boldsymbol{t}}$ factors in the set of $\boldsymbol{D}^{\tau}$ to give real $\boldsymbol{K}^{\boldsymbol{k}}$ and $\boldsymbol{U}^{\boldsymbol{k}}$ which transform like physically irreducible representations.

Appendix F.
Linear Response in Mean Field Theory

To evaluate the stability of a candidate equilibrium configuration of the crystal, we consider the second derivatives with respect to the variables representing the orientations of the molecules, *i.e.*, the order parameters. To facilitate the necessary calculations, we examine how the free energy changes in response to an external field with the system initially in equilibrium.

Consider the response of the order parameters $\langle \boldsymbol{U} \rangle$ in the mean-field system to an infinitesimal external perturbation in the fields $\boldsymbol{h}^{\text{ext}}$, so that

$$\boldsymbol{h} = \boldsymbol{h}^{\text{int}} + \boldsymbol{h}^{\text{ext}}, \tag{92}$$

where $\boldsymbol{h}^{\text{int}} \equiv \{\boldsymbol{h}_1^{\text{int}}, \ldots, \boldsymbol{h}_N^{\text{int}}\}$ is the set of fields from the unperturbed system, as defined in Eq. (75). As explained in Section 2.4., N may be limited to the number of molecules within the kernel of a high–symmetry IR. The $\boldsymbol{h}^{\text{ext}}$ is introduced solely so that $\boldsymbol{h}$ can be perturbed without changing the internal fields $\boldsymbol{h}^{\text{int}}$. It is set to zero later.

Since the field perturbation is infinitesimal, the response is linear with respect to the external fields (Chaikin & Lubensky, 1995),

$$\delta \langle \boldsymbol{U} \rangle = \boldsymbol{\chi} \cdot \delta \boldsymbol{h}^{\text{ext}} = \boldsymbol{\chi}^o \cdot \delta \boldsymbol{h}, \tag{93}$$

where

$$\boldsymbol{\chi} \equiv \frac{\partial \langle \boldsymbol{U} \rangle}{\partial \boldsymbol{h}^{\text{ext}}} \quad \text{and} \quad \boldsymbol{\chi}^o \equiv \frac{\partial \langle \boldsymbol{U} \rangle}{\partial \boldsymbol{h}}\bigg|_o, \tag{94}$$

$\boldsymbol{U} \equiv \{\boldsymbol{U}_1, \ldots, \boldsymbol{U}_N\}$, and the "$o$" indicates the unperturbed system, in which $\boldsymbol{h}^{\text{ext}} = 0$. This assumption of linear response is also called the "random phase approximation" in the literature of many-body problems in Fermi systems (Pines, 1997).

Using Eqs. (75) and (92)-(93), the order parameter response becomes

$$\delta \langle \boldsymbol{U} \rangle = \boldsymbol{\chi}^o \cdot \left(\boldsymbol{K} \cdot \delta \langle \boldsymbol{U} \rangle + \delta \boldsymbol{h}^{\text{ext}} \right), \tag{95}$$

where

$$
\boldsymbol{K} \equiv
\begin{bmatrix}
\boldsymbol{K}_{1,1} & \boldsymbol{K}_{1,2} & \cdots & \boldsymbol{K}_{1,N} \\
\boldsymbol{K}_{2,1} & \boldsymbol{K}_{2,2} & \cdots & \boldsymbol{K}_{2,N} \\
\vdots & \vdots & \ddots & \vdots \\
\boldsymbol{K}_{N,1} & \boldsymbol{K}_{N,2} & \cdots & \boldsymbol{K}_{N,N}
\end{bmatrix},
\tag{96}
$$

and $\boldsymbol{K}_{i,n}$ here indicates a summation of pairwise coupling matrices [Eq. (18)] over all nearest neighbors of molecule type i that belong to type n within the kernel of the high–symmetry IR. Upon rearrangement,

$$
\delta\langle\boldsymbol{U}\rangle = \left(\boldsymbol{\chi}^o - \boldsymbol{K}^{-1}\right)\cdot\delta\boldsymbol{h}^{\text{ext}},
\tag{97}
$$

and taking the limit as the perturbation goes to zero,

$$
\lim_{\delta\to 0}\frac{\delta\langle\boldsymbol{U}\rangle}{\delta\boldsymbol{h}^{\text{ext}}} = \boldsymbol{\chi} = \boldsymbol{\chi}^o - \boldsymbol{K}^{-1}.
\tag{98}
$$

Thus the response of the order parameters in the presence of the external perturbation ($\boldsymbol{\chi}$) can be expressed in terms of the coupling matrices [Eq. (18)] and the unperturbed system response $\boldsymbol{\chi}^o$.

Evaluating the change in the free energy [Eq. (25)] with respect to the external field, we find that

$$
\frac{\partial A_{\text{or}}^{\text{var}}}{\partial\boldsymbol{h}^{\text{ext}}} = \langle\boldsymbol{U}\rangle,
\tag{99}
$$

which implies that the free energy obeys the thermodynamic differential relationship

$$
dA_{\text{or}}^{\text{var}} = -S\,dT + \sum_{i=1}^{N}\langle\boldsymbol{U}_i\rangle\cdot d\boldsymbol{h}_i^{\text{ext}}.
\tag{100}
$$

The thermodynamic potential that is a natural function of the order parameters $\langle\boldsymbol{U}\rangle$ and not of the external fields is obtained by performing a Legendre transformation (Chandler, 1987) on $A_{\text{or}}^{\text{var}}$. Thus we define a new free energy function F,

$$
F \equiv A_{\text{or}}^{\text{var}} - \sum_{i=1}^{N}\langle\boldsymbol{U}_i\rangle\cdot\boldsymbol{h}_i^{\text{ext}},
\tag{101}
$$

that obeys the desired thermodynamic differential relationship

$$
dF = -S\,dT - \sum_{i=1}^{N}\boldsymbol{h}_i^{\text{ext}}\cdot d\langle\boldsymbol{U}_i\rangle.
\tag{102}
$$

Taking the derivative of F with respect to the order parameters, we obtain

$$\frac{\partial F}{\partial \langle U \rangle} = -h^{\text{ext}}, \tag{103}$$

so that F is a function of T and the order parameters, as requested. Taking the second derivative of F,

$$\frac{\partial^2 F}{\partial \langle U \rangle \, \partial \langle U \rangle} = -\frac{\partial h^{\text{ext}}}{\partial \langle U \rangle} \equiv -(\chi)^{-1} = -(\chi^o)^{-1} + K, \tag{104}$$

using the result from Eq. (98). In the limit of vanishing external field, F reduces to the free energy A^{var},

$$\lim_{h^{\text{ext}} \to 0} F = A^{\text{var}}_{\text{or}}. \tag{105}$$

Therefore a crystal structure is stable (*i.e.*, $A^{\text{var}}_{\text{or}}$ is minimized) if the consistency relations are satisfied and the Hessian matrix in Eq. (104) is positive definite.

Appendix G.
Largest Order Parameter Approximation

At high symmetry points of the Brillouin zone the number of independent molecules in the kernel of the IR is manageable. While identifying the $P4_2/nmc$ phase, we had to consider the entire V-line with 256 independent molecules. This large number overwhelmed the codes developed to identify the phases. In this and similar cases a further approximation may be used. This is the largest OP approximation first introduced by James & Keenan (1959). As the fields and thermal average of the rotator functions may be rewritten

$$h_i = \sum_k \frac{e^{i k \cdot t_i}}{\sqrt{N}} E^k \cdot \Lambda^k \cdot \langle Q^k \rangle \tag{106}$$

$$\langle U_i \rangle = \sum_k \frac{e^{i k \cdot t_i}}{\sqrt{N}} E^k \cdot \langle Q^k \rangle, \tag{107}$$

we may approximate that only those $\langle Q^k \rangle$ belonging to the primary order parameter are nonzero. The eigenvalues may be set to zero except for those along the primary

IR and can be brought out of the summation

$$
\begin{aligned}
\boldsymbol{h}_i &= \boldsymbol{\Lambda}_{pri} \cdot \sum_{\boldsymbol{k}} \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{t}_i}}{\sqrt{N}} \boldsymbol{E}^{\boldsymbol{k}} \cdot \langle \boldsymbol{Q}^{\boldsymbol{k}} \rangle \\
&= \boldsymbol{\Lambda}_{pri} \cdot \langle \boldsymbol{U}_i \rangle,
\end{aligned}
\tag{108}
$$

giving only one set of consistency relations to solve for the base molecule

$$
\langle \boldsymbol{U}_0 \rangle = \frac{1}{z_0} \int \boldsymbol{U}_0 \, \exp(-\boldsymbol{U}_0 \cdot \boldsymbol{\Lambda}_{pri} \cdot \langle \boldsymbol{U}_0 \rangle) d(\boldsymbol{\omega}_0).
\tag{109}
$$

Two considerations prevent this technique from general use: (1) it is not as accurate because of the neglect of secondary OP's (2) these consistency relations do not converge as easily to the lowest free energy solution. For the V line there is no secondary OP and the convergence is rapid so that the technique is accurate and efficient.