An incommensurate structure with cubic point group symmetry in rapidly solidified V-Ni-Si alloy

1989 J. Phys.: Condens. Matter 1 3695

(http://iopscience.iop.org/0953-8984/1/23/015)

J. Phys.: Condens. Matter 1 (1989) 3695–3700. Printed in the UK

LETTER TO THE EDITOR

An incommensurate structure with cubic point group symmetry in rapidly solidified V–Ni–Si alloy

Y C Feng, G Lu† and R L Withers‡
Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Chinese Academy of Science, Shenyang 110015, People's Republic of China, and Beijing Laboratory of Electron Microscopy, Chinese Academy of Science, PO Box 2724, Beijing 100080, People's Republic of China

Received 23 March 1989

Abstract. The incommensurate structure with an unusual diffraction pattern in a rapidly solidified $V_6Ni_{16}Si_7$ alloy is analysed and its reciprocal 'lattice' indexed using 18 basis vectors. This structure has some unique features, which are closely related to both conventional incommensurately modulated structures and quasi-crystals. However, it appears to differ from the latter two types of aperiodic structures in some important aspects.

Since the initial discovery of an Al–Mn alloy whose reciprocal lattice exhibited both icosahedral symmetry as well as sharp Bragg reflections (Shechtman *et al* 1984), it has become increasingly clear that conventional notions of condensed matter are in need of considerable generalisation. Not only have icosahedral quasi-crystals been found to occur in a range of transition-metal alloy systems, but new types of quasi-crystalline order, e.g. decagonal (Bendersky 1985, Fung *et al* 1986), octagonal (Wang *et al* 1987) and dodecagonal (Ishimasa *et al* 1985, Chen *et al* 1988), have also been discovered. This broadening of the scope of quasi-crystallinity is potentially of great significance. All these quasi-crystalline phases can be characterised as having good orientational order but no periodic translational order. Incommensurately modulated structures, on the other hand, also possess both these features. The difference is that the orientational order of an incommensurately modulated structure is characterised by a crystallographic point group symmetry rather than the non-crystallographic point group symmetry of the quasi-crystalline phases (Janssen 1986). As far as diffraction patterns are concerned, the conventional modulated structures possess a well defined set of main reflections, which form one (or more in the composite modulation case (Janner and Janssen 1980)) periodic lattice. The accompanying satellite reflections are usually much weaker than the main reflections and the modulation wavevectors normally considerably shorter in magnitude than the reciprocal basis of the parent structure. Quasi-crystalline structures, on the other hand, show no such apparent main reflection lattice.

Recently we briefly reported the observation of unusual diffraction patterns in some rapidly solidified transition-metal–silicon alloys, whose diffraction patterns appeared to be describable in terms of a three-dimensional, incommensurately modulated, conventional cubic structure (Feng *et al* 1987). In this paper, it is shown that these structures

† Also at Physical Department, Wuhan University, 430072 Wuhan, People's Republic of China.

‡ On leave from: Research School of Chemistry, Australia National University, GPO Box 4, Canberra, ACT 2600, Australia.

0953-8984/89/233695 + 06 $02.50

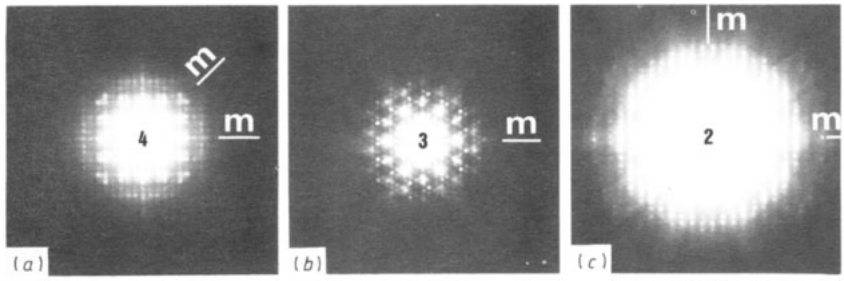

Figure 1. CBED patterns taken down the (*a*) fourfold, (*b*) threefold and (*c*) twofold axes, showing cubic point group symmetry.

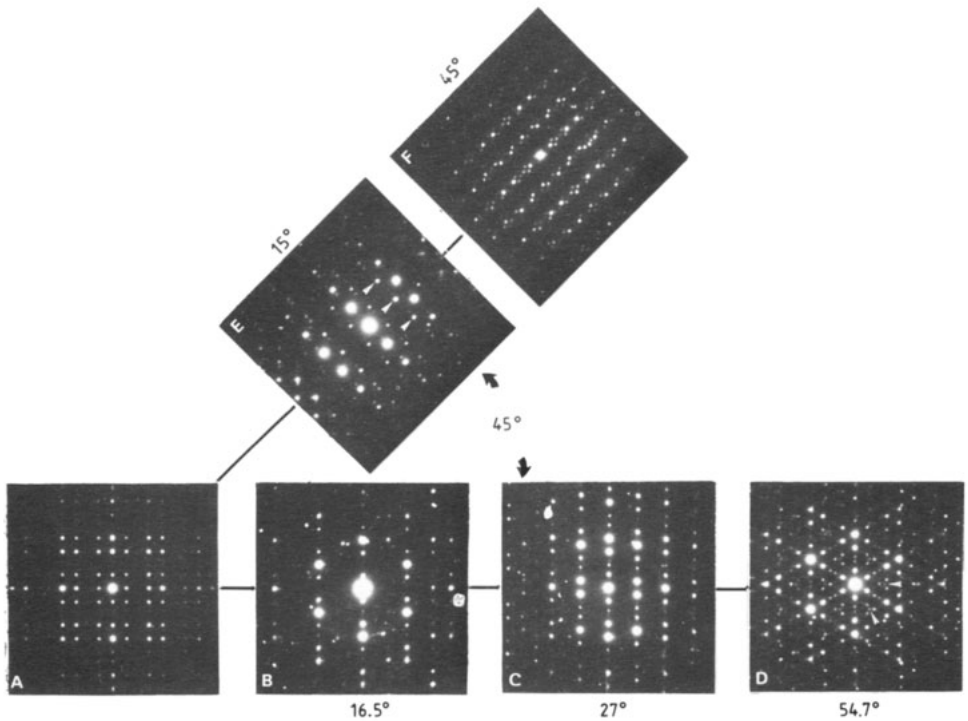

Figure 2. Selected-area diffraction patterns taken from different zone axes covering an orientation triangle of the cubic system (for detail, see the text).

possess some unique characteristic other than conventional modulated structures or known quasi-crystals. One of these phases, the rapidly quenched $V_6Ni_{16}Si_7$, is taken as an example.

Figure 1 shows convergent-beam electron diffraction patterns (CBPS) taken down the fourfold (⟨001⟩), threefold (⟨111⟩), and twofold (⟨110⟩) directions of this reciprocal lattice. The whole pattern symmetries are 4mm, 3m and 2mm (or, perhaps, m) respectively, thus implying a point group symmetry of 432 (or, perhaps, $\bar{4}3m$). Note that these CBPS were taken with a probe size of about 100 Å. Figure 2 shows a representatative sample of zone-axis selected-area electron diffraction patterns (SADPS) encountered on tilting from an [001] zone axis to a [111] zone axis (patterns A to D) and from an [001] zone axis to an [011] zone axis (patterns A, E, F). The inter-zonal angles separating these various zone axes would, in a conventional cubic structure, suggest that the

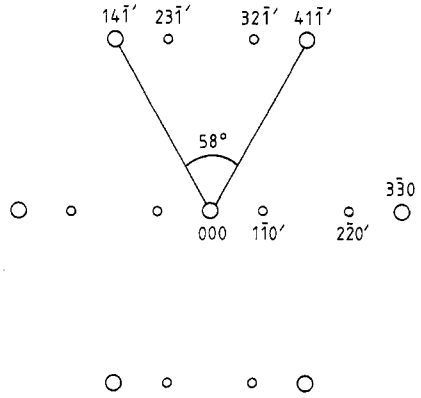

Figure 3. The key diagram corresponding to pattern B in figure 2. Note that the angle between the two $\langle 114\rangle^*$ is not 60°. The indices without primes are exactly indexed, while those with primes are not (see the text).

zone axes for patterns A to D should be indexed as [001], ≃[115], ≃[113], and [111] respectively, while the zone axes for E and F should be indexed as ≃[014] and [011] respectively. The strongest reflections present in all these zone-axis diffraction patterns can indeed be indexed on the above basis, but only if they are labelled as $\{330\}^*$- and $\{114\}^*$-type reflections, and even then only approximately. The magnitude of the reciprocal-lattice vector from the origin to the reflection indexed as $[\bar{3}30]^*$, i.e., $[\bar{3}30]^* = 3\sqrt{2}/a$, is such that a is about 8.8 Å. The reciprocal lattice of this phase therefore bears a strong resemblance to that of γ-brass-type structure (space group $I\bar{4}3m$; see, for example, Bradley and Thewlis 1926). This suggests that the experimentally observed SADPs should be interpreted in terms of linear combinations of the six different $\langle 330\rangle^*$- and twelve different $\langle 114\rangle^*$-type reflections which must be present for a reciprocal lattice that exhibits cubic point group symmetry. The approximate character of this indexing is illustrated in figure 3, which shows schematically the strong reflections in patterns B of figure 2 indexed on the above basis. If the indexing were exact, then the pseudo-hexagonal array of strong reflections presented in this pattern would form an exact hexagonal array. Measurement, however, shows that this is not always the case. The reflections in figure 3 indexed without a prime are exact ones, while those with a prime are not, but shift away from the indexed position. Similar features can be detected in all of the observed SADPs. Thus the 18 strongest 'basis' reflections must all fall very close to, but not exactly upon, the six $\langle 330\rangle^*$ and twelve $\langle 114\rangle^*$ reciprocal-space positions.

Careful analysis of the experimentally observed SADPs shows that the positions and relative intensities of almost all observed reciprocal-lattice reflections can indeed be well understood in terms of linear combinations of 18 such basis vectors $\boldsymbol{q}_i$, $i = 1$ to 18. The reciprocal-space positions of any observed reciprocal-lattice reflection, $\boldsymbol{q}$, can then be indexed as $q = \Sigma_i m_i \boldsymbol{q}_i$, with m_i an integer. The strength of a given reflection appears to be inversely proportional to $S = |\Sigma_i m_i|$, stronger reflections having a small value of S (1, 2 or 3) and weaker reflections a much larger value of S.

The 18 basis vectors $\boldsymbol{q}_i$ are experimentally found to take the forms:

$$
\begin{array}{lll}
\boldsymbol{q}_1 = [330]^* & \boldsymbol{q}_7 = [114]^* + \varepsilon[111]^* & \boldsymbol{q}_{13} = [\bar{1}\bar{4}1]^* + \varepsilon[\bar{1}\bar{1}1]^* \\
\boldsymbol{q}_2 = [033]^* & \boldsymbol{q}_8 = [1\bar{1}4]^* + \varepsilon[1\bar{1}1]^* & \boldsymbol{q}_{14} = [\bar{4}11]^* + \varepsilon[\bar{1}11]^* \\
\boldsymbol{q}_3 = [303]^* & \boldsymbol{q}_9 = [\bar{1}\bar{1}4]^* + \varepsilon[\bar{1}\bar{1}1]^* & \boldsymbol{q}_{15} = [411]^* + \varepsilon[111]^* \\
\boldsymbol{q}_4 = [3\bar{3}0]^* & \boldsymbol{q}_{10} = [\bar{1}14]^* + \varepsilon[\bar{1}11]^* & \boldsymbol{q}_{16} = [1\bar{4}1]^* + \varepsilon[1\bar{1}1]^* \\
\boldsymbol{q}_5 = [03\bar{3}]^* & \boldsymbol{q}_{11} = [141]^* + \varepsilon[111]^* & \boldsymbol{q}_{17} = [\bar{4}\bar{1}1]^* + \varepsilon[\bar{1}\bar{1}1]^* \\
\boldsymbol{q}_6 = [\bar{3}03]^* & \boldsymbol{q}_{12} = [4\bar{1}1]^* + \varepsilon[1\bar{1}1]^* & \boldsymbol{q}_{18} = [\bar{1}41]^* + \varepsilon[\bar{1}11]^*
\end{array}
\qquad (1)
$$

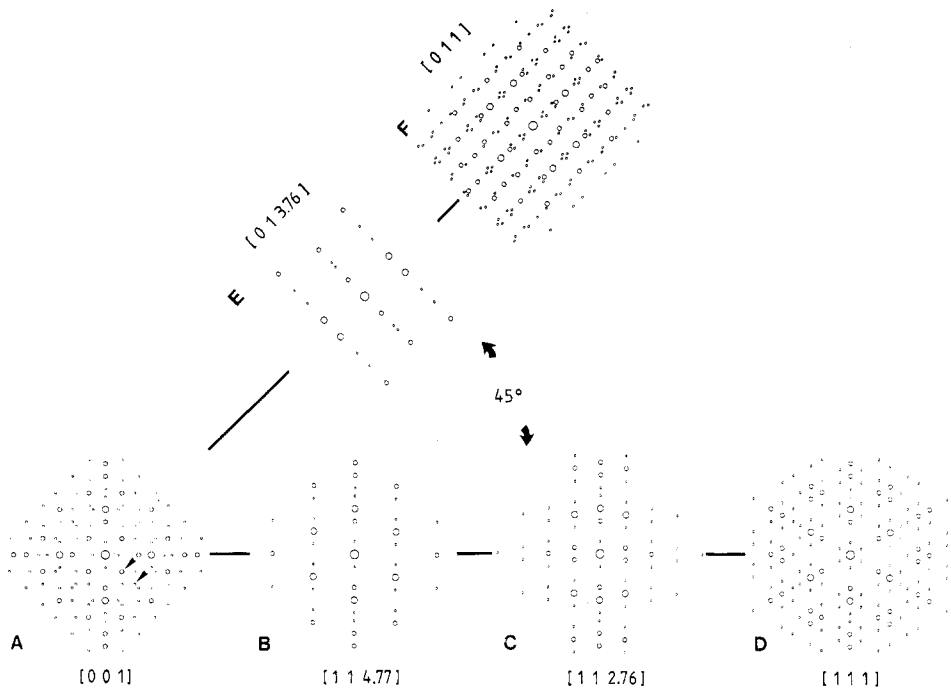

Figure 4. Simulated diffraction patterns corresponding to figure 2, using the 18-vector basis up to the third order.

with ε a dimensionless quantity.

There are various ways of determining ε. One such way is to measure the ratio, R, of the reciprocal-lattice vector out to the two strong reflections—for example, 220′ and 330 as indexed in figure 3. The ratio R is thus $(2 + 2\varepsilon)/3$, since $220' = [114]^* + \varepsilon[111]^* + [11\bar{4}]^* + \varepsilon[11\bar{1}]^*$. The measured R for pattern G in figure 2 indicates that ε for the phase studied is 0.086. When ε changes some zone axes alter slightly. Thus [115] for $\varepsilon = 0$ becomes [1 1 4.77] for $\varepsilon = 0.086$. It is intriguing that when $\varepsilon = 0$, the γ-brass reciprocal lattice is obtained. Indeed small regions with the γ-brass-type structure ($\varepsilon = 0$) have been observed to coexist with the $\varepsilon \neq 0$ phase. Figure 4 shows computer-simulated SADPS produced with these basis vectors and ε-value. The type of weak reflections as arrayed in experimental patterns D (figure 2) are indexed to be of $[\bar{1}\bar{1}2]^* + \varepsilon[222]^*$ and $[\bar{1}\bar{1}2]^* + \varepsilon[\bar{1}\bar{1}\bar{1}]^*$ type; these are a little above or below the $(111)^*$ reciprocal plane, respectively, and are not included in the simulation. Similarly, the weak reflection as arrayed in experimental pattern E are of $[0\bar{3}1]^* + \varepsilon[00\bar{2}]^*$ type; these are slightly out of the $(0\,1\,3.76)^*$ reciprocal plane. In the simulated pattern A the arrayed spots are absent in the experiment. This is probably because of extinction due to some symmetry operations. With the above considerations and allowing dynamical diffraction, the simulation and the experiment are in good qualitative agreement.

The above shifts of the $\langle 114\rangle^*$-type reflections are compatible with 432 (or $\bar{4}3$m) point group symmetry, and do not split the eighteen basis vectors, i.e. relationships of the $\boldsymbol{q}_2 + \boldsymbol{q}_{13} = \boldsymbol{q}_9$ type remain valid. Among these eighteen 'basis' vectors, only seven are linearly independent. These seven can be chosen to be $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$, $\boldsymbol{q}_7$, $\boldsymbol{q}_8$, $\boldsymbol{q}_9$ and $\boldsymbol{q}_{10}$. It is, however, convenient to retain the eighteen basis vectors listed above in order that the rough definition of the strength, S, of a given reflection retains cubic symmetry.

Since there exist a set of reflections corresponding to those of β-brass- (BCC-) type

structure, i.e. those obtained by linear combination of $\boldsymbol{q}_1$, $\boldsymbol{q}_2$ and $\boldsymbol{q}_3$, such as 330, 006 and 336, an alternative way to describe the reciprocal lattice of such a phase is to consider it as an incommensurately modulated β-brass-type structure, with twelve $[114]^* + \varepsilon[111]^*$-type modulating vectors. Among these there are only four independent modulation wavevectors; it is a four-dimensional modulated structure (Perez-Mato *et al* 1986). To retain an indexing system consistent with equation (1), we label the reciprocal basis vector of the parent BCC phase as $\langle 330\rangle^*$ instead of $\langle 110\rangle^*$. If the parent BCC-type reflections are labelled as $\boldsymbol{G}$ then the satellite reflections occur at $\boldsymbol{G} + \Sigma_i m_i \boldsymbol{q}_i$, where $i = 7, 8, 9$ and 10 as defined in (1), and the m_i are integers. Thus the $\varepsilon \neq 0$ phase can be described as an incommensurately modulated structure. When $\varepsilon = 0$, the γ-brass is obtained and can also be described as a modulated β-brass-type structure. Indeed, the atomic types and positions of γ-brass can be obtained from both displacive and compositional modulation of β-brass with an appropriate choice of parameters in the modulation functions. Further work is in progress along these lines. This is, however, beyond the scope of the present Letter.

The phase under study appears to have some unusual features compared with conventional modulated structures. First of all, it seems not to be possible to define one or two sets of main reflection lattices. Secondly, the satellite reflections have intensity of the same order as the main reflections, implying that the modulation waves are unusually strong. Finally the magnitude of the modulation wavevector is the same as (in the $\varepsilon = 0$ case) or slightly greater (when $\varepsilon > 0$) than the reciprocal basis of the parent phase, implying that the wavelength of the modulation wave is similar to or smaller than the dimension of the primitive cell in the parent β-brass-type phase. Modulation waves with such great strength and high frequency cannot really be treated as perturbation to the parent phase. Therefore this structure has some important differences from conventional modulated structures even though it may be formally approached using the methods developed for conventional modulated structures.

On the other hand, this structure resembles quasi-crystalline structures in aspects such as the intensity distribution and the obscurity of the main reflection lattice. The seven-basis-vector model is similar to the six-basis-vector scheme of the icosahedral quasi-crystal, although the numbers of basis vectors are different and the seven basis vectors are of two sets that are not symmetrically equivalent. However, the cubic point group symmetry excludes this phase from the quasi-crystal family, according to the definity of Janssen (1986).

The above analysis presents presumably a type of aperiodic structure, which is closely related to the conventional incommensurately modulated structure and the quasi-crystal, but is strikingly different in some important aspects.

This project was supported by the National Natural Science Foundation of China. The authors are grateful to Professors K H Kuo, H Q Ye, Q B Yang and R H Wang for helpful discussions, and to Mr L G Li for assistance with producing figures 3 and 4. R L Withers thanks Professor K H Kuo for inviting him to work in Shenyang and Beijing. G Lu thanks the National Postdoctoral Committee of China for a postdoctoral fellowship.

References

Bendersky L 1985 *Phys. Rev. Lett.* **55** 1461
Bradley A J and Thewlis J 1926 *Proc. R. Soc.* **112** 678
Chen H, Li D X and Kuo K H 1988 *Phys. Rev. Lett.* **60** 1645

Feng Y C, Zhou D S, Li D L, Dong C, Van Tendeloo G and Kuo K H 1987 *Phil. Mag. Lett.* **55** 221
Fung K K, Yang C Y, Zhou Y Q, Zhao J G, Zhan W S and Shen B G 1986 *Phys. Rev. Lett.* **56** 2060
Ishimasa T, Nissen H-U and Fukano Y 1985 *Phys. Rev. Lett.* **55** 511
Janner A and Janssen T 1980 *Acta Crystallogr.* A **36** 408
Janssen A 1986 *J. Physique Coll.* **47** C3 85
Perez-Mato J M, Madariaga G and Tello M J 1986 *J. Phys. C: Solid State Phys.* **19** 2613
Shechtman D, Blech I, Gratias D and Cahn J W 1984 *Phys. Rev. Lett.* **53** 1951
Wang N, Chen H and Kuo K H 1987 *Phys. Rev. Lett.* **59** 1010