Order Parameters for Reconstructive Phase Transitions

It was recently proposed by Dmitriev *et al.* (DRGT)[1] that the Landau theory of phase transitions can be extended to reconstructive transitions where large-scale displacements of the atoms take place. In these transitions there is no group-subgroup relation between the relevant phases; hence an expansion in powers of displacement around one phase does not guarantee, in general, the proper symmetry around the other phase.

DRGT propose that a certain nonlinear function $\eta(\xi)$ of the displacement ξ can serve as a nonlinear order parameter (NOP). The free energy F is then expanded in powers of η, although ξ is kept as the variational parameter. Thus $F[\eta(\xi)]$ has extrema not only at $\partial F/\partial\eta=0$, as imposed by the symmetry of the $\eta=0$ phase, but also at $\partial\eta/\partial\xi=0$, which can correspond to a high-symmetry phase at large ξ.

We propose here that the NOP is directly related to a density-wave expansion of F, which is a physically motivated, implicit, nonlinear function of ξ containing relevant information on the lattice discreteness.

A lattice in space $\mathbf{r}$ can be described by $\sum_{\mathbf{q}}\rho(\mathbf{q})\times\exp(i\mathbf{q}\cdot\mathbf{r})$, where $\mathbf{q}$ are reciprocal-lattice vectors. In the spirit of Alexander and McTague[2] only the Fourier coefficients $\rho(\mathbf{q})$ with the smallest $\mathbf{q}$ are important and a Landau expansion in powers of these $\rho(\mathbf{q})$ is possible.[2] We consider first $\mathbf{q}\neq 0$ transitions in which the number of atoms per unit cell can change. In particular, in the $\beta\to\omega$ transition,[1] each three consecutive (111) planes, spaced by $a/2\sqrt{3}$ in the β phase, shift in the [111] direction by the amounts 0, ξ, and $-\xi$, respectively. The density wave along $x \parallel [111]$ with $q=4\pi/\sqrt{3a}$ is then

$$\rho(x)=\exp\left[i\frac{4\pi x}{a\sqrt{3}}\right]\left\{1+\exp\left[i\frac{4\pi}{a\sqrt{3}}\left(\frac{a}{2\sqrt{3}}+\xi\right)\right]+\exp\left[i\frac{4\pi}{a\sqrt{3}}\left(\frac{a}{\sqrt{3}}-\xi\right)\right]\right\}=-2\exp\left[i\frac{4\pi}{a\sqrt{3}}\right]\left[\sin\left(\frac{4\pi\xi}{a\sqrt{3}}+\frac{\pi}{6}\right)-\frac{1}{2}\right]. \qquad (1)$$

The term in the last square brackets is *precisely* the NOP of this transition [Eq. (2) of DRGT]. Thus, an expansion in powers of this NOP is equivalent to an expansion in the density wave $\rho(x)$. Note, in particular, that a cubic term is allowed in F since $\rho^3(x)\sim\exp(i4\pi\sqrt{3}x/a)$ couples to a density wave of the β lattice; viz., this is an umklapp term. This formalism can be generalized to allow for unequal displacements with a sequence $0,\xi_1,-\xi_2$. The NOP is then defined as in Eq. (1) with ξ_1 ($-\xi_2$) replacing ξ ($-\xi$). For a given $\xi_1+\xi_2$ the NOP (as well as the cubic term of the free energy) has an extremum at $\xi_1=-\xi_2$, in agreement with the observed ω phase.[3]

Transitions at $\mathbf{q}=0$, i.e., strain is the primary order parameter, involve a shift of the whole reciprocal lattice. New symmetries are formed when the number of reciprocal wave vectors with equal length changes. The procedure for a $\mathbf{q}=0$ transition is therefore more involved in that for each path in phase space one has to choose the relevant density wave from an infinite set.

Consider the simplest case of a two-dimensional square lattice deforming continuously into a triangular lattice. A path in which the two shortest reciprocal wave vectors $\mathbf{q}_1,\mathbf{q}_2$ are kept equal, $|\mathbf{q}_1|=|\mathbf{q}_2|=q$, defines an angle γ between $\mathbf{q}_1$ and $\mathbf{q}_2$; $\gamma=\pi/2$ in the square lattice and becomes $\gamma=2\pi/3$ or $\gamma=\pi/3$ in the triangular lattice. Since $|\mathbf{q}_1\pm\mathbf{q}_2|\to q$ as $\gamma\to 2\pi/3$ (upper sign) or $\gamma\to\pi/3$ (lower sign) the density waves $\rho(\mathbf{q}_1\pm\mathbf{q}_2)$ are essential for describing this transition. Near the triangular lattice the waves with $\mathbf{q}_1\pm\mathbf{q}_2$ are less favored than those with $\mathbf{q}_1$ and $\mathbf{q}_2$ since their gradient energies are $\{\nabla\exp[i(\mathbf{q}_1\pm\mathbf{q}_2)\cdot\mathbf{r}]\}^2\sim(\mathbf{q}_1\pm\mathbf{q}_2)^2>q^2$. We are thus led to the order parameters

$$\eta_\pm=(|\mathbf{q}_1\pm\mathbf{q}_2|^2-q^2)/q^2=1\pm 2\cos\gamma. \qquad (2)$$

To interpolate between the $\pm$ symmetries one may choose $\eta=\eta_+\eta_-$, i.e.,

$$\eta=1-4\cos^2\gamma. \qquad (3)$$

This is a valid NOP since $\eta=0$ is the triangular lattice while $\partial\eta/\partial\gamma=0$ in the square one. The case $\gamma=0$, in which the plane becomes one dimensional, also has $\partial\eta/\partial\gamma=0$. DRGT considered a different $\mathbf{q}=0$ transition and found a periodic function of angle [Eq. (6) of Ref. 1], viz., the same type of NOP as Eq. (3). Note that the choice (3) is not unique since we have no microscopic reasoning for the step from (2) to (3); in fact the minimum-energy path may involve inhomogeneous strains. In this sense, the derivation of the $\mathbf{q}\neq 0$ NOP, as in our Eq. (1), is more fundamental.

Summarizing, a density-wave description of lattices and their displacive transformations can clarify the concept of a NOP.

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