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Configuration-Space Approach to the fcc to hcp Structural Transition

Ian Folkins and M. B. Walker
Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7
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The Shoji-Nishiyama mechanism prescribes a way of continuously distorting an fcc into an hcp structure. We show that the atomic displacements of this deformation mechanism can be considered as the sum of a modulation and a strain. A transition path between these two structures can therefore be characterized by a parametrization of the modulation and strain amplitudes. The free energy as a function of these two amplitudes is shown to be highly constrained and, in particular, is invariant under a two-dimensional space group.

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In a number of cases, an approximate description of a martensitic phase transition can be given in terms of a relatively small number of coordinates called configuration coordinates. For example, the Shoji-Nishiyama mechanism[1] shows how to continuously distort the face-centered-cubic (fcc) structure into the hexagonal-close-packed (hcp) structure. This distortion can be decomposed into two configuration coordinates, one describing a shearing of the crystal, and the other describing a sinusoidal relative displacement of planes of atoms (see Fig. 1). The principal object of this Letter is to show that the free energy of the crystal, when considered as a function of these configuration coordinates, displays a remarkable degree of symmetry. It will be important to exploit this symmetry when constructing a free-energy surface describing the phase transition.

Attempts have been made to construct a Landau theory of martensitic phase transitions. Here, one considers a given reference structure—say the fcc structure in the above example—and expands the free energy in powers of the departures of the configuration coordinates from their reference structure values. This procedure has the fatal difficulty that, although the free energy for configurations close to the fcc structure is well described by such an approach, no expansion having a finite number of terms will give a free energy which even has the correct symmetry at values of the configuration coordinates corresponding to the hcp structure. An example of such a Landau theory, which describes these difficulties, has been given by Gooding and Krumhansl[2] for the body-centered-cubic to 9*R* transition in lithium.

The difficulty just mentioned has been resolved in an interesting way by Dmitriev *et al.*[3] who, for Landau theories of several transitions, write the order parameter as a transcendental function of the (here only one) configuration coordinate. However, the justification for this is not based, as it will be for us, on the symmetries of the various structures which occur in the configuration space. In a later paper,[4] they find that their method is inapplicable, for example, to the fcc to hcp transition,

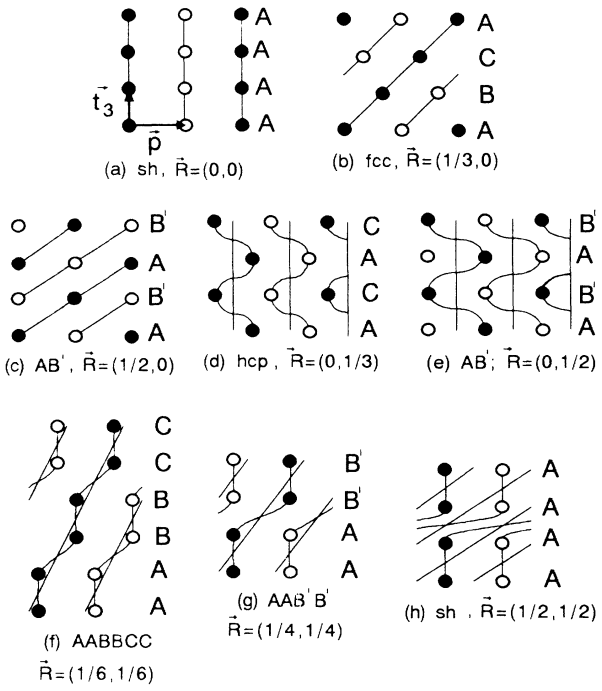

FIG. 1. This figure shows how the various structures in the (η,A) configuration space are derived from the simple hexagonal (sh) structure using the modulation and strain. The Bravais lattice vector $\mathbf{t}_3$ of the sh structure in (a) lies perpendicular to the hexagonal planes and is one-half the modulation wavelength. The orientation of the polarization vector $\mathbf{p}$ of the modulation, with respect to the hexagonal planes, is given in Fig. 3. Solid circles correspond to atoms in the plane of the figure, and open circles to $\frac{1}{2}\mathbf{t}_1$ above or below. The straight lines in each figure represent the effect of the strain, i.e., a vertical line means the shear strain is zero. The modulation, represented by the curved line, shifts planes alternately to the left or right of the positions they would occupy with the shear alone. The planes have been labeled according to their relative positioning along the $\mathbf{p}$ direction. Planes B, B', and C are displaced from A by amounts $\frac{2}{3}\mathbf{p}$, $\mathbf{p}$, and $\frac{5}{3}\mathbf{p}$, respectively. Structures AB', $AAB'B'$, and $AABBCC$ are labeled according to the stacking of their hexagonal planes.

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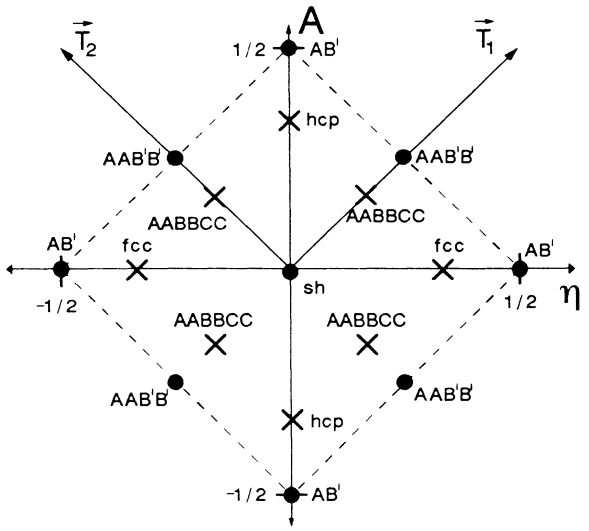

FIG. 2. The unit cell of the (η,A) configuration space. The free energy possesses at least inversion symmetry about structures represented by solid circles. Structures represented by crosses are associated with constraints on the derivatives of the free energy.

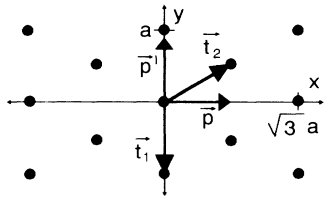

FIG. 3. The solid circles represent a hexagonal layer of a structure in the (η,A) configuration space. The vectors $\mathbf{t}_1,\mathbf{t}_2$, and $\mathbf{p},\mathbf{p}'$ are the Bravais lattice and polarization vectors which lie parallel to these planes.

and devise a different method of tackling this problem.

In defining the configuration coordinates which transform the fcc into the hcp structure, it is convenient to use the simple hexagonal (sh) structure as the reference structure. That is, the sh structure lies at the origin of the configuration space, while the fcc and hcp structures, among others, correspond to nonzero values of the configuration coordinates (see Fig. 2). The sh structure is composed of planes of atoms, arranged hexagonally, stacked directly on top of one another. The Bravais lattice vectors $\mathbf{t}_1$ and $\mathbf{t}_2$, which lie within the hexagonal planes, are shown in Fig. 3. The lattice vector $\mathbf{t}_3$ is perpendicular to the hexagonal planes and has length equal to the interplanar spacing. We note here that the c/a ratio does not enter the discussion below since it does not affect the symmetries of the states [except for the fcc structure, for which $c/a=(8/3)^{1/2}$].

The fcc structure can be generated from the sh structure by shearing its hexagonal planes along the $\hat{\mathbf{x}}$ direction. The hcp structure, on the other hand, can be generated from the sh structure by a modulation which shifts, with alternating sign, the hexagonal planes along the $\hat{\mathbf{x}}$ direction (see Fig. 1). The amplitudes of these two configuration coordinates will be referred to as η and A, respectively. The displacement of an atom from its position at $\mathbf{r}=n_1\mathbf{t}_1+n_2\mathbf{t}_2+n_3\mathbf{t}_3$ in the sh structure, associated with these two coordinates, can then be written as

$$\mathbf{u}(\eta,A,\mathbf{r})=2\eta n_3\mathbf{p}+A\mathbf{p}\cos(\mathbf{Q}\cdot\mathbf{r}). \quad (1)$$

The first term on the right-hand side refers to the shear. It moves each successive hexagonal plane by an additional $2\eta\mathbf{p}$, where $\mathbf{p}=\frac{1}{2}(\mathbf{t}_1+2\mathbf{t}_2)$ (see Fig. 3). The modulation, with wave vector $\mathbf{Q}=(\pi/c)(0,0,1)$, moves the hexagonal planes by, alternatively, $A\mathbf{p}$ or $-A\mathbf{p}$. Neither of the two configuration coordinates changes the ordering of atoms within a hexagonal plane, but only the relative positioning of the planes along the $\mathbf{p}$, or $\hat{\mathbf{x}}$, direction.

In addition to the fcc and hcp structures mentioned above, the two configuration coordinates can generate other special structures. By special we mean a structure whose space-group symmetry is higher than that of those with neighboring η and A. Figure 1 lists these structures and shows how each is generated from the sh structure by giving a cross section in the plane defined by $\mathbf{p}$ and $\mathbf{t}_3$. The remainder of this paper is primarily concerned with finding the constraints on $F(\eta,A)$, the free-energy density as a function of η and A.

Consider the structures with configuration coordinates $(\eta,0)$. Because the sh structure is a Bravais lattice, and because η is a homogeneous strain which does not destroy translational symmetry, these structures will also be Bravais lattices. Their Bravais lattice vectors $\mathbf{t}_i'$ are equal to the $\mathbf{t}_i$ except that $\mathbf{t}_3'=\mathbf{t}_3+2\eta\mathbf{p}$. Distort these structures by adding a modulation, so that (η,A) are the new configuration coordinates. If each atom is then translated by $\mathbf{t}_3'$, the resulting structure will be one having an identical η, but a modulation amplitude A reversed in sign. Hence,

$$F(\eta,A)=F(\eta,-A). \quad (2)$$

In addition to having mirror symmetry about $A=0$, $F(\eta,A)$ also has mirror symmetry about $\eta=0$. This is because structures (η,A) and $(-\eta,A)$ are related to each other by the glide-plane symmetry $\{\sigma_x|\mathbf{t}_3\}$ of the $(0,A)$ structure (this is the symmetry operation which reflects each atom about the plane perpendicular to $\hat{\mathbf{x}}$, and then translates it by $\mathbf{t}_3$):

$$F(\eta,A)=F(-\eta,A). \quad (3)$$

The constraints on the free energy given by Eqs. (2) and (3) can be formulated somewhat differently. Let $\mathbf{R}=(\eta,A)$, and define $[\sigma_A|0]\mathbf{R}=(\eta,-A)$ and $[\sigma_\eta|0]\mathbf{R}=(-\eta,A)$. From Eqs. (2) and (3), the free energy $F(\mathbf{R})$ is invariant under these two operations. The free energy is also invariant under translations of $\mathbf{R}$. From

Fig. 2, $\mathbf{R}=(\frac{1}{2},\frac{1}{2})$ as well as $\mathbf{R}=(0,0)$ corresponds to the sh structure. The point-group symmetry $[\sigma_\eta|0]$ implies that $\mathbf{R}=(-\frac{1}{2},\frac{1}{2})$ also corresponds to the sh structure. Let $\mathbf{T}_1=(\frac{1}{2},\frac{1}{2})$ and $\mathbf{T}_2=(-\frac{1}{2},\frac{1}{2})$. Then if $[E|\mathbf{T}_1]\mathbf{R}=\mathbf{R}+\mathbf{T}_1$ and $[E|\mathbf{T}_2]\mathbf{R}=\mathbf{R}+\mathbf{T}_2$, $F(\mathbf{R})$ is invariant under the two-dimensional space-group *pmm*, with generators $[\sigma_A|0]$, $[\sigma_\eta|0]$, $[E|\mathbf{T}_1]$, and $[E|\mathbf{T}_2]$. Multiplication of these generators is defined in the usual way. If $[P|\mathbf{v}]$ denotes an arbitrary element of *pmm*,

$$F([P|\mathbf{v}]\mathbf{R})=F(\mathbf{R}). \tag{4}$$

The symmetries of three structures, denoted in Fig. 2 by fcc, *AABBCC*, and hcp, impose additional constraints not implied by the space-group constraints of Eq. (4). They are associated with the fact that each possesses a threefold axis perpendicular to the hexagonal planes. The generator of this axis can be referred to as $\{C_3|0\}$. This symmetry forces the partial derivatives of $F(\mathbf{R})$ with respect to η and A, evaluated at these three structures, to be zero. The argument for the case of A is as follows. (The case of η is analogous.) Consider the following two ways of distorting any of the three structures: The first, a change δA in the amplitude of its configuration coordinate A, and, the second, the addition of a modulation with amplitude $\delta A'$, whose wave vector is the same as that of A, but whose polarization is perpendicular. The displacement of an atom at $\mathbf{r}$ from its position in fcc, *AABBCC*, or hcp, due to these two distortions, is

$$\delta\mathbf{u}(\delta A,\delta A',\mathbf{r})=\delta A\mathbf{p}\cos(\mathbf{Q}\cdot\mathbf{r})+\delta A'\mathbf{p}'\cos(\mathbf{Q}\cdot\mathbf{r}). \tag{5}$$

The new polarization vector $\mathbf{p}'=-(\sqrt{3}/2)\mathbf{t}_1$ is shown in Fig. 3. The modulation amplitudes δA and $\delta A'$ transform into one another under $\{C_3|0\}$ like coefficients of orthogonal basis vectors,

$$\begin{aligned}\{C_3|0\}\delta A&=-\frac{1}{2}\delta A-\frac{\sqrt{3}}{2}\delta A',\\ \{C_3|0\}\delta A'&=\frac{\sqrt{3}}{2}\delta A-\frac{1}{2}\delta A'.\end{aligned} \tag{6}$$

These transformation properties can be shown to imply that no linear combination of δA and $\delta A'$ is invariant under $\{C_3|0\}$. The derivatives of $F(\mathbf{R})$ with respect to A, evaluated at fcc, *AABBCC*, and hcp, must therefore vanish. Since the same holds true for derivatives with respect to η, it would appear that we have six new constraints on $F(\mathbf{R})$. However, two of the six are already implied by the invariance of $F(\mathbf{R})$ under *pmm*. The four new constraints are given below:

$$\left.\frac{\partial F(\mathbf{R})}{\partial A}\right|_{\text{hcp}}=\left.\frac{\partial F(\mathbf{R})}{\partial A}\right|_{AABBCC}=\left.\frac{\partial F(\mathbf{R})}{\partial \eta}\right|_{\text{fcc}}=\left.\frac{\partial F(\mathbf{R})}{\partial \eta}\right|_{AABBCC}=0. \tag{7}$$

It can be shown that the invariance of the free energy under *pmm* requires $F(\mathbf{R})$ to be of the form

$$F(\eta,A)=\sum_{m,n}A_{m,n}\cos(2\pi m\eta)\cos(2\pi nA), \qquad m,n\geq 0,\ m+n \text{ even}. \tag{8}$$

The four constraints on the derivatives of $F(\mathbf{R})$ can be expressed as constraints on the $A_{m,n}$. The substitution of the above free energy into Eq. (7) gives, respectively, the four equations

$$\begin{aligned}&\sum_{m,n}nA_{m,n}\sin(2\pi n/3)\\ &\quad=\sum_{m,n}nA_{m,n}\cos(\pi m/3)\sin(\pi n/3)=0,\\ &\sum_{m,n}mA_{m,n}\sin(2\pi m/3)\\ &\quad=\sum_{m,n}mA_{m,n}\sin(\pi m/3)\cos(\pi n/3)=0.\end{aligned} \tag{9}$$

Some combinations of the parameters $A_{m,n}$ can be related to experiment by noting that, for the hcp phase, for example, the second derivatives of the free energy with respect to η (or A) gives the elastic constant C_{44} (or a $\mathbf{q}=0$ transverse-optical phonon frequency); similar remarks apply to the fcc phase.

Further progress depends on a knowledge of the parameters $A_{m,n}$. Ultimately, one would hope to be able to calculate these coefficients by an extension to nonzero temperatures of first-principles frozen-phonon total-energy-type calculations (such as those used to study the pressure-induced bcc to hcp transition in barium[5]). In the absence of such information on the $A_{m,n}$ we introduce an arbitrary approximation, motivated primarily by its simplicity, in order to give an illustrative example of the application of the theory to the determination of the fcc to hcp phase transition. We expect that the $A_{m,n}$ will decrease in magnitude as the m and n become large (since there is a limit to how rapidly the energy will vary as η and A are varied). This leads us to consider models for which $A_{m,n}=0$ for $m+n\geq N$. Henceforth, we restrict ourselves to the case $N=6$, which is the simplest such model consistent with the symmetry constraints derived above, and which has nine nonzero parameters. Dropping A_{00}, and using the constraints on the derivatives of $F(\eta,A)$ results in four independent parameters.

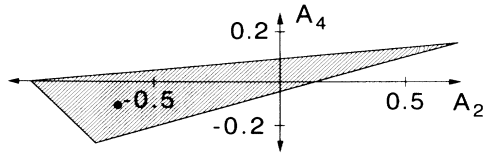

FIG. 4. The region of the (A_2,A_4) parameter space where fcc and hcp are the global free-energy minima (for $A_{22}\geq 0$, $\Delta=0$). The free energy of the point shown is plotted in Fig. 5.

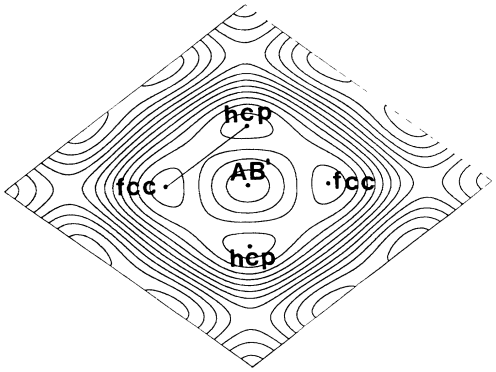

FIG. 5. The unit-cell free-energy landscape of $(A_2,A_4)=(-0.65,-0.1)$. The η and A directions are as shown in Fig. 2. However, the origin has been located at the AB' structure to show a transition between the fcc and hcp structures, the global minima, more clearly. The line between fcc and hcp is the transition path of the Shoji-Nishiyama relation.

We will use A_{22}, $\Delta=\frac{1}{2}(A_{20}-A_{02})$, $A_2=\frac{1}{2}(A_{20}+A_{02})$, and $A_4=\frac{1}{2}(A_{40}+A_{04})$. It can be shown that for $\Delta=0$, $A_{m,n}=A_{n,m}$. In this case, the free energy $F(\eta,A)$ is symmetric under interchange of η and A and the fcc and hcp free energies are degenerate. For $\Delta\neq 0$, however, $F(\frac{1}{3},0)\neq F(0,\frac{1}{3})$. To this order in $A_{m,n}$ the transition temperature between the fcc and hcp structures is determined by the temperature dependence of the asymmetry parameter Δ, the transition, which is first order, occurring when $\Delta=0$. The free-energy landscape at the transition temperature is then determined by the values of the three parameters A_2, A_4, and A_{22}. Since the form of the free energy is unchanged by a proportionality constant, we can set $A_{22}=1$. (A similar analysis holds for $A_{22}=-1$.) Restrictions on the values of A_2 and A_4 may be obtained by noting that fcc and hcp must be the global minima of $F(\eta,A)$ at a transition between these two structures. The region of the (A_2,A_4) parameter space for which this is satisfied is shown in Fig. 4. The free-energy landscape generated by one of the points in this parameter space is represented by a contour diagram in Fig. 5.

This paper has been primarily concerned with the fcc to hcp transition. However, the configuration-space approach itself is obviously much more general. We suggest that, when combined with a microscopic approach, as in Ref. 5, it may be a powerful tool with which to analyze martensitic phase transitions.

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