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Rapidly quenched $V_6Ni_{16}Si_7$—a three-dimensional, incommensurately modulated structure

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Abstract. $V_6Ni_{16}Si_7$ has a very unusual reciprocal lattice, closely related to that of γ-brass but requiring a minimum of six basis vectors in order to index all observed reflections. It can be decribed formally as a three-dimensional, incommensurately modulated β-brass structure. Characteristic satellite extinction conditions observed at $\langle 001 \rangle$ zone axes imply the presence of certain six-dimensional super-space group symmetry operations which can be used to develop a modulated structure approach to the structural description of $V_6Si_{16}Si_7$ and to provide a structural comparison with γ-brass.

1. Introduction

Recently we have reported the results of a detailed electron diffraction study of the crystallography characteristic of a rather remarkable material, namely rapidly solidified $V_6Ni_{16}Si_7$ (Feng *et al* 1989). Its reciprocal lattice exhibits conventional cubic point group symmetry but requires a minimum of six basis vectors in order to index all the observed reflections. Cubic point group symmetry splits this set of six basis vectors into two sets of vectors—a first set of three symmetry-related vectors defining an FCC, 'average structure' reciprocal lattice (and thus labelled $(110)^*$, $(011)^*$ and $(101)^*$ respectively) followed by a further set of three symmetry-related vectors ($\boldsymbol{q}_1 = \frac{1}{3}(114)^* + \varepsilon(111)^*$, $\boldsymbol{q}_2 = \frac{1}{3}(1\bar{1}4)^* + \varepsilon(1\bar{1}1)^*$ and $\boldsymbol{q}_3 = \frac{1}{3}(\bar{1}\bar{1}4) + \varepsilon(\bar{1}\bar{1}1)^*$) corresponding to independent, incommensurate, primary modulation wavevectors of the BCC, average structure (Perez-Mato *et al* 1986). There are, of course, six equivalent $\{110\}^*$-type and 12 equivalent $\{\frac{1}{3}(114) + \varepsilon(111)\}^*$-type reflections for cubic point group symmetry. Only six of these 18 'basis vectors', however, are linearly independent. (Note that in our earlier paper (Feng *et al* 1989), it was incorrectly asserted that seven of these 18 'basis vectors' were linearly independent. Note also the different notation used to describe these basis vectors in that paper). Any reflection can be indexed as an integer linear combination

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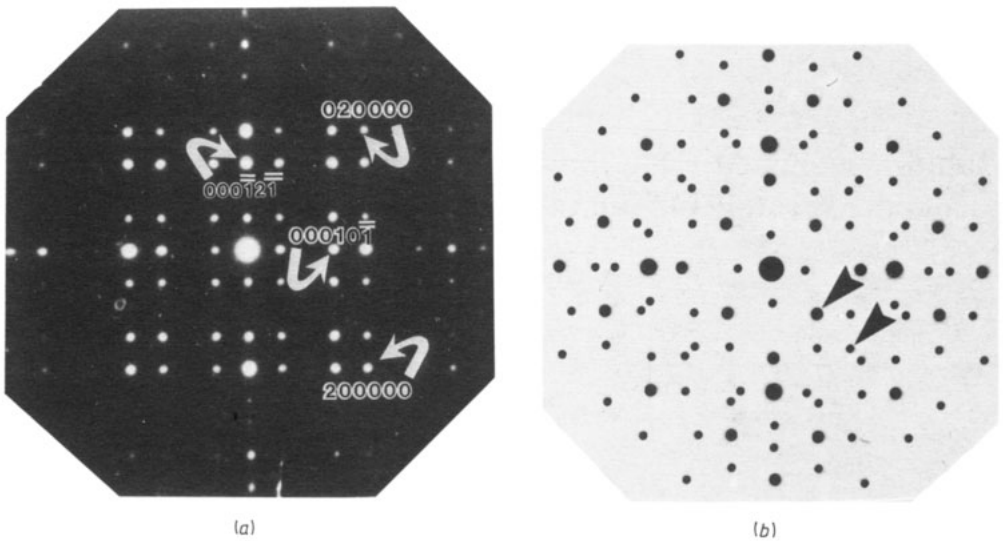

Figure 1. (*a*) The experimentally observed $\langle 001 \rangle_{BCC}$ zone axis selected area diffraction pattern (SADP) of rapidly quenched $V_6Ni_{16}Si_7$. (*b*) The corresponding simulated SADP (see text for a description of the simulation). Note the experimental absence of reflections of the type $(h, k, 0, m, -m + n, -n)$ where $m + n \neq 2q$ (shown by arrow in (*b*)).

of these six basis vectors. Following de Wolff *et al* (1981), a general reflection can be indexed as

$$(h, k, l, m_1, m_2, m_3,) \equiv ha^* + kb^* + lc^* + \sum_{i=1}^{3} m_i \boldsymbol{q}_i$$

where h, k, l, and the m_i are integers and $\boldsymbol{a}^* \equiv (100)^*$ etc. (see figure 1). The FCC reciprocal lattice of the average structure implies the extinction condition $F(h, k, l, m_1, m_2, m_3) = 0$ unless $h + k + l = 2n$.

Figure 2(*a*) shows selected area electron diffraction patterns of the major zone axes encountered on tilting from an $\langle 001 \rangle_{BCC}$- to a $\langle 111 \rangle_{BCC}$-type zone axis (patterns A to D) and from an $\langle 001 \rangle_{BCC}$- to an $\langle 011 \rangle_{BCC}$-type zone axis (patterns A, E, F). Figure 2(*b*) shows a corresponding simulation of the diffraction patterns to be expected if the six equivalent $\{100\}^*$- and 12 equivalent $\{\frac{1}{3}(114) + \varepsilon(111)\}^*$-type vectors are used as 'basis vectors'. The larger the circle size of a particular reflection, the lower the order of the minimum linear combination of these 18 basis vectors required to reach its position in reciprocal space. In general, agreement is excellent except between the experimental and simulated $\langle 001 \rangle_{BCC}$-type zone axis diffraction patterns (see figure 1). (The apparent extra reflections (arrowed) in patterns D and E of figure 2(*a*) are due to reflections which are very close to, but not quite in, the plane perpendicular to the zone axis orientation. They occur in the experimental pattern due to the shape transform effect.) The absence of approximately half the reflections to be expected at $\langle 001 \rangle_{BCC}$-type zone axes is a characteristic satellite extinction condition, the origin and structural implications of which will be spelt out below.

Experimentally, the BCC unit cell has a lattice paramater $a \sim 2.95$ Å while the incommensurability parameter $\varepsilon \sim 0.028$. Isomorphous phases have been found to occur in a

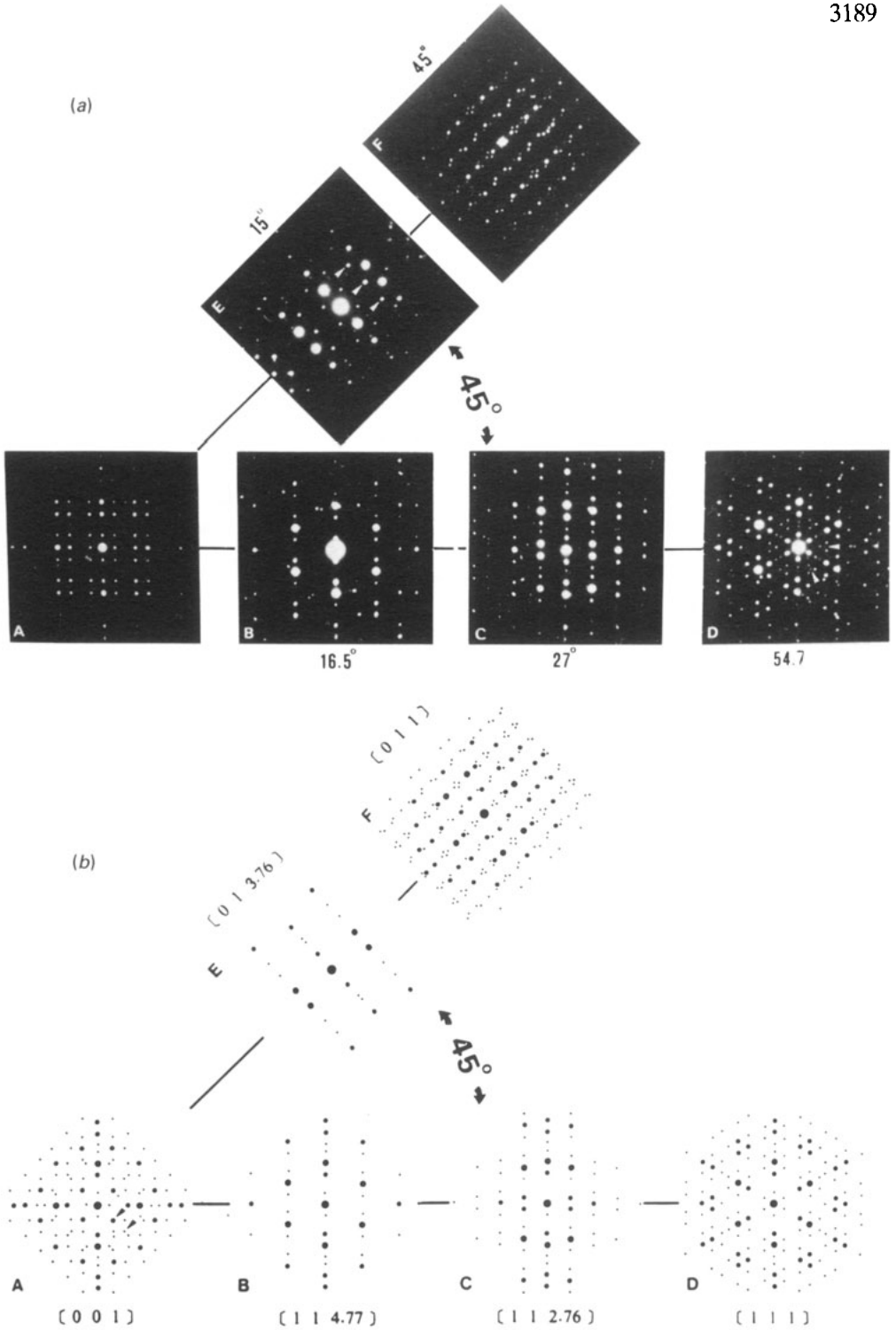

Figure 2. (*a*) SADPs of the major zone axes encountered on tilting from ⟨001⟩ to a ⟨111⟩ zone axis (patterns A to D) and from a ⟨001⟩ to a ⟨011⟩ zone axis (patterns A, E, F) along with (*b*) the corresponding simulated SADPs. The zone axis labelling in (*b*) is with respect to the BCC average structure.

range of rapidly quenched, ternary, transition-metal–silicon alloy systems (Feng *et al* 1987). The incommensurability parameters, ε, vary correspondingly.

All such structures can be described as three-dimensional, incommensurately modulated, BCC structures (see, for example, Perez-Mato *et al* 1986). Unlike most known type I modulated structures, however, it is not experimentally possible to separate 'satellite reflections' from 'matrix reflections' (i.e., those corresponding to the underlying average BCC parent structure) on the basis of intensity, even close in to the origin of reciprocal space (see figure 1). This feature of the reciprocal space of this remarkable family of materials seems more closely related to the reciprocal lattices of the (icosahedral, decagonal, . . .) quasi-crystalline phases.

It is interesting to note that the apparent space group symmetry (and even cell dimensions) of the average structure is identical to that for disordered β-brass (space group $Im\bar{3}m$, $a \sim 2.95$ Å). Similarly the reciprocal lattice of $V_6Ni_{16}Si_7$ is very closely related to that of γ-brass. The structure of γ-brass can, of course, be derived from a disordered β-brass parent structure via appropriate compositional and displacive modulation, as will be shown below. The appropriate 'primary' modulation wavevectors are again $\boldsymbol{q}_1$, $\boldsymbol{q}_2$ and $\boldsymbol{q}_3$, but this time with ε put to zero. The purpose of this paper is threefold: firstly, to explain the existence of the characteristic satellite extinction conditions observed at $\langle 001 \rangle$ zone axes in terms of six-dimensional super-space group symmetry operations; secondly, to use these symmetry operations to develop a modulated structure approach to the structural description of $V_6Ni_{16}Si_7$; thirdly, to provide a structural comparison of $V_6Ni_{16}Si_7$ with γ-brass.

2. Characteristic satellite extinction conditions and 6D super-space group symmetry

Characteristic satellite extinction conditions, such as $F(\boldsymbol{G}_{\text{basal}} + m(\boldsymbol{q}_1 - \boldsymbol{q}_2) + n(\boldsymbol{q}_2 - \boldsymbol{q}_3)) \equiv F(h, k, 0, m, -m + n, -n)$ $0 = unless\ h + k = 2p,\ m + n = 2q\ where\ m, n, p$ and q are all integers, occur at all three $\langle 001 \rangle_{\text{BCC}}$-type zone axes (see figure 1(*a*)). Such characteristic satellite extinction conditions require the existence of super-space group symmetry operations $\{\sigma_x, \mathbf{0}|\tau_1, \tau_1 - \frac{1}{2}, \frac{1}{2} - \tau_1\}$, $\{\sigma_y, \mathbf{0}|\tau_2, -\tau_2, \frac{1}{2} - \tau_2\}$ and $\{\sigma_z, 0|\tau_3, \tau_3 - \frac{1}{2}, \tau_3\}$ (using the notation of Perez-Mato *et al* 1986). Another, and equivalent, way of writing such super-space group symmetry operations is in the form $\{\sigma_x|\boldsymbol{T}_1\}$, $\{\sigma_y|\boldsymbol{T}_2\}$ and $\{\sigma_z|\boldsymbol{T}_3\}$ (Withers 1989) where $\boldsymbol{T}_1$, $\boldsymbol{T}_2$ and $\boldsymbol{T}_3$ are Bravais lattice symmetry translations of the average structure satisfying the following constraints:

$$\begin{aligned}
&-\boldsymbol{q}_1 \cdot \boldsymbol{T}_1 = \tau_1 && -\boldsymbol{q}_1 \cdot \boldsymbol{T}_2 = \tau_2 && -\boldsymbol{q}_1 \cdot \boldsymbol{T}_3 = \tau_3 \\
&-\boldsymbol{q}_2 \cdot \boldsymbol{T}_1 = \tau_1 - \tfrac{1}{2} && -\boldsymbol{q}_2 \cdot \boldsymbol{T}_2 = -\tau_2 && -\boldsymbol{q}_2 \cdot \boldsymbol{T}_3 = \tau_3 - \tfrac{1}{2} \\
&-\boldsymbol{q}_3 \cdot \boldsymbol{T}_1 = \tfrac{1}{2} - \tau_1 && -\boldsymbol{q}_3 \cdot \boldsymbol{T}_2 = \tfrac{1}{2} - \tau_2 && -\boldsymbol{q}_3 \cdot \boldsymbol{T}_3 = \tau_3 \ldots
\end{aligned} \tag{1}$$

That such super-space group symmetry operations give rise to the observed satellite extinction conditions can be shown as follows. Consider any arbitrary atom in the structure at $\boldsymbol{r} = x\boldsymbol{a} + y\boldsymbol{b} + z\boldsymbol{c}$. There must then exist an identical atom in the structure at $\{\sigma_z|\boldsymbol{T}_3\}\boldsymbol{r} = \boldsymbol{r}' = x\boldsymbol{a} + y\boldsymbol{b} - z\boldsymbol{c} + \boldsymbol{T}_3$. The separation of these two equivalent atoms is thus given by $\Delta\boldsymbol{r} = \boldsymbol{r}' - \boldsymbol{r} = -2z\boldsymbol{c} + \boldsymbol{T}_3$. The structure factor, $F(\boldsymbol{k})$, of any reflection $\boldsymbol{k}$ is then proportional to $1 + \exp(-i2\pi\boldsymbol{k} \cdot \Delta\boldsymbol{r})$. In particular:

$$F(\boldsymbol{G}_{\text{basal}} + m(\boldsymbol{q}_1 - \boldsymbol{q}_2) + n(\boldsymbol{q}_2 - \boldsymbol{q}_3)) \propto 1 + \exp[-i2\pi(\boldsymbol{G}_{\text{basal}} + m(\boldsymbol{q}_1 - \boldsymbol{q}_2) + n(\boldsymbol{q}_2 - \boldsymbol{q}_3)) \cdot (-2z\boldsymbol{c}2 + \boldsymbol{T}_3)]$$

$$= 1 + \exp[-i\pi(-m + n) = 0$$

unless $m + n = 2q$ as observed. The satellite extinction conditions thus obtained are the same as those obtained via application of equation (17) of Perez-Mato *et al* (1986).

Such six-dimensional super-space group symmetry operations severely constrain the form of compositional and/or displacement eigenvectors associated with the various 'harmonics' of the primary modulation wavevectors, as will be shown below for the strongest modulation harmonics.

3. A representation theory approach to the structural description of rapidly quenched $V_6Ni_{16}Si_7$

A representation theory approach to the structural description of rapidly quenched $V_6Ni_{16}Si_7$ requires the definition of an underlying, unmodulated (or prototype) parent structure, the incommensurate modulation of which gives rise to the resultant modulated structure. The various incommensurate modulation wavevectors then need to be specified, followed by the transformation properties of their corresponding compositional and displacement eigenvectors under the symmetry operations belonging to the appropriate little group (see, for example, Bradley and Cracknell 1972). Having specified the form of the eigenvectors associated with each of the various modulation harmonics, one must finally consider how the modulated structure as a whole transforms under a general symmetry operation of the parent structure.

3.1. The parent structure

The underlying average structure of rapidly quenched $V_6Ni_{16}Si_7$ is BCC with a lattice parameter ~2.9 Å. The 4 mm, 3 m and 2 mm whole pattern symmetries observed in convergent beam electron diffraction patterns taken down the four-, three- and two-fold axes (see Feng *et al* 1989) suggests an average structure space group symmetry the same as that of disordered β-brass, namely $Im\bar{3}m$. In turn, the $(\sqrt{3}/2)a \sim 2.5$ Å body-centring separation distance implies that there can only be one atomic site per primitive unit cell of the average structure—at 0, 0, 0. Thus the prototype parent structure appears to be the same as that for disordered β-brass except that the atomic scattering factor of this one average atom is given by $\bar{f}_\mu \sim \frac{1}{29}(6f_V + 16f_{Ni} + 7f_{Si})$, and not $\bar{f}_\mu \sim \frac{1}{27}(10f_{Cu} + 16f_{Zn})$ as in the case of disordered β-brass. The resultant modulated structure can now be described in terms of a summation of compositional and displacive modulations of this prototype parent structure. Such modulations, for a particular modulation wavevector $\boldsymbol{q}$, take the form:

$$\delta f_\mu(\boldsymbol{T}) = \bar{f}_\mu a_\mu(\boldsymbol{q}) \cos(2\pi \boldsymbol{q} \cdot \boldsymbol{T} + \theta_\mu(\boldsymbol{q}))$$

and

$$\boldsymbol{U}_\mu(\boldsymbol{T}) = \sum_{\alpha = x,y,z} \boldsymbol{\alpha} \varepsilon_{\mu\alpha}(\boldsymbol{q}) \cos(2\pi \boldsymbol{q} \cdot \boldsymbol{T} + \theta_{\mu\alpha}(\boldsymbol{q})) \ldots . \tag{2}$$

In the above equation, $\delta f_\mu(\boldsymbol{T})$ represents the periodic deviation from its average value, $\bar{f}_\mu$, of the atomic scattering factor of the μth atom site in the $\boldsymbol{T}$th unit cell while $\boldsymbol{\mu}_\mu(\boldsymbol{T})$ represents the atomic displacement away from its average position of the μth atom site in the $\boldsymbol{T}$th unit cell.

The number of higher-order harmonic modulations which will need to be included in order to obtain a good approximation to the real structure is clearly going to be significant due to the obviously large amplitudes of the primary ($\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$, $\boldsymbol{q}_4$) modulation harmonics. Nevertheless, experimentally, it is clear that the amplitude associated with the various modulations does drop off sharply with increasing order.

3.2. Modulation wavevectors

Although cubic m3m point group symmetry gives rise to ±12 equivalent wavevectors of the form $\frac{1}{3}\{114\}^* + \varepsilon\{111\}^*$, only three of these wavevectors are rationally independent, i.e., only three are required, in conjunction with the average structure reciprocal lattice basis vectors, in order to index all the observed reflections. These primary modulation wavevectors can be chosen to be $\boldsymbol{q}_1 = \frac{1}{3}(114)^* + \varepsilon(111)^*$, $\boldsymbol{q}_2 = \frac{1}{3}(1\bar{1}4)^* + \varepsilon(1\bar{1}1)^*$ and $\boldsymbol{q}_3 = \frac{1}{3}(\bar{1}\bar{1}4)^* + \varepsilon(\bar{1}\bar{1}1)^*$. Of the 12 equivalent wavevectors, $\boldsymbol{q}_4 = \frac{1}{3}(\bar{1}14)^* + \varepsilon(\bar{1}11)^* = \boldsymbol{q}_1 - \boldsymbol{q}_2 + \boldsymbol{q}_3$ and hence is not rationally independent. The remaining eight wavevectors can be obtained by appropriate linear combinations of $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$ and $\boldsymbol{q}_4$ with reciprocal lattice vectors of the BCC average structure, e.g., $\boldsymbol{q}_3 - (101)^* = \frac{1}{3}(\bar{4}\bar{1}1)^* + \varepsilon(\bar{1}\bar{1}1)^*$ etc., and hence are also not rationally independent.

Because $\varepsilon \neq 0$ for $V_6Ni_{16}Si_7$, there exist an infinite series of higher-order harmonic modulation wavevectors, e.g. $\boldsymbol{q}_i \pm \boldsymbol{q}_j$, $2\boldsymbol{q}_i$, ... In the case of commensurately modulated γ-brass, however, all higher-order harmonic modulation wavevectors become equivalent to one of the four $\boldsymbol{q}_i$s or to one of the nine, 'second harmonic', modulation wavevectors of the form $(\boldsymbol{q}_i \pm \boldsymbol{q}_j)$.

Such $(\boldsymbol{q}_i \pm \boldsymbol{q}_j)$ modulation wavevectors fall into two separate, symmetry-related classes. The first class consists of

$$\boldsymbol{q}_5 \equiv \boldsymbol{q}_2 - \boldsymbol{q}_3 = (\tfrac{1}{3} + \varepsilon)(200)^*$$

$$\boldsymbol{q}_6 \equiv \boldsymbol{q}_1 - \boldsymbol{q}_2 = (\tfrac{1}{3} + \varepsilon)(020)^*$$

$$\boldsymbol{q}_7 \equiv \boldsymbol{q}_1 + \boldsymbol{q}_3 - (002)^* = (\tfrac{1}{3} + \varepsilon)(002)^*.$$

The second class consists of the six wavevectors:

$$\boldsymbol{q}_8 \equiv \boldsymbol{q}_1 - \boldsymbol{q}_3 = (\tfrac{1}{3} + \varepsilon)(220)^*$$

$$\boldsymbol{q}_9 \equiv \boldsymbol{q}_1 + \boldsymbol{q}_4 - (002)^* = (\tfrac{1}{3} + \varepsilon)(022)^*$$

$$\boldsymbol{q}_{10} \equiv \boldsymbol{q}_1 + \boldsymbol{q}_2 - (002)^* = (\tfrac{1}{3} + \varepsilon)(202)^*$$

$$\boldsymbol{q}_{11} \equiv \boldsymbol{q}_2 - \boldsymbol{q}_4 = (\tfrac{1}{3} + \varepsilon)(2\bar{2}0)^*$$

$$\boldsymbol{q}_{12} \equiv -\boldsymbol{q}_2 - \boldsymbol{q}_3 + (002)^* = (\tfrac{1}{3} + \varepsilon)(02\bar{2})^*$$

$$\boldsymbol{q}_{13} \equiv \boldsymbol{q}_3 + \boldsymbol{q}_4 = (\tfrac{1}{3} + \varepsilon)(\bar{2}02)^*.$$

In the following section, the general form of compositional and displacive modulations associated with these 13 strongest modulation harmonics will be derived and the above super-space group symmetry operations used to determine their relative phasing. A Fourier decomposition of the known γ-brass structure in terms of modulations associated with the same 13 modulation wavevectors provides an illuminating structural comparison.

Table 1. Multiplication table for the little co-group associated with the 'primary' modulation wavevectors, $\boldsymbol{q}_1 \ldots \boldsymbol{q}_4$.

	E	$C_3^{\pm}$	σ_{di}
R_1	1	1	$\underline{1}$
R_2	1	$\underline{1}$	$\underline{1}$
R_3	2	$\underline{1}$	0

3.3. Irreducible representations and modulation functions assocated with $\boldsymbol{q}_1, \ldots, \boldsymbol{q}_{13}$

3.3.1. Irreducible representations associated with the 'primary' modulation wavevectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$, $\boldsymbol{q}_4$. The little co-group associated with $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$ and $\boldsymbol{q}_4$ is $3m(C_{3v}) = E, C_3^{\pm}, \delta_{di}$ (see Bradley and Cracknell 1972). The corresponding multiplication table is given in table 1.

Compositional modulation is symmetry constrained to only be associated with an R_1 representation. The m3m point group symmetry of reciprocal space, in conjunction with the existence of the above super-space group symmetry operations, ensures that displacive modulation is likewise associated only with an R_1 irreducible representation. the corresponding displacement eigenvectors are given by

$$\boldsymbol{e}^{R_1}(\boldsymbol{q}_1) = (e_1, e_1, e_1) \qquad \boldsymbol{e}^{R_1}(\boldsymbol{q}_2) = (e_2, \bar{e}_2, e_2)$$

$$\boldsymbol{e}^{R_1}(\boldsymbol{q}_3) = (\bar{e}_3, \bar{e}_3, e_3) \qquad \boldsymbol{e}^{R_1}(\boldsymbol{q}_4) = (\bar{e}_4, e_4, e_4)$$

where the complex amplitudes e_j (describing atomic shifts along the $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ axes) $\equiv \varepsilon_{\mu\alpha} \exp(i\theta_{\mu\alpha})$ (see equation (2) above).

The compositional and displacement modulation functions associated with these symmetry-equivalent, primary modulation harmonics are therefore given by

$$\delta f_\mu(\boldsymbol{T}) = f_\mu[a_{11} \cos(2\pi \boldsymbol{q}_1 \cdot \boldsymbol{T} + \theta'_{11}) + a_{12} \cos(2\pi \boldsymbol{q}_2 \cdot \boldsymbol{T} + \theta'_{12}) + a_{13} \cos(2\pi \boldsymbol{q}_3 \cdot \boldsymbol{T} + \theta'_{13}) + a_{14} \cos(2\pi \boldsymbol{q}_4 \cdot \boldsymbol{T} + \theta'_{14})] \tag{3}$$

and

$$\boldsymbol{U}_\mu(\boldsymbol{T}) = \varepsilon_{11}(\boldsymbol{a} + \boldsymbol{b} + \boldsymbol{c}) \cos(2\pi \boldsymbol{q}_1 \cdot \boldsymbol{T} + \theta_{11}) + \varepsilon_{12}(\boldsymbol{a} - \boldsymbol{b} + \boldsymbol{c}) \cos(2\pi \boldsymbol{q}_2 \cdot \boldsymbol{T} + \theta_{12}) + \varepsilon_{13}(-\boldsymbol{a} - \boldsymbol{b} + \boldsymbol{c}) \cos(2\pi \boldsymbol{q}_3 \cdot \boldsymbol{T} + \theta_{13}) + \varepsilon_{14}(-\boldsymbol{a} + \boldsymbol{b} + \boldsymbol{c}) \cos(2\pi \boldsymbol{q}_4 \cdot \boldsymbol{T} + \theta_{14}). \tag{4}$$

Application of $\{\sigma_x|\boldsymbol{T}_1\}$, $\{\sigma_y|\boldsymbol{T}_2\}$ and $\{\sigma_z|\boldsymbol{T}_3\}$ to $\delta f_\mu(\boldsymbol{T})$ requires:

$$a_{11} = a_{12} = a_{13} = a_{14} = a_1 \tag{5}$$

and

$$\theta'_{11} = \theta'_{14} + 2\pi\tau_1 = \theta'_{12} + 2\pi\tau_2 = -\theta'_{13} + 2\pi\tau_3$$

$$\theta'_{12} = \theta'_{13} + 2\pi\tau_1 - \pi = \theta'_{11} - 2\pi\tau_2 = -\theta'_{14} + 2\pi\tau_3 - \pi$$

$$\theta'_{13} = \theta'_{12} - 2\pi\tau_1 + \pi = \theta'_{14} - 2\pi\tau_2 + \pi = -\theta'_{12} + 2\pi\tau_3$$

$$\theta'_{14} = \theta'_{11} - 2\pi\tau_1 = \theta'_{13} + 2\pi\tau_2 + \pi = -\theta'_{12} + 2\pi\tau_3 + \pi. \tag{6}$$

Table 2. Symmetry decomposition of the known structure of γ-brass in terms of commensurate modulations of a β-brass-like parent phase.

$a_1 \cos\theta_1 = (5f_{Zn} - 7f_{Cu})/(10f_{Cu} + 16f_{Zn})$ $\quad$ $\varepsilon_1 \cos\theta_1 = -0.0454$

$a_1 \sin\theta_1 = (-3\sqrt{3}f_{Zn} + 3\sqrt{3}f_{Cu})/(10f_{Cu} + 16f_{Zn})$ $\quad$ $\varepsilon_1 \sin\theta_1 = -0.0346$

$a_2 = a_3 = (2f_{Cu} - 4f_{Zn})/(10f_{Cu} + 16f_{Zn})$ $\quad$ $\varepsilon_2 = 0.0174$, $\varepsilon_3 = -0.0194$, $\varepsilon_3' = 0.0177$.

	$\boldsymbol{q}_1$	$\boldsymbol{q}_2$	$\boldsymbol{q}_3$	$\boldsymbol{q}_4$	$\boldsymbol{q}_5$	$\boldsymbol{q}_6$	$\boldsymbol{q}_7$	$\boldsymbol{q}_8$	$\boldsymbol{q}_9$	$\boldsymbol{q}_{10}$	$\boldsymbol{q}_{11}$	$\boldsymbol{q}_{12}$	$\boldsymbol{q}_{13}$
a_κ	a_1	a_1	a_1	a_1	a_2	a_2	a_2	a_3	a_3	a_3	a_3	a_3	a_3
θ_κ	θ_1	$-\theta_1$	θ_1	$-\theta_1$	0°	0°	0°	0°	0°	0°	0°	0°	0°
$\varepsilon_{\kappa x}$	ε_1	ε_1	$-\varepsilon_1$	$-\varepsilon_1$	ε_2	0	0	ε_3	ε_3'	ε_3	ε_3	$-\varepsilon_3'$	$-\varepsilon_3$
$\theta_{\kappa x}$	θ_1	$180° - \theta_1$	θ_1	$180° - \theta_1$	90°			+90°	0°	+90°	+90°	0°	+90°
$\varepsilon_{\kappa y}$	ε_1	$-\varepsilon_1$	$-\varepsilon_1$	ε_1	0	ε_2	0	ε_3	ε_3	ε_3'	$-\varepsilon_3$	ε_3	$-\varepsilon_3'$
$\theta_{\kappa y}$	θ_1	$180° - \theta_1$	θ_1	$180° - \theta_1$		90°		+90°	+90°	0°	+90°	+90°	0°
$\varepsilon_{\kappa z}$	ε_1	ε_1	ε_1	ε_1	0	0	ε_2	ε_3'	ε_3	ε_3	$-\varepsilon_3'$	$-\varepsilon_3$	ε_3
$\theta_{\kappa z}$	θ_1	$180° - \theta_1$	θ_1	$180° - \theta_1$			90°	0°	+90°	+90°	0°	+90°	+90°

Application to $\boldsymbol{u}_\mu(\boldsymbol{T})$ requires:

$$\varepsilon_{11} = \varepsilon_{12} = \varepsilon_{13} = \varepsilon_{14} = \varepsilon_1 \tag{7}$$

and

$$\begin{aligned}
\theta_{11} &= \theta_{14} + 2\pi\tau_1 = \theta_{12} + 2\pi\tau_2 = -\theta_{13} + 2\pi\tau_3 + \pi \\
\theta_{12} &= \theta_{13} + 2\pi\tau_1 - \pi = \theta_{11} - 2\pi\tau_2 = -\theta_{14} + 2\pi\tau_3 \\
\theta_{13} &= \theta_{12} - 2\pi\tau_1 + \pi = \theta_{14} - 2\pi\tau_2 + \pi = -\theta_{11} + 2\pi\tau_3 + \pi \\
\theta_{14} &= \theta_{11} - 2\pi\tau_1 = \theta_{13} + 2\pi\tau_2 + \pi = -\theta_{12} + 2\pi\tau_3.
\end{aligned} \tag{8}$$

Note that $(\boldsymbol{q}_1 + \boldsymbol{q}_3) - (\boldsymbol{q}_2 + \boldsymbol{q}_4) = \boldsymbol{0}$. Thus $(\theta_{11}' + \theta_{13}') - (\theta_{12}' + \theta_{14}')\,(= \pi)$ and $(\theta_{11} + \theta_{13}) - (\theta_{12} + \theta_{14})\,(= \pi)$ are invariant under an origin shift by a Bravais lattice translation vector, unlike the individual phase angles themselves. Note further that the values of these invariant combinations of phase angles are exactly as would be expected from a Landau theoretical point of view (see section 4).

For comparison purposes, the Fourier decomposition of the known $I\bar{4}3m$ γ-brass structure in terms of compositional and displacive modulations associated with the $\boldsymbol{q}_1, \ldots \boldsymbol{q}_{13}$ modulation wavevectors is given in table 2. Thus, for example:

$$\begin{aligned}
&\varepsilon_{11} = \varepsilon_{12} = \varepsilon_{13} = \varepsilon_{14} = \varepsilon_1 = -0.0571\ (|\varepsilon_1| \equiv 0.168\ \text{Å}) \\
&\theta_{11} = \theta_{13} = 37.25° \\
&\theta_{12} = \theta_{14} = 180° - 37.25°
\end{aligned}$$

and

$$(\theta_{11} + \theta_{13}) - (\theta_{12} + \theta_{14}) = 149°$$

in the case of γ-brass.

Table 3. Multiplication table for the little co-group associated with wavevector $\boldsymbol{q}_6$.

	E	C_{2y}	$C^{\pm}_{4y}$	σ_x, σ_z	σ_{dc}, σ_{de}
R_1	1	1	1	1	1
R_2	1	1	1	$\bar{1}$	$\bar{1}$
R_3	1	1	$\bar{1}$	1	$\bar{1}$
R_4	1	1	$\bar{1}$	$\bar{1}$	1
R_5	2	$\bar{2}$	0	0	0

Table 4. Multiplication table for the little co-group associated with $\boldsymbol{q}_8$.

	E	C_{2a}	σ_z	σ_{db}
R_1	1	1	1	1
R_2	1	1	$\bar{1}$	$\bar{1}$
R_3	1	$\bar{1}$	1	$\bar{1}$
R_4	1	$\bar{1}$	$\bar{1}$	1

3.3.2. Irreducible representations associated with the second harmonic modulation wavevectors $\boldsymbol{q}_5$, $\boldsymbol{q}_6$, $\boldsymbol{q}_7$. The little co-group associated with $\boldsymbol{q}_5$, $\boldsymbol{q}_6$, $\boldsymbol{q}_7$ is 4mm (C_{4v}). In the case of $\boldsymbol{q}_6$, this little co-group is given by E, C_{2y}, $C^{\pm}_{4y}$, σ_X, σ_z σ_{dc} and σ_{de} (see Bradley and Cracknell 1972). The corresponding multiplication table is given in table 3.

The observed m3m point group symmetry of reciprocal space again ensures that compositional and displacive modulation can only be associated with the totally symmetric R_1 irreducible representation. The displacement eigenvectors are given by

$$\boldsymbol{e}^{R_1}(\boldsymbol{q}_5) = (e_1, 0, 0) \qquad \boldsymbol{e}^{R_1}(\boldsymbol{q}_6) = (0, e_2, 0) \qquad \boldsymbol{e}^{R_1}(\boldsymbol{q}_7) = (0, 0, e_3)$$

while the corresponding compositional and displacive modulation functions are given by

$$\delta f_\mu(\boldsymbol{T}) = \bar{f}_\mu[a_{21}\cos(2\pi\boldsymbol{q}_5\cdot\boldsymbol{T} + \theta'_{21}) + a_{22}\cos(2\pi\boldsymbol{q}_6\cdot\boldsymbol{T} + \theta'_{22}) + a_{23}\cos(2\pi\boldsymbol{q}_7\cdot\boldsymbol{T} + \theta'_{23})] \tag{9}$$

and

$$\boldsymbol{U}_\mu(\boldsymbol{T}) = \varepsilon_{21}\boldsymbol{a}\cos(2\pi\boldsymbol{q}_5\cdot\boldsymbol{T} + \theta_{21}) + \varepsilon_{22}\boldsymbol{b}\cos(2\pi\boldsymbol{q}_6\cdot\boldsymbol{T} + \theta_{22}) + \varepsilon_{23}\boldsymbol{c}\cos(2\pi\boldsymbol{q}_7\cdot\boldsymbol{T} + \theta_{23}). \tag{10}$$

Application of the known super-space group symmetry operations, however, requires that $a_{21} = a_{22} = a_{23} = 0$ and $\varepsilon_{21} = \varepsilon_{22} = \varepsilon_{23} = 0$, i.e., modulations associated with $\boldsymbol{q}_5$, $\boldsymbol{q}_6$, $\boldsymbol{q}_7$ are specifically forbidden for $V_6Ni_{16}Si_7$. In the case of γ-brass, however, such is not the case (see table 2).

3.3.3. Irreducible representations associated with $\boldsymbol{q}_8$, $\boldsymbol{q}_9$, $\boldsymbol{q}_{10}$, $\boldsymbol{q}_{11}$, $\boldsymbol{q}_{12}$, $\boldsymbol{q}_{13}$. The little co-group associated with $(\frac{1}{3} + \varepsilon)\{220\}^*$-type modulation wavevectors (i.e., $\boldsymbol{q}_8, \ldots \boldsymbol{q}_{13}$) is mm2 ($C_{2v}$). In the specific case of $\boldsymbol{q}_8$, it is E, C_{2a}, σ_z, σ_{db}. The corresponding multiplication table is given in table 4.

The observed m3m point group of reciprocal space, in conjunction with the super-space group symmetry operations of section 2, again ensures that compositional and displacive modulation can only be associated with the R_1 irreducible representation. (In the case of γ-brass, compositional and displacive modulation associated with both R_1 and R_4 irreducible representations occur (see table 2), i.e., both irreducible representations are consistent with the $I\bar{4}3m$ resultant space group symmetry of γ-brass). The displacement eigenvectors for R_1 symmetry are given by

$$e^{R_1}(q_8) = (e_1, e_1, 0) \qquad e^{R_1}(q_9) = (0, e_2, e_2) \qquad e^{R_1}(q_{10}) = (e_3, 0, e_3)$$

$$e^{R_1}(q_{11}) = (e_4, \bar{e}_4, 0) \qquad e^{R_1}(q_{12}) = (0, e_5, \bar{e}_5) \qquad e^{R_1}(q_{13}) = (\bar{e}_6, 0, e_6)$$

The corresponding compositional and displacement modulation functions are thus given by

$$\begin{aligned}\delta f_\mu(\boldsymbol{T}) = \bar{f}_\mu[&a_{31}\cos(2\pi \boldsymbol{q}_8 \cdot \boldsymbol{T} + \theta'_{31}) + a_{32}\cos(2\pi \boldsymbol{q}_9 \cdot \boldsymbol{T} + \theta'_{32}) \\ &+ a_{33}\cos(2\pi \boldsymbol{q}_{10} \cdot \boldsymbol{T} + \theta'_{33}) + a_{34}\cos(2\pi \boldsymbol{q}_{11} \cdot \boldsymbol{T} + \theta'_{34}) \\ &+ a_{35}\cos(2\pi \boldsymbol{q}_{12} \cdot \boldsymbol{T} + \theta'_{35}) + a_{36}\cos(2\pi \boldsymbol{q}_{13} \cdot \boldsymbol{T} + \theta'_{36})] \end{aligned} \tag{11}$$

and

$$\begin{aligned}\boldsymbol{u}_\mu(\boldsymbol{T}) = &\varepsilon_{31}(\boldsymbol{a} + \boldsymbol{b})\cos(2\pi \boldsymbol{q}_8 \cdot \boldsymbol{T} + \theta_{31}) + \varepsilon_{32}(\boldsymbol{b} + \boldsymbol{c})\cos(2\pi \boldsymbol{q}_9 \cdot \boldsymbol{T} + \theta_{32}) \\ &+ \varepsilon_{33}(\boldsymbol{a} + \boldsymbol{c})\cos(2\pi \boldsymbol{q}_{10} \cdot \boldsymbol{T} + \theta_{33}) \\ &+ \varepsilon_{34}(\boldsymbol{a} - \boldsymbol{b})\cos(2\pi \boldsymbol{q}_{11} \cdot \boldsymbol{T} + \theta_{34}) + \varepsilon_{35}(\boldsymbol{b} - \boldsymbol{c})\cos(2\pi \boldsymbol{q}_{12} \cdot \boldsymbol{T} + \theta_{35}) \\ &+ \varepsilon_{36}(-\boldsymbol{a} + \boldsymbol{c})\cos(2\pi \boldsymbol{q}_{13} \cdot \boldsymbol{T} + \theta_{36}). \end{aligned} \tag{12}$$

Application of the above super-space group symmetry operations to $\delta f_\mu(\boldsymbol{T})$ requires that

$$a_{31} = a_{34} \qquad a_{32} = a_{35} \qquad a_{33} = a_{36} \tag{13}$$

and

$$\begin{aligned}\theta'_{31} &= -\theta'_{34} + 2\pi(2\tau_1) + \pi = \theta'_{34} + 2\pi(2\tau_2) + \pi = \theta'_{31} \\ \theta'_{32} &= \theta'_{32} = -\theta'_{35} + 2\pi(2\tau_2) + \pi = \theta'_{35} + 2\pi(2\tau_3) + \pi \\ \theta'_{33} &= \theta'_{36} + 2\pi(2\tau_1) + \pi = \theta'_{33} = -\theta'_{36} + 2\pi(2\tau_3) - \pi \\ \theta'_{34} &= -\theta'_{31} + 2\pi(2\tau_1) + \pi = \theta'_{31} - 2\pi(2\tau_2) - \pi = \theta'_{34} \\ \theta'_{35} &= \theta'_{35} = -\theta'_{32} + 2\pi(2\tau_2) + \pi = \theta'_{32} - 2\pi(2\tau_3) - \pi \\ \theta'_{36} &= \theta'_{33} - 2\pi(2\tau_1) - \pi = \theta'_{36} = -\theta'_{33} + 2\pi(2\tau_3) + \pi. \end{aligned} \tag{14}$$

Application to $\boldsymbol{U}_\mu(\boldsymbol{T})$ requires

$$\varepsilon_{31} = \varepsilon_{34} \qquad \varepsilon_{32} = \varepsilon_{35} \qquad \varepsilon_{33} = \varepsilon_{36} \tag{15}$$

and

$$\begin{aligned}\theta_{31} &= -\theta_{34} + 2\pi(2\tau_1) = \theta_{34} + 2\pi(2\tau_2) + \pi = \theta_{31} \\ \theta_{32} &= \theta_{32} = -\theta_{35} + 2\pi(2\tau_2) = \theta_{35} + 2\pi(2\tau_3) + \pi \\ \theta_{33} &= \theta_{36} + 2\pi(2\tau_1) - \pi = \theta_{33} = -\theta_{36} + 2\pi(2\tau_3)\end{aligned}$$

$$\theta_{34} = -\theta_{31} + 2\pi(2\tau_1) = \theta_{31} - 2\pi(2\tau_2) - \pi = \theta_{34}$$

$$\theta_{35} = \theta_{35} = -\theta_{32} + 2\pi(2\tau_2) = \theta_{32} - 2\pi(2\tau_3) + \pi$$

$$\theta_{36} = \theta_{33} - 2\pi(2\tau_1) + \pi = \theta_{36} = -\theta_{33} + 2\pi(2\tau_3). \tag{16}$$

Note that invariant phase angle combinations again take values that might be expected from simple Landau theoretical arguments (see section 4) e.g.

$$(\boldsymbol{q}_8 - \boldsymbol{q}_{11}) - (\boldsymbol{q}_9 + \boldsymbol{q}_{12}) = \mathbf{0} \qquad (\theta_{31} - \theta_{34}) - (\theta_{32} + \theta_{325}) = \pi.$$

Similarly

$$\boldsymbol{q}_1 - \boldsymbol{q}_3 - \boldsymbol{q}_8 = \mathbf{0} \qquad \theta_{11} - \theta_{13} - \theta_{31} = -\pi/2.$$

4. Landau theoretical considerations

It is possible to interpret simply many of the above phase relationships with the use of a Landau free energy expansion. In constructing a Landau free energy expansion purporting to represent the free energy difference between the modulated and unmodulated (i.e. disordered β-brass) structures, we follow Landau by expanding in terms of order parameters. The appropriate order parameters for each independent modulation wavevector are the complex amplitudes of the corresponding compositional and displacive modulations, which we label $P(\boldsymbol{q})$ and $Q(\boldsymbol{q})$ respectively (see, for example, Moncton *et al* 1977). We will not attempt to construct a general such free energy expansion but concentrate upon the lowest-order phase-dependent terms.

In general, a free energy term $\Delta F^{(n)} = \mathrm{Re}\, BQ(\boldsymbol{q}_1) \ldots Q(\boldsymbol{q}_n)$ will exist if $\boldsymbol{q}_1 + \ldots + \boldsymbol{q}_n = \boldsymbol{G}$, where $\boldsymbol{G}$ is an allowed reciprocal lattice vector of the unmodulated parent structure (see Kwok and Miller 1966). The free energy coefficient, B, is in general complex but the requirement that the free energy expansion should be invariant under the space group symmetry operations of the parent structure (see, for example, Jacobs and Walker 1980) will mean that such coefficients are usually either real or imaginary.

4.1. Landau theoretical considerations applied to rapidly quenched $V_6Ni_{16}Si_7$ ($\varepsilon \neq 0$).

The lowest-order phase-dependent free energy terms are Re $B_1Q(\boldsymbol{q}_1)$ $Q(\boldsymbol{q}_2)^*Q(\boldsymbol{q}_3)Q(\boldsymbol{q}_4)^*$ and Re $B_2P(\boldsymbol{q}_1)P(\boldsymbol{q}_2)^*P(\boldsymbol{q}_3)P(\boldsymbol{q}_4)^*$. Because $P(\boldsymbol{q}) \rightarrow P(\boldsymbol{q})^*$ and $Q(\boldsymbol{q}) \rightarrow -Q(\boldsymbol{q})^*$ under inversion (see equation (2)), both coefficients B_1 and B_2 are real. Thus the above terms reduce to

$$B_1\varepsilon_1^4 \cos(\theta_{11} - \theta_{12} + \theta_{13} - \theta_{14})$$

and

$$B_2a_1^4 \cos(\theta'_{11} - \theta'_{12} + \theta'_{13} - \theta'_{14}).$$

For B_1 and B_2 positive, such free energy terms are minimised for $(\theta_{11} - \theta_{12} + \theta_{13} - \theta_{14}) = \pi$, and $(\theta'_{11} - \theta'_{12} + \theta'_{13} - \theta'_{14}) = \pi$, just as required by the superspace group symmetry operations $\{\sigma_x|\boldsymbol{T}_1\}$, $\{\boldsymbol{\sigma}_y|\boldsymbol{T}_2\}$ and $\{\boldsymbol{\sigma}_z|\boldsymbol{T}_3\}$.

Similarly, consider the lowest-order free energy terms capable of inducing the displacive component of the second harmonic modulations $\boldsymbol{q}_5$, $\boldsymbol{q}_6$, $\boldsymbol{q}_7$:

$$\Delta F = \mathrm{Re}\, C_1[Q(\boldsymbol{q}_5)^*(Q(\boldsymbol{q}_2)Q(\boldsymbol{q}_3)^* + Q(\boldsymbol{q}_1)Q(\boldsymbol{q}_4)^*) + Q(\boldsymbol{q}_6)^*(Q(\boldsymbol{q}_1)Q(\boldsymbol{q}_2)^* + Q(\boldsymbol{q}_3)^*Q(\boldsymbol{q}_4)) + Q(\boldsymbol{q}_7)^*(Q(\boldsymbol{q}_1)Q(\boldsymbol{q}_3) + Q(\boldsymbol{q}_2)Q(\boldsymbol{q}_4))].$$

Invariance of the free energy under inversion implies C_1 is purely imaginary. Thus

$$\Delta F = C_1\varepsilon_1^2\varepsilon_2[\sin(\theta_{12} - \theta_{13} - \theta_{21}) + \sin(\theta_{11} - \theta_{14} - \theta_{21}) + \sin(\theta_{11} - \theta_{12} - \theta_{22}) + \sin(-\theta_{13} + \theta_{14} - \theta_{22}) + \sin(\theta_{11} + \theta_{13} - \theta_{23}) + \sin(\theta_{12} + \theta_{14} - \theta_{23})]$$

Because $(\theta_{11} - \theta_{12} + \theta_{13} - \theta_{14}) = \pi$, $[\ ] = 0$ and hence there is no free energy to be gained by having a non-zero amplitude for these $(\boldsymbol{q}_5, \boldsymbol{q}_6, \boldsymbol{q}_7)$ second harmonic displacive modulations, i.e., one would expect $\varepsilon_2 = 0$. Again this is precisely what the super-space group symmetry operations require. A similar argument holds for the compositional component of the modulations associated with modulation wavevectors $\boldsymbol{q}_5$, $\boldsymbol{q}_6$ and $\boldsymbol{q}_7$.

The lowest-order free energy terms capable of inducing the displacive $\boldsymbol{q}_8, \ldots, \boldsymbol{q}_{13}$ modulations are:

$$\Delta F^{(4)} = \mathrm{Re}\, C_2[Q(\boldsymbol{q}_1)Q(\boldsymbol{q}_2)Q(\boldsymbol{q}_{10})^* + Q(\boldsymbol{q}_1)Q(\boldsymbol{q}_3)^*Q(\boldsymbol{q}_8)^* + Q(\boldsymbol{q}_1)Q(\boldsymbol{q}_4)Q(\boldsymbol{q}_9)^* + Q(\boldsymbol{q}_2)Q(\boldsymbol{q}_3)Q(\boldsymbol{q}_{12}) + Q(\boldsymbol{q}_2)Q(\boldsymbol{q}_4)^*Q(\boldsymbol{q}_{11})^* + Q(\boldsymbol{q}_3)Q(\boldsymbol{q}_4)Q(\boldsymbol{q}_{13})^*].$$

Invariance under inversion again implies an imaginary C_2. Thus

$$\Delta F^{(4)} = |C_2|\varepsilon_1^2[\varepsilon_{33}\sin(\theta_{11} + \theta_{12} - \theta_{33}) + \varepsilon_{31}\sin(\theta_{11} - \theta_{13} - \theta_{31}) + \varepsilon_{32}\sin(\theta_{11} + \theta_{14} - \theta_{32}) + \varepsilon_{32}\sin(\theta_{12} + \theta_{13} + \theta_{35}) + \varepsilon_{31}\sin(\theta_{12} - \theta_{14} - \theta_{34}) + \varepsilon_{33}\sin(\theta_{13} + \theta_{14} - \theta_{36})].$$

Thus one would expect the arguments of all six sine functions to equal either $+\pi/2$ or $-\pi/2$. Judicious use of equations (8) and (16) shows that this is exactly what application of the super-space group symmetry operations $\{\sigma_x|\boldsymbol{T}_1\}$, $\{\sigma_y|\boldsymbol{T}_2\}$ and $\{\sigma_z|\boldsymbol{T}_3\}$ requires.

The compositional equivalent of the above free energy term is given by:

$$|C_2'|a_1^2[a_{33}\cos(\theta_{11}' + \theta_{12}' - \theta_{33}') + a_{31}\cos(\theta_{11}' - \theta_{13}' - \theta_{31}') + a_{32}\cos(\theta_{11}' + \theta_{14}' - \theta_{32}') + a_{32}\cos(\theta_{12}' + \theta_{13}' + \theta_{35}') + a_{31}\cos(\theta_{12}' - \theta_{14}' - \theta_{34}') + a_{33}\cos(\theta_{13}' + \theta_{14}' - \theta_{36}')]$$

(The reason that cosine functions appear instead of sine functions is that C_2' is real rather than imaginary). Thus one would expect the argument of all six cosine functions to equal either 0° or 180°, dependent upon the sign of $C_2'\,a_{3j}$. Judicious use of equations (6) and (14) again shows that this is precisely what the super-space group symmetry requires. Thus many of the experimental observations seem to be well described within the framework of such a free energy expansion.

4.2. Landau theoretical considerations applied to γ-brass (ε = 0)

For the commensurate ($\varepsilon = 0$) γ-brass case, there exist additional low-order free energy terms of the form

$$\mathrm{Re}\, A_1(Q(\boldsymbol{q}_1)^3 + Q(\boldsymbol{q}_2)^3 + Q(\boldsymbol{q}_3)^3 + Q(\boldsymbol{q}_4)^3)$$

and

$$\mathrm{Re}\, A_2(P(\boldsymbol{q}_1)^3 + P(\boldsymbol{q}_2)^3 + P(\boldsymbol{q}_3)^3 + P(\boldsymbol{q}_4)^3).$$

Invariance under inversion implies A_1 is purely imaginary and A_2 real. Thus the above terms reduce to

$$-A_1\varepsilon_1^3\{\sin 3\theta_{11} + \sin 3\theta_{12} + \sin 3\theta_{13} + \sin 3\theta_{14}\}$$

and

$$A_2 a_1^3\{\cos 3\theta'_{11} + \cos 3\theta'_{12} + \cos 3\theta'_{13} + \cos 3\theta'_{14}\}.$$

Experimentally, $\theta_{11} = \theta_{13} = 37.25°$ and $\theta_{12} = \theta_{14} = 180° - 37.25°$.

Thus

$$\sin 3\theta_{11} = \sin 3\theta_{12} = \sin 3\theta_{13} = \sin 3\theta_{14} = \sin(90° + 21.75°)$$

while

$$\cos(\theta_{11} - \theta_{12} + \theta_{13} - \theta_{14}) = \cos(180° - 31°).$$

The experimentally observed values of the primary modulation phase angles can be understood in terms of a trade-off between the above free energy terms and the fourth-order $\cos(\theta_{11} - \theta_{12} + \theta_{13} - \theta_{14})$ term. The above free energy terms would be minimised for $\theta_{11} = \theta_{13} = 30°$, $\theta_{12} = \theta_{14} = 180° - 30°$ whereas the $\cos(\theta_{11} - \theta_{12} + \theta_{13} - \theta_{14})$ term is minimised for $\theta_{11} = \theta_{13} = 45°$, $\theta_{12} = \theta_{14} = 180° - 45°$. Experimentally, the compromise choice of 37.25° occurs. That $(\theta_{11} - \theta_{12} + \theta_{13} - \theta_{14})$ no longer exactly equals π implies that second-order compositional and displacive modulations characterised by the modulation wavevectors $\boldsymbol{q}_5$, $\boldsymbol{q}_6$ and $\boldsymbol{q}_7$ no longer need have zero amplitude (i.e., $\varepsilon_2, a_2 \neq 0$)—as observed in γ-brass (see table 2). Thus the experimental differences in phase angle relationships between rapidly quenched $V_6Ni_{16}Si_7$ and γ-brass can also be easily rationalised within the framework of a Landau-like free energy expansion.

5. Conclusions

$V_6Ni_{16}Si_7$ is representative of a family of rapidly quenched transition metal–silicon alloy systems whose reciprocal lattices are closely related to that of γ-brass. In real space, the γ-brass structure consists of a BCC packing of clusters formed of bi-capped stellar quadrangulae. Structures which can be described in terms of the regular packing of clusters based on stellar quadrangulae are quite well known in solid state chemistry (see, for example, Nyman and Andersson 1979, Hyde and Andersson 1989). Presumably the local structure of rapidly quenched $V_6Ni_{16}Si_7$ must also consist of such clusters. Their size, distribution and connectivity must, however, await the results of a full x-ray, structure refinement when, and if, a large enough single 'crystal' can be grown.

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