Unusual structural modification in the $Ti_{68}Fe_{26}Ni_1Si_5$ quasicrystalline phase

M. A. Shaz and N. P. Lalla
Physics Department, Banaras Hindu University, Varanasi 221 005, India

R. K. Mandal
School of Material Science and Technology, Banaras Hindu University, Varanasi 221 005, India

O. N. Srivastava
Physics Department, Banaras Hindu University, Varanasi 221 005, India

(Received 23 May 1996; revised manuscript received 13 November 1996)

We report here the formation of a class of materials in the rapidly solidified $Ti_{68}Fe_{26}Ni_1Si_5$ system based on transmission electron microscopic exploration of the electropolished melt-spun ribbons. The phase reported here pertains to a modification of the icosahedral phase leading to tetrahedral symmetry with no discernible periodicities, unlike those of earlier known rational approximant phases. The analysis of the selected area diffraction patterns of these phases revealed variable linear phason strains in the shifted spots of undistorted twofold reciprocal rows. The experimentally observed reciprocal vectors in these directions have been suggested to arise owing to their dependence on both the physical and pseudospace components *vis-à-vis* that of the icosahedral phase. It has been argued that such a dependence may arise owing to the presence of the nonlinear motif having components in both the spaces in the higher-dimensional structural description. [S0163-1829(97)01713-X]

INTRODUCTION

Ever since the seminal finding of icosahedral quasicrystals (IQC's) in the rapidly solidified $Al_{86}Mn_{14}$ alloy,[1] a surfeit of structures related to these phases has been reported. These include (i) decagonal and pentagonal, the two-dimensional (2D) quasicrystals (QC's), (ii) trigonal and digonal, the 1D-QC, and (iii) rational approximant structures (RAS's).[2–4] They display 1D, 2D, and 3D periodicity, respectively, and their diffraction patterns manifest striking similarity with those of 3D-QC in some of the reciprocal rows. Owing to this, they are referred to as icosahedrally related structures (IRS's).[5] Aluminum transition-metal- (TM) based binary and ternary alloys lead to the formation of an entire gamut of IRS's with slight modifications in composition and/or experimental condition. However, unlike the Al-based QC systems, such a possibility does not get readily realized for Ti-TM-based systems.[6,7] Owing to experimental difficulty in the synthesis of alloys in this system and also lack of observation of a stable and a perfect phase in them, they remain less explored *vis-à-vis* Al-TM systems.[7–9] The Ti-TM-based systems display the formation of IQC, RAS (Fibonacci and non-Fibonacci) phases. The non-Fibonacci approximant phases differ in the nature of characteristic modifications of golden mean (τ) from those of Fibonacci ones. These are successive approximants of (τ) for the latter and correspond to 1/1, 2/1, 3/2, 5/3, ... However, for the non-Fibonacci ones, they are any ratio in between these.[10,11] Apart from the above, Ti-TM systems show ordered cells with a large lattice parameter along the ordering direction[12] and the IQC phases formed in them display secondary features in diffraction patterns.[13]

In the course of development of quasicrystallography, several models for understanding their structural details have been suggested, out of which the higher dimensional method seems to be one that is general and can provide economy of description of IRS's.[5,14,15] It has been argued that a series of periodic structures can be generated by sectioning the higher dimensional crystal, having a linear motif lying in pseudospace by the physical spaces whose orientations are rational. If the physical space orientations are fixed by replacing the golden mean τ at any of its approximant values mentioned above, the resulting structures are RAS's.[16] The detailed atomic structure of the RAS is governed by the shape, chemistry, and position around a 6D lattice point of the pseudospace motif. All these affect the physical space structures. These features are unique to aperiodic crystals and give rise to phason modes in addition to the usual phonon modes. Owing to the relaxation of the former by a diffusive mode, the quenched-in phason defects are found in IQC's. Ishii[17] has suggested that the linear strain due to these defects may lead to spontaneous symmetry breaking and a range of IRS's may result. The RAS can, therefore, be thought of as a consequence of mode locking of the linear phason strains. The symmetry of the phason matrix governs the nature of RAS's. It has been shown that the systematic nonlinear term dependence of physical space components on pseudospace components can be made compatible with $m\bar{3}\bar{5}$ and also its subgroups. The 6D motif, therefore, will possess extension in pseudospace and physical space, both. Various physical cuts of such a 6D crystal will generate a different class of materials related to IQC's. However, linear term dependence of the physical space component on the phason part necessarily breaks the icosahedral symmetry. This situation has been encountered more frequently under experimental conditions.

The present paper deals with the occurrence of some modifications of the QC phase in a Ti-Fe-Ni-Si system. These have been found to correspond to variable linear pha-

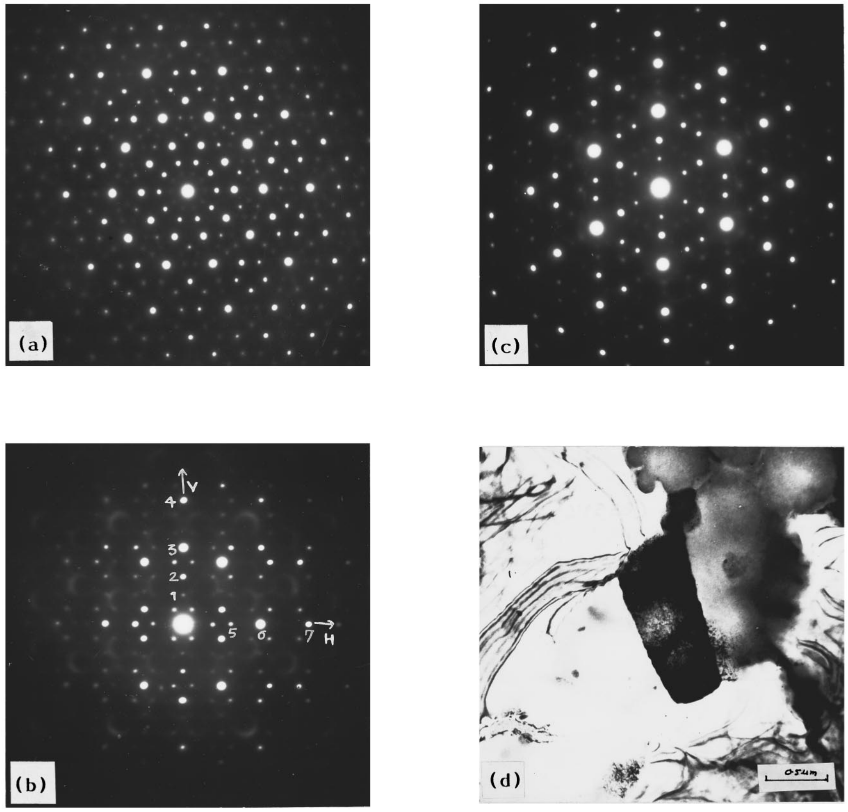

FIG. 1. (a) Fivefold, (b) twofold, and (c) threefold SAD patterns taken from the region whose microstructure is shown in (d). These SAD patterns reveal the icosahedral symmetry of the phase present in that particular region.

son strains, and hence may be termed ''variable strain approximants'' (VSA's). The observation and analysis of these phases reveal that the kind of modification reported here may be a commonly found structure along with the QC phases. The mechanism of VSA's has been outlined in terms of a variable phason strain mode locking and is different from that leading to RAS's discussed in literature.

EXPERIMENT

Alloy ingots of $Ti_{68}Fe_{26}Ni_1Si_5$ were prepared by RF-induction melting of a corresponding stoichiometric mixture of 99.9% pure Ti, Fe, Ni, and Si in purified graphite crucibles under an inert argon atmosphere. The alloy ingots were then subjected to rapid solidification employing melt spinning at various tangential speeds ranging from 25 to 40 m/s. After rapid solidification, 30–40-μm-thick and 1–2-cm-long ribbons were formed. The ribbons were then subjected to extensive structural characterization, employing first powder x-ray diffraction (Phillips PW1710), and then rigorous transmission electron microscopy (TEM, Phillips-EM CM-12). For TEM, the ribbons were electropolished using 5% $HC10_4$ in methanol as electrolyte at $-20\,°C$. TEM of the samples was carried out in various modes like selected area diffraction pattern (SADP) and bright field imaging, and the results are discussed in the following section.

RESULT AND DISCUSSION

The rapidly solidified melt-spun ribbons of $Ti_{68}Fe_{26}Ni_1Si_5$ alloy were electropolished and investigated in both diffraction and imaging modes by TEM. The presence of quasicrystalline and related phases were observed. Figures 1(a)–1(c) depict the fivefold, twofold, and threefold SADP's recorded by utilizing the double tilt facility of the specimen holder corresponding to the bright field image [Fig. 1(d)]. Mutual orientations of these SADP's were in conformity with the icosahedral symmetry. The bright field micrograph was taken in fivefold orientation and shows the characteristic mottled features observed in IQC phases. Apart from such regions having icosahedral symmetry, microstructural features with sectorial contrast were also noticed. Figure 2(a) shows such a microstructure having orientation nearly parallel to the fivefold IQC. Figure 2(b) is the SADP recorded from the central region of the grain, and Figs. 2(c)–2(g) are the SADP's corresponding to the five sectors of the nodule, but sufficiently away from the central region. All these SADP's look similar to the fivefold pattern of IQC [viz., Fig. 1(a)], but they differ in details. This pertains to the shape of spots and also their shifts *vis-à-vis* the IQC phase. The occurrence of these kinds of features have been attributed to the presence of phason strains leading to various approximant phases.

Various other representative zone patterns were also taken from the nodular grain with sectorial contrast and are shown in Figs. 3(a)–3(d), which resembles twofold and threefold patterns of the icosahedral phase. For a detailed and comparative study of these features, various other regions having microstructural features analogous to Fig. 1(d) were investigated, and the fivefold like pattern from some of them are shown in Figs. 4(a)–4(c). A close comparison of the patterns reveals significant differences between them. In the litera-

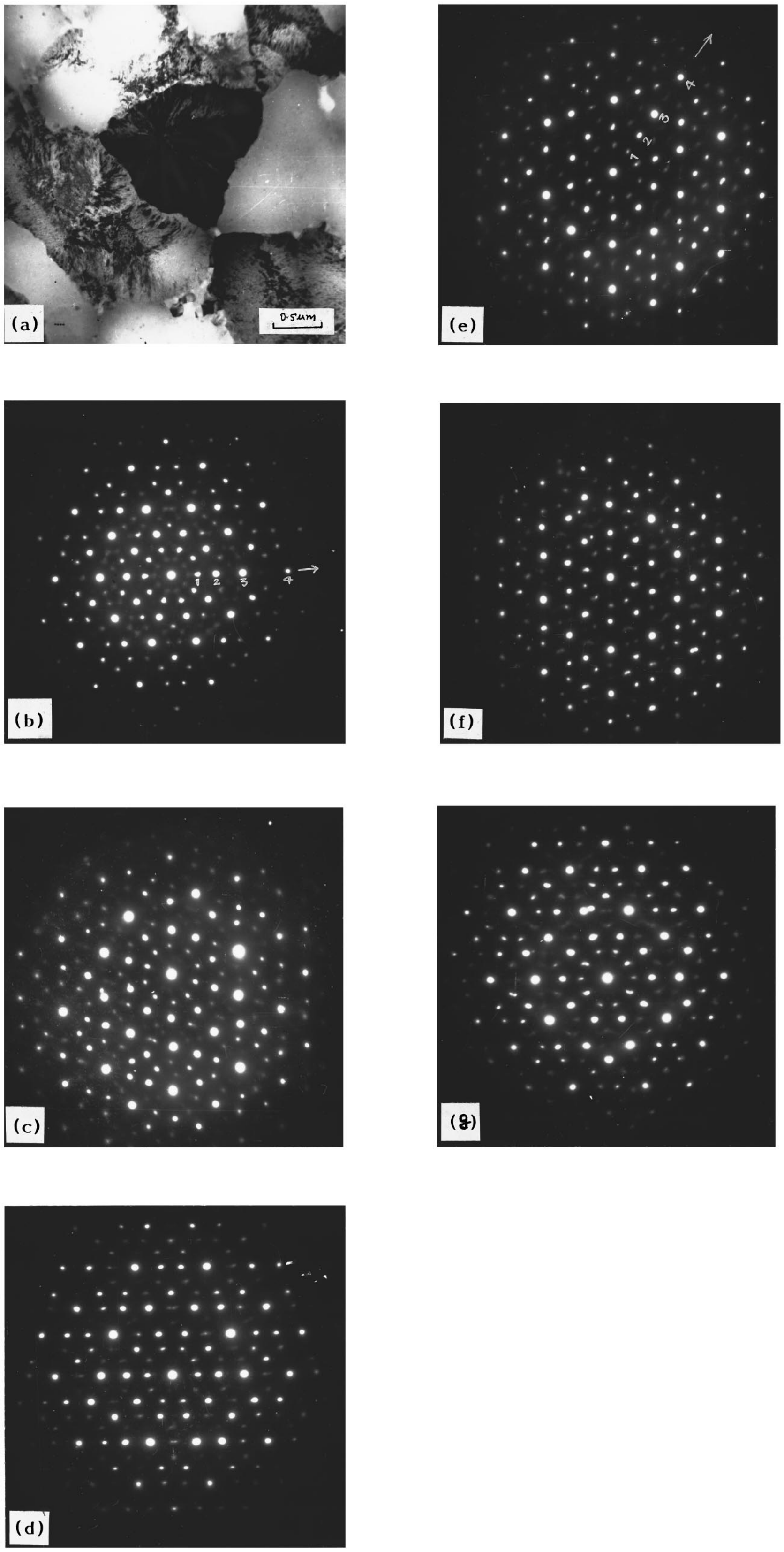

FIG. 2. (a) Microstructure revealing the sectorial contrast emerging radially from the central region of the grain, (b) SAD pattern from close to the central region. (c)–(g) represent the SAD patterns from the different sectors of the same grain. These represent the pseudofive-fold (or broken) symmetry. The difference between various patterns can be observed by comparing the directions of the shifts of spots. In each pattern there is only one direction, i.e., [100]-type direction, along which the spots suffer only linear shifts. This direction has been indicated by an arrow in (b) and (e) whose spots along this direction have been used for calculation of the γ value of the phason strain matrix [as given in Eq. (1)].

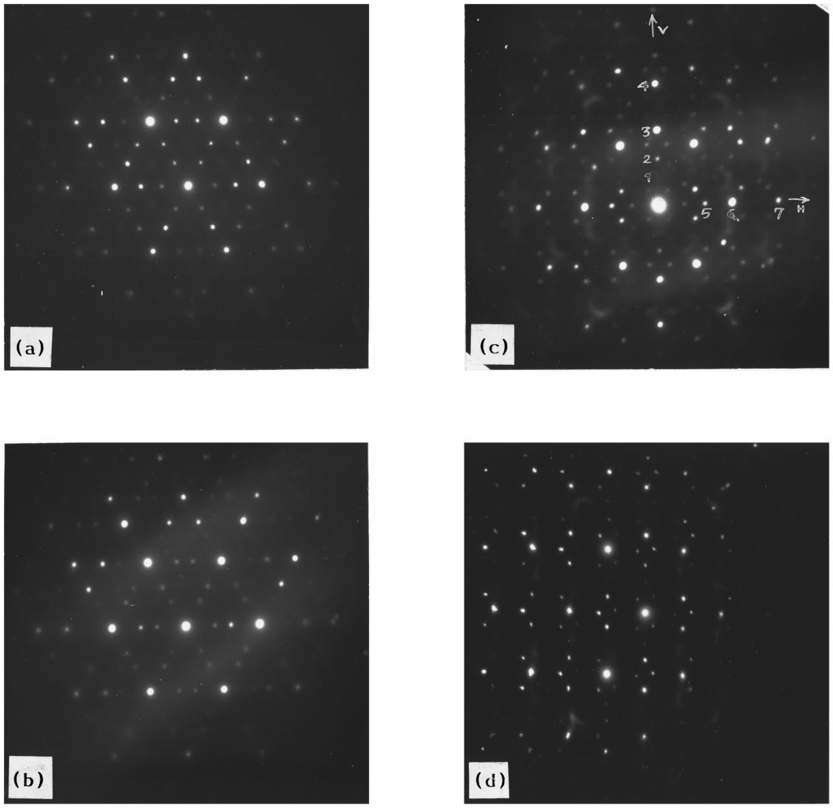

FIG. 3. (a) and (b) represent the SAD patterns revealing the proper threefold and improper (or pseudo) threefold, respectively, expected from a tetrahedrally modified icosahedral phase. (c) and (d) represent the proper and improper twofold from the same phase. The arrows as marked in (c) indicate the vertically and horizontally oriented proper twofold direction along which the spots have been used for measurement for the γ value of the phason strain matrix.

ture, the occurrence of diffraction patterns displaying shifts in the spot position and variation in their intensity *vis-à-vis* that of IQC has been attributed to the presence of phason strains in the latter. They modify the atomic arrangements, and hence their diffraction features. As discussed in the beginning of this presentation, the phason strain is equivalent to fixing the orientation of the physical space for the linear case.

Any orientation other than that required for IQC necessarily breaks the icosahedral symmetry in physical space structure both for the linear[17] and nonlinear motifs.[18] If the physical space orientation is made rational with the help of successive approximants of τ, the resulting structure is RAS for the former case. In contrast to this, if some other rational numbers are chosen for fixing the physical space, then they give rise to various modifications of the icosahedral phase. They have been referred to as non-Fibonacci phases in the literature.[11]

The orientation of a physical space can be experimentally determined by comparing the diffraction of rationally modified RAS phases with that of IQC's. This is accomplished by following the well-known relationship for cubic phases with $m3$ point group and is given by

$$\begin{pmatrix} G_x^{\parallel} \\ G_y^{\parallel} \\ G_z^{\parallel} \end{pmatrix}_{\text{Expt}} = \begin{pmatrix} G_x^{\parallel} \\ G_y^{\parallel} \\ G_z^{\parallel} \end{pmatrix}_{\text{Icos}} + \begin{pmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \gamma \end{pmatrix} \begin{pmatrix} G_x^{\perp} \\ G_y^{\perp} \\ G_z^{\perp} \end{pmatrix} \quad (1)$$

where $G_x^{\parallel} G_y^{\parallel} G_z^{\parallel}$ and $G_x^{\perp} G_y^{\perp} G_z^{\perp}$ are, respectively, physical and pseudospace Cartesian components of any 6D reciprocal lattice vectors, γ is the coefficient of the phason matrix, the subscript ''Icos'' and ''Expt'' refer, respectively, to icosahedral structure and experimentally observed vectorial distances with respect to the transmitted spot.

As indicated in the Introduction, the phason matrix can have a number of nonzero elements, depending on the symmetry of the observed structure appearing in Eq. (1), which relates p/q in the description of RAS (Ref. 19) by the following equation:

$$\gamma = \frac{(\tau - T)}{(1 + \tau T)} \quad (\text{for } T = p/q). \quad (2)$$

Any particular rational orientation of a physical space having tetrahedral symmetry ($m3$) can be chosen in five independent ways to give rise to five related variants. This has been observed in the present investigation (see Fig. 2). The diffraction patterns taken from various sectors of a single grain reveal only five different orientations and are obvious in Figs. 2(c)–2(g). Such a transformation can occur through symmetry breaking of the icosahedral phase in the solid state in rapidly solidified materials. The transformation from the icosahedral phase to the tetrahedral one can arise owing to the introduction of isotropic quenched-in phason strains. The degree of such strains may lead to the formation of structures with $m3$ phases having different periodicities and in prin-

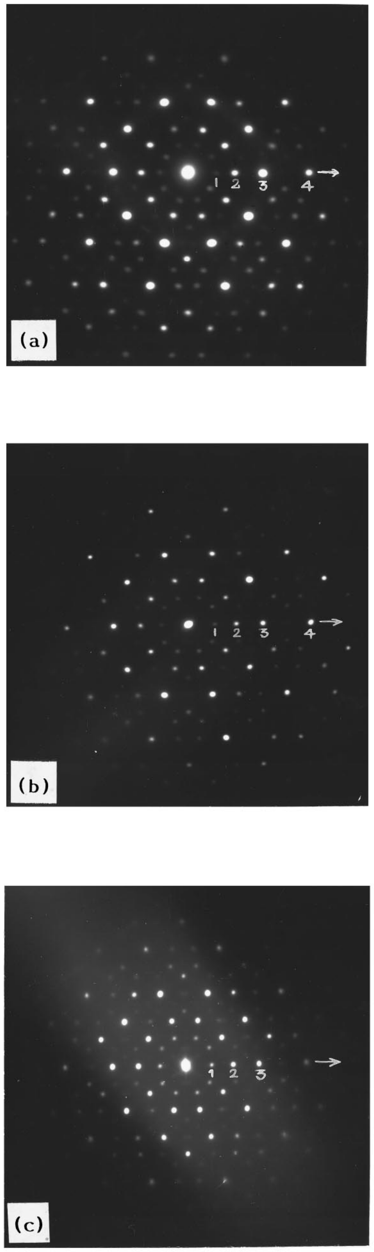

FIG. 4. (a), (b), and (c) represent the SAD pattern representing the pseudofivefold symmetry from different tetrahedrally modified phase grains. The arrows indications are similar to those in Fig. 2(b) and 2(c).

ciple can be aperiodic.[20] The presence of a varied degree of strains has been noted in the present investigation [see Figs. 4(a)–4(c)].

All the six fivefold axes of IQC will transform into twofold (or pseudofivefold) and out of ten threefold, only four will remain as cubic threefold of the [111]-type, whereas the other six will behave as pseudothreefold. Similarly, out of 15 twofold, only three will be acting as cubic [100]. The $m\bar{3}$ will result with the above minimal symmetry.

Figures 3(a) and 3(b) correspond to the [111]-type threefold and pseudothreefold, respectively, from the modified phase displaying sectorial contrast. Similarly, Fig. 3(c) corresponds to the [100]-type proper twofold. The spots along the other two directions, [010]* and [001]*, are only linearly shifted as compared to the twofold pattern from IQC, as shown in Fig. 1(b). Figure 3(d) shows a pseudotwofold pattern from the same region. Their mutual orientations in the tilting experiment conform to those required for tetrahedral symmetry. This led us to conclude that we are dealing with a phase having tetrahedral symmetry. Now we wish to quantify the value of γ. This can be determined by identifying the row without any angular deviation. Utilizing Eqs. (1) and (2), corresponding values of $T=p/q$ can be determined. Following this, Mukhopadhyay *et al.*[19] and Zhang *et al.*[11] have determined p/q experimentally. The values are either the ratio of Fibonacci integers 1/1, 2/1, 3/2, . . . , or lying in between these values. The phases corresponding to the latter has been termed as non-Fibonacci approximants. We have adopted a parallel procedure to determine the value of p/q for the observed approximant phases in the present investigation. For this, a careful measurement of shift in position of diffraction spots *vis-à-vis* IQC was carried out. The indexing of the spots was accomplished following Elser.[21] The $G^{\parallel}$ and $G^{\perp}$ components corresponding to the sextuplet were determined for the icosahedral case by choosing a quasilattice constant equal to 4.6 Å.[11] These values, in combination with the measurement of the experimentally observed reciprocal distances, led to the different values of γ. Table I(a) gives $G^{\parallel}$ and $G^{\perp}$ values of all the relevant reflections of IQC based on the above quasilattice constants. Table I(b) gives $G^{\parallel}_{\mathrm{Expt}}$, and the calculated γ values for all the SADP's displaying pseudofivefold symmetry. For these calculations, a true twofold direction in these SADP's was identified. This has been done to realize the effects of phason strains leading to tetrahedral symmetry. It is important to note here that pseudoaxes do not contain any information about the symmetry and should not be considered for delineating the point group of the phases. Apart from this, identification of $G^{\parallel}_{\mathrm{Expt}}$ *vis-à-vis* $G^{\parallel}_{\mathrm{Icos}}$ for the same indices along any of the improper symmetry axes will be difficult and erroneous, since these suffer radial as well as angular shifts in spots, unlike proper symmetry axes which have only radial shifts. The twofold reciprocal axes of twofold SADPs [Fig. 3(d)] have been analyzed to see the consistency of our assertion that they [Figs. 3(a)–3(d)] have been recorded from the same nodular regions. Figure 4(a) obviously matches with those of vertical twofold direction in Table I(c). The scrutiny of γ's reveals that none of the γ values coming out from any pattern are equal, which would have been the case for the normal mode locking of linear phasons leading to RAS. The variable nature of γ will, therefore, mean a variable linear phason strain, and can be termed a variable strain approximant (VSA) structure. The foregoing discussion obviously shows that $G^{\parallel}_{\mathrm{Expt}}$ does not have a linear dependence on $G^{\perp}$. Such behavior can be understood in a better way by exploring the exact form of nonlinear dependence of $G^{\parallel}_{\mathrm{Expt}}$. Such a dependence has been discussed[18] for a general case in a qualitative way. The quantitative details pertaining to the present case are being explored further.

Once we have determined the point group of the diffraction patterns under the assumption of the Friedel law, we now proceed to understand the translational invariance of the reciprocal rows considered so far. The measurements have revealed the ratio of the first two reciprocal vectors are not simple rational numbers (e.g., 1.846, 1.556, and 1.565), respectively, for Figs. 2(c)–2(g), Fig. 2(b) and Figs. 4(a) and 4(b), these numbers vary for the various regions observed by

TABLE I. (a) Values of $G^{\parallel}$ and $G^{\perp}$ in Å^{-1} for selected spots of the IQC pattern. (b) Values of $G^{\parallel}_{\text{Expt}}$ and γ for various pseudofivefold patterns. (c) Values of $G^{\parallel}_{\text{Expt}}$ and γ for the twofold pattern.

(a)

Spot number	Indices of reflection	$G^{\parallel}$	$G^{\perp}$
1	100010	1.102	+0.680
2	101011	1.799	−0.419
3	201021	2.902	+0.261
4	302032	4.717	−0.159
5	011101	1.799	−0.4192
6	021201	2.9017	+0.2606
7	032302	4.7167	−0.1586

(b)

Spot number	Fig. 2(b)		Figs. 2(c)–2(g)		Fig. 4(a)		Fig. 4(b)		Fig. 4(c)	
	$G^{\parallel}_{\text{Expt}}$	γ	$G^{\parallel}_{\text{Expt}}$	γ	$G^{\parallel}_{\text{Expt}}$	γ	$G^{\parallel}_{\text{Expt}}$	γ	$G^{\parallel}_{\text{Expt}}$	γ
1	1.012	−0.131	0.993	−0.160	1.051	0.074	1.012	−0.131	0.973	−0.189
2	1.870	−0.168	1.791	+0.018	1.791	+0.018	1.811	−0.028	1.811	−0.027
3	2.902	−0.001	2.882	−0.075	2.843	−0.224	2.823	+0.298	2.765	−0.523
4	4.732	−0.101	4.693	+0.147	4.551	+1.044	4.596	+0.761		

(c)

Spot number	Vertical direction		Spot number	Horizontal direction	
	$G^{\parallel}_{\text{Expt}}$	γ		$G^{\parallel}_{\text{Expt}}$	γ
1	1.051	−0.074	5	1.752	0.111
2	1.791	+0.018	6	2.843	−0.224
3	2.843	−0.224	7	4.558	−0.100
4	4.551	+1.044			

us. We therefore conclude that there is no discernible periodicity within the limit of our experimental techniques. We further note the ratio has a tendency to change its value. This is easily comprehended by recalling that there is no restriction on this by the point group symmetry. Following the annotation of Steinhart and Ostlund,[22] this class of materials will fall in the category of incommensurate phases. Here it can be pointed out that a similar kind of aperiodic structure, but with cubic point group symmetry, had been reported by Feng *et al.*[23] in a V-Ni-Si alloy system.

CONCLUSIONS

We have thus shown experimental evidence of tetrahedral phases in the Ti-Fe-Ni-Si system. They seem to arise owing to slight modification of the icosahedral phase and do not have any linear phason strain dependence normally discussed in the literature so far in reciprocal space. The different values of γ in the present investigation indicate the origin of these phases in the phason freezing in local regions during the rapid solidification process. Further investigation on the origin of these phases and possible analysis in terms of the nonlinear dependence of $G^{\parallel}_{\text{Expt}}$ are being explored. These phases do not have an discernible periodicity within the limit of our observation.

ACKNOWLEDGMENTS

The authors are grateful to Professor A. L. Mackay (London), Professor A. R. Verma (NPL-Delhi), Professor R. P. Rastogi (Lucknow), Professor H. P. Gautam (BHU), Professor S. Ranganathan, Professor T. V. Ramakrishanan (Bangalore), Dr. N. K. Mukhopadhyay (NML, Jamshedpur), and Professor C. Dong (People's Republic of China) for helpful discussion and encouragement.

[1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[2] L. Bendersky, Phys. Rev. Lett. **55**, 1461 (1985).

[3] S. Ranganathan and K. Chattopadhyay, Annu. Rev. Mater. Sci. **21**, 437 (1991).

[4] A. I. Goldmann and K. F. Kelton, Rev. Mod. Phys. **65**, 213 (1993).

[5] R. K. Mandal and S. Lele, in *Proceedings of the International Conference on Aperiodic Crystals*, edited by G. Chapuis and W. Paciorek (World Scientific, Singapore, 1995), p. 97.

[6] R. A. Dunlap and K. Dini, Can. J. Phys. **63**, 1267 (1985).
[7] K. F. Kelton, in *Proceedings of the International Conference on Aperiodic Crystals* (Ref. 5), p. 505.
[8] A. P. Tasai, A. Inoue, and T. Masumoto, J. Mater. Sci. Lett. **8**, 253 (1989).
[9] N. P. Lalla, R. S. Tiwari, and O. N. Srivastava, J. Mater. Res. **7**, 53 (1992).
[10] N. K. Mukhopadhyay, K. N. Ishihara, S. Ranganathan, and K. Chattopadhyay, Acta Metall. **39**, 1151 (1990).
[11] X. Zhang, R. M. Stroud, J. L. Libbert, and K. F. Kelton, Philos. Mag. B **70**, 927 (1994).
[12] P. Mandal, R. K. Mandal, R. S. Tewari, and O. N. Srivastava, Phys. Rev. B **45**, 7521 (1992).
[13] K. F. Kelton and P. C. Gibbons, Philos. Mag. B **66**, 639 (1992).
[14] P. Bak and A. I. Goldmann, in *Introduction to Quasicrystals*, edited by M. Jaric (Academic, New York, 1988).
[15] C. Janot, Int. J. Mod. Phys. B **7**, 310 (1993).
[16] J. W. Cahn, D. Gratias, and B. Mozer, J. Phys. (France) **4**, 1225 (1988).
[17] Y. Ishii, Phys. Rev. B **39**, 11 862 (1989).
[18] S. Lele and R. K. Mandal, in *Proceedings of the Advances in Physical Metallurgy*, edited by S. Banerjee and R. V. Ramanujan (Gordon and Breach, New York, 1995), Vol. 89.
[19] N. K. Mukhopadhay, G. C. Weatherly, D. J. Lloyd, and J. D. Embury, J. Non-Cryst. Solids **63**, 153 (1993).
[20] R. Lifshitz and N. D. Mermin, in *Proceedings of the 5th International Conference of Quasicrystals, France*, edited by C. Janot and R. Mosseri (World Scientific, Singapore, 1995).
[21] V. Elser, Phys. Rev. B **32**, 4892 (1985).
[22] P. J. Steinhardt and S. Ostlund, *Physics of Quasicrystals* (World Scientific, Singapore, 1988).
[23] Y. C. Feng, G. Lu, H. Q. Ye, K. H. Kuo, R. L. Withers, and G. Van Tendeloo, J. Phys. Condens. Matter **2**, 9749 (1990).