A group theoretical consideration of the diffraction patterns of $Nd_{1+\ epsilon}\ Fe_4B_4$ compounds

1992 J. Phys.: Condens. Matter 4 9221

(http://iopscience.iop.org/0953-8984/4/47/004)

J. Phys.: Condens. Matter 4 (1992) 9221–9234. Printed in the UK

A group theoretical consideration of the diffraction patterns of $Nd_{1+\epsilon}Fe_4B_4$ compounds

Z B Zhao and Shane Y Hong

Department of Mechanical and Materials Engineering, Wright State University, Dayton, OH 45435, USA

Received 18 May 1992, in final form 17 August 1992

Abstract. The entire crystal structure of each member of the series of $R_{1+\epsilon}Fe_4B_4$ compounds is built up from the interpenetration of two incommensurable substructures: the R substructure and the Fe–B substructure. In their $[uv0]$ electron diffraction patterns, satellite reflections due to the modulation occur in addition to the basic reflections corresponding to either the Fe–B substructure or the Nd substructure. To study the systematic extinction conditions for the observed x-ray and electron diffraction patterns, symmetry analyses have been performed by means of two approaches—by considering the three-dimensional space group of the commensurate supercells, and by considering the four-dimensional superspace group developed by de Wolff *et al* . The individual symmetry of the substructure has served as the basis for each approach in this paper. Examination of the symmetry under the commensurate approximation is the crucial step for the structure analysis of the Vernier structures. However, the occurrence and distribution of satellite reflections in the electron diffraction patterns cannot be interpreted within this framework. The superspace group characterization of these compounds provides a method of giving some insight into the general features of the conditions of the systematic extinction observed in the diffraction patterns of $R_{1+\epsilon}Fe_4B_4$ compounds.

1. General features of $R_{1+\epsilon}Fe_4B_4$ compounds

Several experimental and theoretical investigations concerning the crystal structural aspects of $R_{1+\epsilon}Fe_4B_4$ (R represents rare-earth elements, e.g. R = Ce, Pr, Nd, Sm, Gd and Tb) compounds have been reported in recent years (Braun *et al* 1982, Bezinge *et al* 1985, 1987, Givord *et al* 1985, 1986a,b, Tian *et al* 1988, Zhao and Ma 1988, 1989, Zhao *et al* 1989a,b,c,d). Based on the atomic parameters reported by Kuźma and Bilonizhbo (1975) and Givord *et al* (1986b), the (001) and (110) crystallographic projections of $Nd_{10}(Fe_4B_4)_9$ and $NdCo_4B_4$ are visualized in figure 1. The entire crystal structure is formed by the interpenetration of two substructures. One is the Fe–B substructure, a three-dimensional framework consisting of edge-sharing iron tetrahedra and boron atom pairs. The other one is the R substructure, which is defined by R atoms in the form of infinite chains along the c axis. These two substructures, both of tetragonal symmetry, have the same dimensions in the tetragonal basal plane. However, their periods in the c direction do not match each other. Moreover, the value of $c(\text{Fe–B})/c(\text{R})$ as a function of composition x in $R_xFe_4B_4$ alloys is approximately expressed by ratios of two relatively small integers. Such a feature can be characterized by the chimney–ladder structure or

0953-8984/92/479221+14$07.50

the Vernier structure, which was also found to occur in $MnSi_{2-x}$ (e.g. Knott *et al* 1967, Jeitschko and Parthé 1967) and $Ba_{1+x}Fe_2S_4$ (e.g. Grey 1974, Hoggins and Steinfink 1977). Electron diffraction and electron microscopic studies on $R_{1+\epsilon}Fe_4B_4$ compounds with R = Pr (Tian *et al* 1988) and R = Nd (Zhao *et al* 1989a,b,c,d) revealed the incommensurability of their crystal structures. Despite the fact that more and more incommensurately modulated crystal structures have been found in solid materials, compounds which consist of two or more mutually incommensurable crystallographic subsystems, such as $Nd_{1+\epsilon}Fe_4B_4$, are less common. Also, it was reported by Zhao *et al* (1989d) that these compounds where R = Nd present a novel example of the infinitely adaptive structures proposed by Anderson (1973, 1977). Since the periodicity mismatch happens only in the c direction (see figures 1(*b*) and 1(*c*)), the most characteristic electron diffraction patterns for $R_{1+\epsilon}Fe_4B_4$ compounds are the $[uv0]$ sections in which the satellite reflections appear simultaneously with the basic reflections. The occurrence and distribution of the systematic extinction conditions in the observed diffraction patterns of $R_{1+\epsilon}Fe_4B_4$ compounds, generally associated with the symmetry of their crystal structures, have not been well interpreted as yet. In order to characterize the symmetry of $R_{1+\epsilon}Fe_4B_4$ compounds, and then to understand their diffraction patterns, two approaches are attempted in the following sections. The fundamentals for each approach will be briefly summarized separately.

2. Three-dimensional space group in the commensurate supercell

Strictly speaking, the periodicity of $R_{1+\epsilon}Fe_4B_4$ compounds should be defined by two translation vectors c(Fe–B) and c(R). In spite of this, one can always choose a number of pairs of integers p and q, within a specified tolerance, to meet the need of the relation $p/q = c(\text{Fe–B})/c(\text{R})$. Consequently, an artificial superstructure $R_p(Fe_4B_4)_q$ whose c dimension is defined by the smallest common multiple of c(Fe–B) and c(R) (i.e. $c = pc(\text{R}) = qc(\text{Fe–B})$), can be constructed. In such a way, one recovers the translational symmetry of the compounds and, hence, three-dimensional space group characterization applies.

2.1. Commensurate models and their space groups

The symmetry relation between a derivative crystal structure and its parent structure has been discussed by Buerger (1947). It was proposed that the symmetry of a derivative structure is a subgroup of the space group of the parent structure. In the case of $R_{1+\epsilon}Fe_4B_4$ compounds, the symmetry of the entire crystal structure must be compatible with the individual symmetry of both the substructures. Either the Fe–B substructure or the R substructure can be regarded as the parent structure of the commensurate superstructure $R_p(Fe_4B_4)_q$. Consequently, the highest symmetry of $R_p(Fe_4B_4)_q$ is the maximum common subgroup of the space groups of the Fe–B substructure and the R substructure. As reported by Givord *et al* (1985), the symmetry of the Fe–B substructure is $P4_2/ncm$ and that of the R substructure is $I4/mmm$. In view of the centrosymmetries of both substructures, it is reasonable to suppose that the superstructure $R_p(Fe_4B_4)_q$ is also centrosymmetric, and one should superimpose its symmetry centre onto those of $I4/mmm$ and $P4_2/ncm$. Here the space groups of the substructures are expressed in terms of the space group generators and the translation vectors. If we define $2/m$ at $(\frac{1}{4}, -\frac{1}{4}, \frac{1}{4})$ with respect to $\bar{4}$ as the origin of $P4_2/ncm$, one may divide its symmetry elements into two parts:

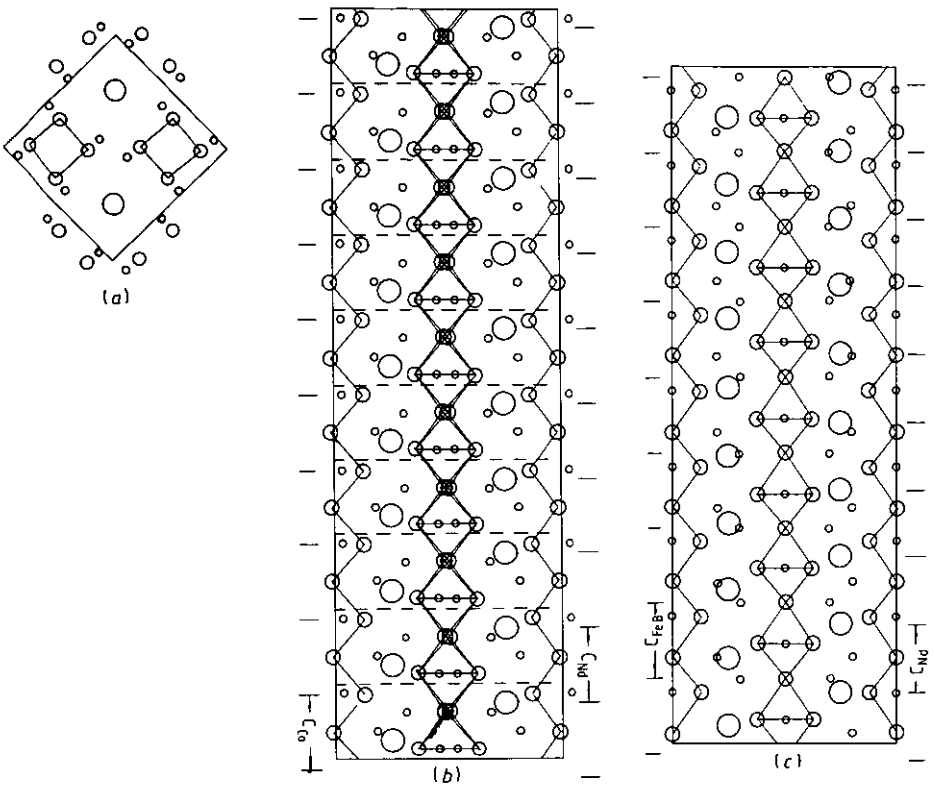


Figure 1. (*a*) The (001) crystallographic projection of $NdCo_4B_4$ (that for $Nd_{1+\epsilon}Fe_4B_4$ is slightly different). (*b*) and (*c*) The (110) crystallographic projections of $NdCo_4B_4$ and $Nd_{1+\epsilon}Fe_4B_4$, respectively, which visualize the feature of a Vernier structure or a chimney–ladder structure. Large circle, Nd atom; medium circle, Fe (or Co) atom; small circle, B atom. (The figures were produced by using the structural parameters of Kuźma and Bilonizhbo (1975) and Givord *et al* (1986b).)

(a) a translation part

$$(1, 0, 0) \qquad (0, 1, 0) \qquad (0, 0, 1/q) \tag{2.1}$$

(b) an orthogonal part

$$\begin{aligned}
&x, y, z \qquad \tfrac{1}{2} - x, \tfrac{1}{2} - y, z \qquad \tfrac{1}{2} - y, x, 1/2q + z \qquad y, \tfrac{1}{2} - x, 1/2q + z \\
&\bar{x}, \tfrac{1}{2} + y, 1/2q - z \qquad \tfrac{1}{2} + x, \bar{y}, 1/2q - z \qquad \tfrac{1}{2} + y, \tfrac{1}{2} + x, \bar{z} \qquad \bar{y}, \bar{x}, \bar{z} \\
&\bar{x}, \bar{y}, \bar{z} \qquad \tfrac{1}{2} + x, \tfrac{1}{2} + y, \bar{z} \qquad \tfrac{1}{2} + y, \bar{x}, 1/2q - z \qquad \bar{y}, \tfrac{1}{2} + x, 1/2q - z \\
&x, \tfrac{1}{2} - y, 1/2q + z \qquad \tfrac{1}{2} - x, y, 1/2q + z \qquad \tfrac{1}{2} - y, \tfrac{1}{2} - x, z \qquad y, x, z.
\end{aligned} \tag{2.2}$$

In the case of the R substructure, the $2/m$ which is at $(\frac{1}{4}, -\frac{1}{4}, \frac{1}{4})$ with respect to $4/mmm$ is also chosen as the origin of $I4/mmm$. Then it follows that:

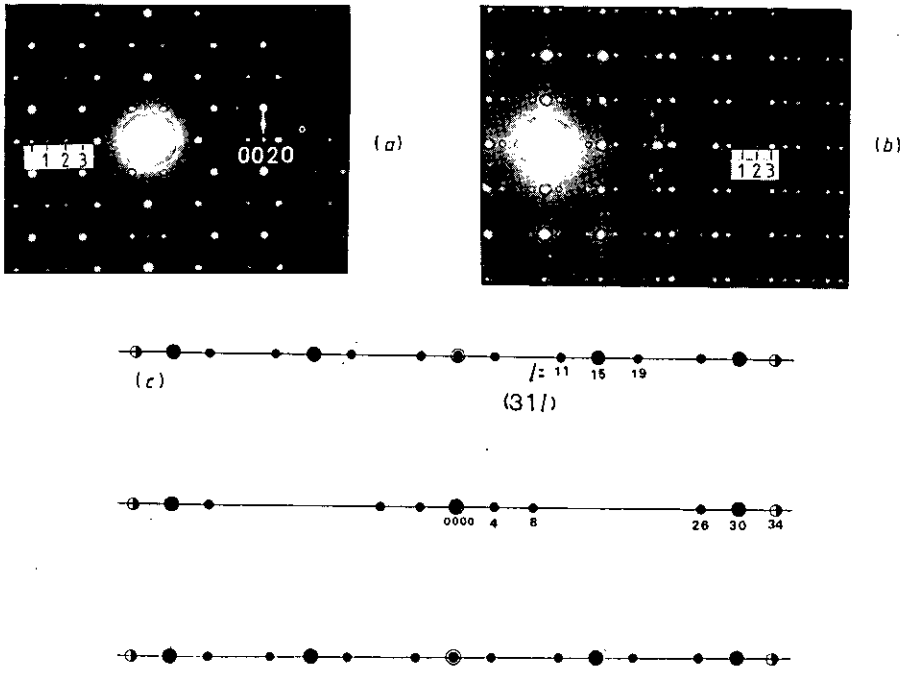


Figure 2. (*a*) and (*b*) Two examples of diffraction patterns which can be simulated by the commensurate models $R_{2j+1}(Fe_4B_4)_{2j-1}$: (*a*) for $j = 8$ and (*b*) for $j = 9$. (*c*) Systematics of the $[\bar{1}\,3\,0]$ pattern for the superstructure $R_{17}(Fe_4B_4)_{15}$. Note the selection rule of $l = 15f + 17j$, as discussed in the text.

(a) for the translation part

$$(1, 0, 0) \qquad (0, 1, 0) \qquad (0, 0, 1/p) \qquad (\tfrac{1}{2}, \tfrac{1}{2}, 1/2p) \tag{2.3}$$

(b) for the orthogonal part

$$\begin{array}{llll} x, y, z & \bar{x}, \bar{y}, 1/2p + z & \bar{y}, \tfrac{1}{2} + x, z & \tfrac{1}{2} + y, \bar{x}, z \\ \bar{x}, \tfrac{1}{2} + y, \bar{z} & \tfrac{1}{2} + x, \bar{y}, \bar{z} & y, x, \bar{z} & \bar{y}, \bar{x}, 1/2p - z \\ \bar{x}, \bar{y}, \bar{z} & x, y, 1/2p - z & y, \tfrac{1}{2} - x, \bar{z} & \tfrac{1}{2} - y, x, \bar{z} \\ x, \tfrac{1}{2} - y, z & \tfrac{1}{2} - x, y, z & \bar{y}, \bar{x}, z & y, x, 1/2p + z. \end{array} \tag{2.4}$$

The maximum number of common subgroups should be formed by the maximum number of mathematical intersections of operations (2.1)-(2.4). By proper repetition of the translation operations in (2.1) and (2.3), common translation vectors for both space groups can be easily obtained, which are expressed as

$$(1, 0, 0) \qquad (0, 1, 0) \qquad (0, 0, 1). \tag{2.5}$$

with regard to the orthogonal generators, the parity of p and q needs to be taken into account. By applying the translational vector $(\frac{1}{2}, \frac{1}{2}, 1/2p)$ p times to $(\frac{1}{2} + y, \bar{x}, z)$, for instance, one has the transformation form for $I4/mmm$:

$$(\tfrac{1}{2}, \tfrac{1}{2}, 1/2p)^p(\tfrac{1}{2} + y, \bar{x}, z) \rightarrow ((p + 1)/2 + y, p/2 - x, \tfrac{1}{2} + z). \tag{2.6}$$

When p is odd, the resultant in (2.6) is $(y, \frac{1}{2}-x, \frac{1}{2}+z)$. Its equi-point, on the other hand, can also be readily obtained from $P4_2/ncm$ by applying the translation vector $(0, 0, 1/q)$ to $(y, \frac{1}{2}-x, \frac{1}{2}+z)$ $((q-1)/2)$ times if q is supposed odd.

Similarly, it can be shown that the obtained intersections of the orthogonal generators may be classified into the following three categories.

(1) p odd and q odd

$$\begin{array}{llll} x, y, z & \frac{1}{2}-x, \frac{1}{2}-y, z & \frac{1}{2}-y, x, \frac{1}{2}+z & y, \frac{1}{2}-x, \frac{1}{2}+z \\ \bar{x}, \bar{y}, \bar{z} & \frac{1}{2}+x, \frac{1}{2}+y, \bar{z} & \frac{1}{2}+y, \bar{x}, \frac{1}{2}-z & \bar{y}, \frac{1}{2}+x, \frac{1}{2}-z. \end{array} \tag{2.7}$$

Apparently, the orthogonal generators in (2.7) combine with the translation vectors in (2.5) and are actually the entire generators of the space group $P4_2/n$. Known examples for this case are $Ce_{37}(Fe_4B_4)_{33}$, $Pr_{21}(Fe_4B_4)_{19}$, $Nd_{41}(Fe_4B_4)_{39}$, $Sm_{17}(Fe_4B_4)_{15}$, $Gd_{33}(Fe_4B_4)_{29}$ and $Tb_{31}(Fe_4B_4)_{27}$ (Parthé and Chabot 1984, Bezinge *et al* 1985). Indeed the practical structure refinement of $Sm_{17}(Fe_4B_4)_{15}$ was made utilizing the same space group assignment (Bezinge *et al* 1985). The diffraction patterns given in figures 2(*a*) and (*b*), which can be ascribed to $Nd_{17}(Fe_4B_4)_{15}$ and $Nd_{19}(Fe_4B_4)_{17}$, also belong to this category.

(2) p even and q odd

$$\begin{array}{llll} x, y, z & \frac{1}{2}-x, \frac{1}{2}-y, z & \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z & \frac{1}{2}+x, \bar{y}, \frac{1}{2}-z \\ \bar{x}, \bar{y}, \bar{z} & \frac{1}{2}+x, \frac{1}{2}+y, \bar{z} & x, \frac{1}{2}-y, \frac{1}{2}+z & \frac{1}{2}-x, y, \frac{1}{2}+z. \end{array} \tag{2.8}$$

Obviously, the operations in (2.5) and (2.8) constitute an orthorhombic space group $Pccn$. Givord *et al* (1985, 1986a,b) have performed the structure refinements for two commensurate superstructures $Nd_{10}(Fe_4B_4)_9$ and $Gd_8(Fe_4B_4)_7$ just based on this space group.

(3) p odd and q even

$$\begin{array}{llll} x, y, z & \frac{1}{2}-x, \frac{1}{2}-y, z & y, x, \frac{1}{2}+z & \frac{1}{2}+y, \frac{1}{2}+x, \frac{1}{2}-z \\ \bar{x}, \bar{y}, \bar{z} & \frac{1}{2}+x, \frac{1}{2}+y, \bar{z} & \bar{y}, \bar{x}, \frac{1}{2}-z & \frac{1}{2}-y, \frac{1}{2}-x, \frac{1}{2}+z. \end{array} \tag{2.9}$$

Unlike the cases in categories (1) and (2), the orthogonal operations in (2.9), when combined with (2.5), cannot form either a tetragonal space group or an orthorhombic space group. The generators in (2.9), however, reveal the existence of several symmetry operations, such as centrosymmetry and two *c*-glide planes along the diagonals. Thus an alternative treatment was attempted by choosing an enlarged supercell with $\boldsymbol{A} = \boldsymbol{a} + \boldsymbol{b}$, $\boldsymbol{B} = \boldsymbol{b} - \boldsymbol{a}$ and $\boldsymbol{C} = \boldsymbol{c}$. For such a selected supercell, $P4_2/ncm$ and $I4/mmm$ then take the forms of '$C4_2/nmc$' and '$F4/mmm$', respectively. Using a similar procedure to the one mentioned above, the intersection of their orthogonal part under the implication of odd p and even q can be obtained, which is expressed as

$$\begin{array}{llll} x, y, z & \frac{1}{2}-x, \bar{y}, z & \bar{x}, y, \frac{1}{2}-z & \frac{1}{2}+x, \bar{y}, \frac{1}{2}-z \\ \bar{x}, \bar{y}, \bar{z} & \frac{1}{2}+x, y, \bar{z} & x, \bar{y}, \frac{1}{2}+z & \frac{1}{2}-x, y, \frac{1}{2}+z. \end{array} \tag{2.10}$$

By noting the extra non-primitive translation $(\frac{1}{2}, \frac{1}{2}, 0)$ with reference to $(\boldsymbol{A}, \boldsymbol{B}, \boldsymbol{C})$, it readily known that the space group for this case is '$Ccca$' in the

revised supercell. Up until now, no structure analysis has been made using this space group. However, the actual structures of $Nd_{1+\epsilon}Fe_4B_4$ compounds inevitably make several numbers of their infinitely adapted structures fall into or approach such a category as the commensurate model owing to the quasi-continuous variation of $c(Fe–B)/c(R)$ as a function of x in $R_xFe_4B_4$. Examples of this case include $Nd_9(Fe_4B_4)_8$, $Nd_{11}(Fe_4B_4)_{10}$, $Nd_{13}(Fe_4B_4)_{12}$ and $Nd_{15}(Fe_4B_4)_{14}$, which were observed by electron diffraction (Zhao *et al* 1989d).

As demonstrated above, the symmetry of the commensurate superstructures $R_q(Fe_4B_4)_q$ depends on the parity of p and q, which can be explained by $P4_2/n$, $Pccn$ and '$Ccca$' respectively, for three different parity combinations of p and q.

2.2. *The selection rule of satellite reflections*

Besides the systematic extinctions associated with their space groups, the satellite reflections $(H\ K\ l)$ or $(h\ k\ l)$ always exhibit the selection rule for all superstructures $R_p(Fe_4B_4)_q$ as

$$l = qf + pj \tag{2.11}$$

where f and j are integers. This is a unique feature of the Vernier structures (see, for example, Flieher *et al* 1967, Johnson and Watson 1976, Völlenkle *et al* 1967). For the case $p - q = 1$, which was exemplified by the diffraction patterns modelled by $R_p(Fe_4B_4)_{p-1}$ (Zhao *et al* 1989d), this selection rule is true but not obvious. If $p - q \neq 1$, however, the selection rule can be clearly observed. Figures 2(*a*) and 2(*b*) are two diffraction patterns which can be described by the commensurate models $R_{2j+1}(Fe_4B_4)_{2j-1}$. As indicated in their insets, the satellite spacing represented by 12 is approximately 25% larger than the one represented by 23. Thus figures 2(*a*) and 2(*b*) actually represent the diffraction patterns of $Nd_{17}(Fe_4B_4)_{15}$ and $Nd_{19}(Fe_4B_4)_{17}$. Figure 2(*c*) is the systematics of the $[\bar{1}\,30]$ pattern of $Nd_{17}(Fe_4B_4)_{15}$, shown to indicate the selection rule $l = 15f + 17j$. The selection rule of $R_p(Fe_4B_4)_q$ is also evident in these x-ray diffraction patterns (Givord *et al* 1986a).

3. Superspace group characterization

The satellite spacings of the electron diffraction patterns of $Nd_{1+\epsilon}Fe_4B_4$ are variable rather than definite, and one usually has to choose different commensurate models to adapt the variation of the satellite spacings. If the difference in the satellite spacings is ignored, the general features of the same zone $[uv0]$ diffraction patterns, which have to be described by the different commensurate superstructures, are quite similar. This implies that it is possible to utilize a unified characterization within a certain framework to describe the symmetry of $Nd_{1+\epsilon}Fe_4B_4$ compounds.

As is well known, a typical feature of incommensurate crystal structures is the absence of their translation periodicity, and thus three-dimensional space groups no longer apply to their symmetry characterization. As well as the usual method of commensurate approximation, several approaches aiming at describing the symmetry of incommensurate crystal structures have been developed. These include superspace group theory (e.g. de Wolff 1974, 1977, Janner and Janssen 1977), the irreducible representations of ordinary space groups within the framework of Landau theory (e.g.

Janssen and Janner 1984) the dualistic approach (de Wolff 1984), etc. Superspace group theory, like other approaches, has been undergoing relatively frequent applications. Our discussion in the following sections is mainly based on the work of Janner and Janssen (1980, hereafter referred to as JJ).

3.1. Supersymmetry of $R_{1+\epsilon}Fe_4B_4$ compounds

The lattice of the $R_{1+\epsilon}Fe_4B_4$ crystal consists of two sublattices: the primitive tetragonal Fe–B sublattice (Λ_1) and the body centred tetragonal R sublattice (Λ_2), which can be represented by the following basis vectors:

$$\Lambda_1^*: \qquad a_{11}^* = (1, 0, 0)^* \qquad a_{12}^* = (0, 1, 0)^* \qquad a_{13}^* = (0, 0, q)^* \tag{3.1}$$

$$\Lambda_2^*: \qquad a_{21}^* = (1, 0, 0)^* \qquad a_{22}^* = (0, 1, 0)^* \qquad a_{23}^* = (0, 0, p)^*. \tag{3.2}$$

Here p and q are no longer restricted to being integers in the superspace group description. A minimal set of vectors

$$a_1^* = (1, 0, 0)^* \qquad a_2^* = (0, 1, 0)^* \qquad a_3^* = (0, 0, q)^* \qquad a_4^* = (0, 0, p)^* \tag{3.3}$$

are chosen as the basis for union of Λ_1^* and Λ_2^*. Thus every $a_{\nu j}$ ($\nu = 1, 2$; $j = 1, 2, 3$) can be represented as the integral linear combination of vectors in (3.3), and the matrices $\mathbf{Z}^\nu$ defined by equation (2) of JJ are

$$\mathbf{Z}^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \qquad \mathbf{Z}^2 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{3.4}$$

Consequently, the linear projections (defined by equation (6) of JJ) which map the 'internal space' vector b belonging to the superspace onto the three-dimensional space appear as

$$\pi_1 b = 0 \qquad \pi_2 b = a_{23}. \tag{3.5}$$

Furthermore, one can obtain the matrix σ defined in equation (5) of JJ

$$\sigma = (0, 0, \gamma) \tag{3.6}$$

where γ is defined as q/p. Four-dimensional superspace therefore is spanned by (equation (4) of JJ) the basis vectors

$$(a_1, 0) \qquad (a_2, 0) \qquad (a_3, -\gamma b) \qquad (0, b). \tag{3.7}$$

According to the notation in JJ, the atomic positions of the supercrystal can be expressed in terms of

$$(n_\nu + r_{\nu j} - \pi_\nu t, t) \qquad \nu = 1, 2 \tag{3.8}$$

where $n \in \Lambda_\nu$ and t is a vector defined in internal space. Representing a symmetry operator of the superspace group by $\{(R_E, R_I/(v_E, v_I)\}$, one may write the symmetry condition as

$$R_E(n_\nu + r_{\nu j} - \pi_\nu t) + v_E = n_{\nu'} + r_{\nu' j'} - \pi_{\nu'} t' \tag{3.9}$$

and

$$R_I t + v_I = t'. \tag{3.10}$$

An equivalent form of (3.9) and (3.10) can be written as

$$R_E(n_\nu + r_{\nu j}) + v_E + \pi_{\nu'} v_I = n_{\nu'} + r_{\nu' j'} \tag{3.11}$$

and

$$R_E \pi_\nu t = \pi_{\nu'} R_I t. \tag{3.12}$$

Also the invariance of each sublattice under the operation of a point group requires

$$R_E \Lambda_\nu = \Lambda_{\nu'}. \tag{3.13}$$

Hence relations (3.11)–(3.13) determine the holohedrism of the Bravais lattice.

With regard to $R_{1+\epsilon}Fe_4B_4$ compounds, two substructures consist of different atoms. Therefore, one necessarily has $\nu = \nu'$. As a consequence, equation (3.13) is always fulfilled. Furthermore, equation (3.11) may be divided into

$$R_E(n_1 + r_{1j}) + v_E + \pi_1 v_I = n_1 + r_{1j'} \tag{3.14}$$

$$R_E(n_2 + r_{2j}) + v_E + \pi_2 v_I = n_2 + r_{2j'}. \tag{3.15}$$

It can be shown that the holohedrism of the Bravais lattice spanned by the basis vectors in (3.7) is not compatible with tetragonal symmetry. Taking $\bar{4}$ of $P4_2/ncm$, for example, as the $R_E|v_E$ of the superspace group, one easily knows that (3.14) is satisfied owing to $\pi_1 b = 0$. However, for any v_I, the needs of (3.15) are by no means met. Such a situation also applies for other tetragonal symmetry operations. In other words, such a tetragonal symmetry related operator as $((R_E, R_I)|(v_E, v_I))$ does not exist that has equations (3.14) and (3.15) satisfied simultaneously. Therefore, one has to choose the basis vectors as selected in section 2 again. Under the newly chosen basis vectors $A = a+b$, $B = b-a$ and $C = c$, it can be easily demonstrated that the linear projections (3.5) and the matrix in (3.6) remain unchanged. Thus, the Bravais lattice of the superspace group is spanned by the basis vectors

$$a_1 = (A, 0) \qquad a_2 = (B, 0) \qquad a_3 = (C, -\gamma b) \qquad a_4 = (0, b). \tag{3.16}$$

In the notation of de Wolff *et al* (1981), the Bravais lattice can be represented by $P^{Cmmm}_{11\bar{1}}$.

The C centre in external space can be easily understood to be attributed to the non-primitive translation vector $(\frac{1}{2}, \frac{1}{2}, 0)$ which both '$C4_2/nmc$' and '$F4/mmm$' commonly possess. The holohedrism of the Bravais lattice is then generated by the following orthogonal generators:

$$\begin{aligned} &R_1 = (M_x, 1) \qquad R_2 = (2_x, -1) \qquad R_3 = (M_y, 1) \\ &R_4 = (2_y, -1) \qquad R_5 = (M_z, -1) \qquad R_6 = (2_z, 1). \end{aligned} \tag{3.17}$$

An implication of (3.17) is that the symmetry condition (3.12) has already been satisfied. Accordingly, one only needs to consider equations (3.14) and (3.15).

As an example, taking $v_E = (\frac{1}{2}, 0, 0)$ and $v_I = \frac{1}{2}b$ as the translation vector for the orthogonal transformation $R_1 = (M_x, 1)$, one finds that equation (3.14) is actually equivalent to a symmetry operation $M_x|(\frac{1}{2}, 0, 0)$ of the space group '$C4_2/nmc$' owing to $\pi_\nu b = 0$ for $\nu = 1$. On the other hand, the operation $\{(M_x, 1)|(\frac{1}{2}, 0, 0, \frac{1}{2})\}$ is equivalent to $(x, y, z) \rightarrow (\frac{1}{2} - x, y, \frac{1}{2} + z)$, a symmetric operation of the space group '$F4/mmm$', because of the relation $\pi_2 v_I = \frac{1}{2}a_{23}$. This means that equation (3.15) can also be met in such a case. Therefore, $g_1 = \{(M_x, 1)|(\frac{1}{2}, 0, 0, \frac{1}{2})\}$ is shown to be a generator of the superspace group of $R_{1+\epsilon}Fe_4B_4$ compounds. Similarly, one can also obtain the other generators of the superspace group. They are expressed as follows:

$$\begin{aligned} &g_2 = \{(2_x, -1)|(\tfrac{1}{2}, 0, 0, \tfrac{1}{2})\} \qquad g_3 = \{(M_y, 1)|(0, 0, 0, \tfrac{1}{2})\} \\ &g_4 = \{(2_y, -1)|(0, 0, 0, \tfrac{1}{2})\} \qquad g_5 = \{(M_z, -1)|(\tfrac{1}{2}, 0, 0, 0)\} \\ &g_6 = \{(2_z, 1)|(\tfrac{1}{2}, 0, 0, 0)\}. \end{aligned} \tag{3.18}$$

For the generators to the superspace group, their $\{R_E|v_E\}$ part in three-dimensional space gives rise to the following equi-points:

$$\begin{aligned} &x, y, z \qquad \tfrac{1}{2} - x, \bar{y}, z \qquad \bar{x}, y, \bar{z} \qquad \tfrac{1}{2} + x, \bar{y}, \bar{z} \\ &\bar{x}, \bar{y}, \bar{z} \qquad \tfrac{1}{2} - x, y, \bar{z} \qquad x, \bar{y}, z \qquad \tfrac{1}{2} - x, y, z. \end{aligned} \tag{3.19}$$

Additionally, considering the non-primitive translation $(\frac{1}{2}, \frac{1}{2}, 0)$ common to both '$C4_2/nmc$' and '$F4/mmm$', one can determine that all the $(R_E|v_E)$s of the superspace group form a three-dimensional space group '$Cmma$'. In the notation of de Wolff *et al* (1981), the superspace group of $R_{1+\epsilon}Fe_4B_4$ compounds can thus be represented by $P^{Cmma}_{ss\bar{1}}$. Its Bravais lattice has the basis vectors:

$$(1, 0, 0, 0) \qquad (0, 1, 0, 0) \qquad (0, 0, 1, -\gamma) \qquad (0, 0, 0, 1) \qquad (\tfrac{1}{2}, \tfrac{1}{2}, 0, 0). \tag{3.20}$$

The equi-points generated by this superspace group are

$$\begin{aligned} &x, y, z, t \qquad \tfrac{1}{2} - x, \bar{y}, z, t \qquad \bar{x}, y, \bar{z}, \tfrac{1}{2} - t, \qquad \tfrac{1}{2} + x, \bar{y}, \bar{z}, \tfrac{1}{2} - t \\ &\bar{x}, \bar{y}, \bar{z}, \bar{t} \qquad \tfrac{1}{2} + x, y, \bar{z}, \bar{t}, \qquad x, \bar{y}, z, \tfrac{1}{2} + t, \qquad \tfrac{1}{2} - x, y, z, \tfrac{1}{2} + t. \end{aligned} \tag{3.21}$$

Apparently the superspace group $P^{Cmmm}_{ss\bar{1}}$ is centrosymmetric.

3.2. Systematic extinctions associated with the superspace group

First of all, the Bravais lattice of the superspace group $P^{Cmma}_{ss\bar{1}}$, as with a non-primitive three-dimensional Bravais lattice, leads to a systematic extinction condition

$$F(H\ K\ f\ j) = 0 \qquad \text{unless } H + K = 2n \qquad \text{for } n \text{ integers.} \tag{3.22}$$

The characteristic sets of systematic extinctions related to certain operations of four-dimensional superspace groups have been tabulated by de Wolff *et al* (1981). With

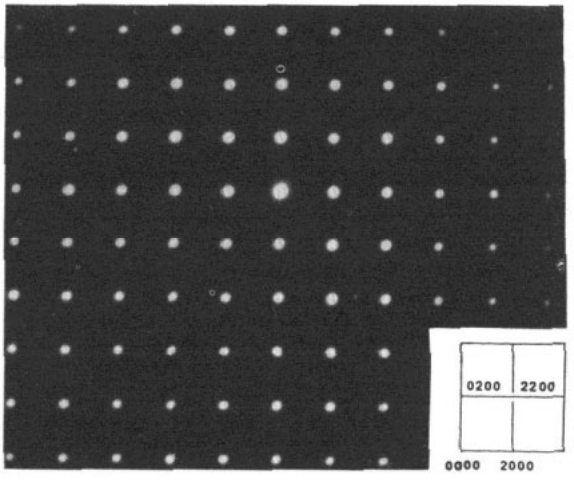


Figure 3. The [0 0 1] electron diffraction pattern of $Nd_{1+\epsilon}Fe_4B_4$. The indices in its inset are based on the diffraction vector $D = HA^* + KB^* + Lc^*(\text{Fe–B}) + jq$. Note the extinction rules $H + K = 2n$ and $H = 2n$.

regard to the superspace group of $R_{1+\epsilon}Fe_4B_4$ compounds, the operator $(\frac{a}{1})$ gives rise to

$$F(H\ K\ 0\ 0) = 0 \qquad \text{unless } H = 2n \qquad \text{for } n \text{ integers.} \tag{3.23}$$

Associated with the two symmetry elements (^m_s) along A and B one also has the following respective systematic extinction conditions

$$F(0\ K\ f\ j) = 0 \qquad \text{unless } j = 2n \qquad \text{for } n \text{ integers.} \tag{3.24}$$

and

$$F(H\ 0\ f\ j) = 0 \qquad \text{unless } j = 2n \qquad \text{for } n \text{ integers.} \tag{3.25}$$

By simple mathematical transformation, one finds that the indices H and K, corresponding to the rechosen basis vectors A, B and C, are related to the indices h and k, corresponding to the basis vectors a, b and c in the form

$$H = h + k \tag{3.26}$$

and

$$K = h - k. \tag{3.27}$$

Therefore it can be easily understood that the systematic extinction condition in (3.22) is ascribed to the rechosen basis vectors. In view of the fact that $(H\ K\ 0\ 0)$ represents basic reflections in diffraction patterns, the related systematic extinction condition should only be determined by the space groups of each substructure. Thus the condition $H = 2n$ in (3.23) is actually equivalent to the extinction condition $h + k = 2n$ for $(h\ k\ 0\ 0)$ reflections, the common requirement of both $P4_2/ncm$ and $I4/mmm$.

According to equation (3.3), the diffraction vectors of $R_{1+\epsilon}Fe_4B_4$ compounds can be represented by

$$\boldsymbol{D} = H\boldsymbol{A}^* + K\boldsymbol{B}^* + f\boldsymbol{c}^*(\text{Fe–B}) + j\boldsymbol{c}^*(R). \tag{3.28}$$

By a simple transformation, one has a new form of the diffraction vector

$$\boldsymbol{D} = H\boldsymbol{A}^* + K\boldsymbol{B}^* + L\boldsymbol{c}^*(\text{Fe–B}) + jq \tag{3.29}$$

where $L = f + j$ and $q = \boldsymbol{c}^*(\text{R}) - \boldsymbol{c}^*(\text{Fe–B})$. In such a case, the superspace group of the $R_{1+\epsilon}Fe_4B_4$ compounds changes its form into $N^{Cmma}_{ss\bar{1}}$ in the notation of de Wolff *et al* (1981).

4. Experimental results

Examples of typical electron diffraction patterns are presented in figures 4(*a*) and 5(*a*). The diffraction of $Nd_{1+\epsilon}Fe_4B_4$ compounds shows a strong dynamic effect (Zhao *et al* 1989a), which can be actually confirmed by a significant variation of satellite reflections in the (0 0 1) row of the different $[uv0]$ patterns, obtained by tilting the same crystal fragment. The multi-diffraction must be taken into account before the systematic extinction conditions can be extracted from the observed diffraction patterns. Figures 4(*b*) and 5(*b*) are the systematics of the diffraction patterns given in figures 4(*a*) and 5(*a*), respectively, and they are indexed in terms of the diffraction vectors given in (3.29). The observed extinction conditions are summarized as follows:

$$F(H\ K\ L\ j) = 0 \qquad \text{unless } H + K = 2n \qquad \text{for } n \text{ integers} \tag{4.1}$$

$$F(H\ k\ 0\ 0) = 0 \qquad \text{unless } H = 2n\ (K = 2n) \qquad \text{for } n \text{ integers} \tag{4.2}$$

$$F(H\ 0\ L\ j) = 0 \qquad \text{unless } j = 2n \qquad \text{for } n \text{ integers} \tag{4.3}$$

and

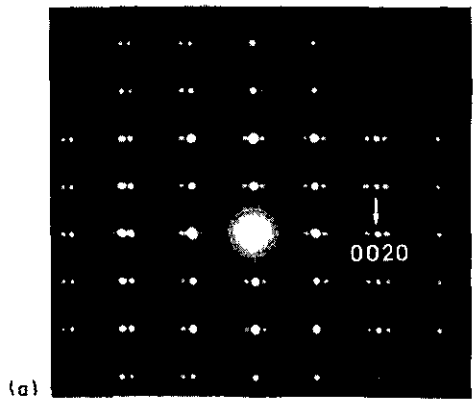
$$F(0\ 0\ l\ j) = 0 \qquad \text{unless } j = 2n \qquad \text{for } n \text{ integers.} \tag{4.4}$$

In comparison with those in (3.22)–(3.25), one finds that the predicted systematic extinction conditions associated with the superspace group are basically in agreement with those extracted from the observed diffraction patterns.

In the case of the commensurate superstructures $R_p(Fe_4B_4)_q$, only three indices $(H\ K\ l)$ are needed. Their diffraction vectors, by transformation from relation (3.28), can be represented by

$$\boldsymbol{D} = H\boldsymbol{A}^* + K\boldsymbol{B}^* + (qf + pj)\boldsymbol{c}^* \tag{4.5}$$

where $\boldsymbol{c}^*$ is equal to $\boldsymbol{c}^*(\text{Fe–B})/p$ or $\boldsymbol{c}^*(\text{R})/q$. Therefore, the index l in the case of commensurate superstructure models $R_p(Fe_4B_4)_q$ is always equal to $qf + pj$, where f and j are integers. This is the selection rule described by (2.11).



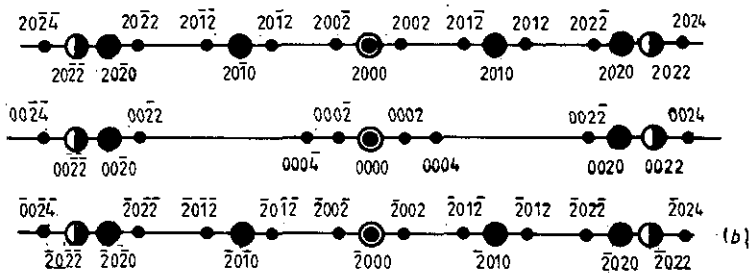
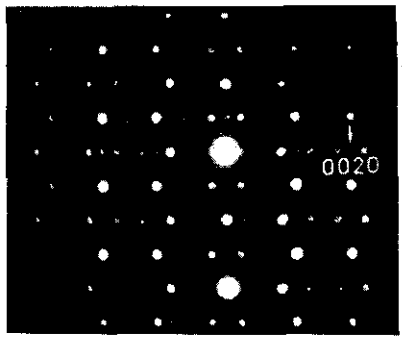


Figure 4. (*a*) An example of the [0100] electron diffraction pattern. The indices are based on the Fe–B sublattice. (*b*) Systematics of the [0100] pattern, indexed in terms of the diffraction vector $\boldsymbol{D} = H\boldsymbol{A}^* + K\boldsymbol{B}^* + L\boldsymbol{c}^*(\text{Fe–B}) + j\boldsymbol{q}$.



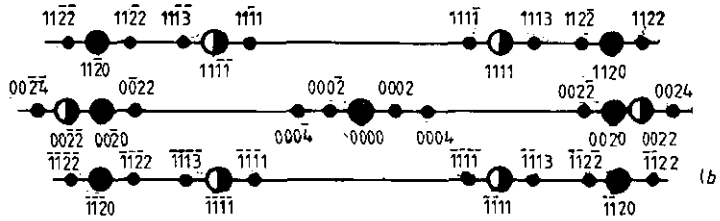


Figure 5. (*a*) An example of the $[\bar{1}100]$ electron diffraction pattern. The indices are based on the Fe–B sublattice. (*b*) Systematics of the $[\bar{1}100]$ pattern, indexed in terms of the diffraction vector $\boldsymbol{D} = H\boldsymbol{A}^* + K\boldsymbol{B}^* + L\boldsymbol{c}^*(\text{Fe–B}) + j\boldsymbol{q}$.

5. Concluding remarks

It has been shown that the symmetries of the superstructures $R_p(Fe_4B_4)_q$ can be

either $P4_2/n$, or $Pccn$, or '$Ccca$', depending on the parity combinations of integers p and q. In the demonstration of the superspace approach, however, it is not stated that p and q must be strict integers. Therefore, the characterization of superspace group symmetry is obviously a unified one. The symmetry of each member of the infinitely adaptive structures (either the truly incommensurate structures or the unusual long-period superstructures) in the $R_{1+\epsilon}Fe_4B_4$ series can be described by a four-dimensional superspace group. The related systematic extinction conditions can be utilized to understand the observation of both basic reflections and satellite reflections in the diffraction patterns. One may regard the translation symmetry of the $R_{1+\epsilon}Fe_4B_4$ compounds as concealed in the superspace and recovered by the superspace group. In accordance with this point, the systematic extinction conditions of these compounds may also be concealed in the superspace. It should be pointed out that in both approaches, the interaction between the two substructures was not taken into account. In fact, the two substructures modulate each other; the twist modulation of the Fe tetrahedra has been reported by Bezinge *et al* (1985) and Givord *et al* (1985, 1986a,b). In the case of $R_{1+\epsilon}Fe_4B_4$ compounds, however, ignoring this modulation leads to results agreeable with the experimental space group assignments in the case of the commensurate approximation. Furthermore, the observed systematic extinctions are actually somewhat more than those predicted by the superspace group P^{Cmma}_{ssi}. This implies that $R_{1+\epsilon}Fe_4B_4$ compounds may be of even higher symmetry than that assumed in this paper. It may be reasonable to think that the modulation may not have an effect on the superspace group of $R_{1+\epsilon}Fe_4B_4$ compounds; as a matter of fact, such a situation has been found to occur for $(TTF)_7I_{5-x}$ (Janner and Janssen 1980).

References

Anderson J S 1973 *J. Chem. Soc., Dalton* 1107

—— 1977 *J. Physique* C **7** 17

Bezinge A, Braun H F, Muller J and Yvon K 1985 *Solid State Commun.* **55** 131

Bezinge A, Yvon K, Braun H F, Muller J and Nissen H U 1987 *Phys. Rev.* B **36** 1406

Braun H F, Pelizzone M and Yvon K 1982 *Proc. 7th Int. Conf. on Solid Compounds of Transition Elements (Grenoble)* IIB11

Buerger M J 1947 *J. Chem. Phys.* **15** 1

de Wolff P M 1974 *Acta Crystallogr.* A **30** 777

—— 1977 *Acta Crystallogr.* A **33** 493

—— 1984 *Acta Crystallogr.* A **40** 30

de Wolff P M, Janssen T and Janner A 1981 *Acta Crystallogr.* A **37** 625

Flieher G, Völlenkle H and Nowotny H 1967 *Mh. Chem.* **98** 176

Givord D, Moreau J M and Tenaud P 1985 *Solid State Commun.* **55** 303

Givord D, Tenaud P and Moreau J M 1986a *J. Less-Common Met.* **115** L7

—— 1986b *J. Less-Common Met.* **123** 109

Grey I E 1974 *J. Solid State Chem.* **11** 128

Hoggins J T and Steinfink H 1977 *Acta Crystallogr.* B **33** 673

Janner A and Janssen T 1977 *Phys. Rev.* B **15** 643

—— 1980 *Acta Crystallogr.* A **36** 408

Janssen T and Janner A 1984 *Physica* A **126** 163

Jeitschko W and Parthé E 1967 *Acta Crystallogr.* **22** 417

Johnson C K and Watson C R Jr 1976 *J. Chem. Phys.* **64** 2271

Knott H W, Mueller M H and Heaton L 1967 *Acta Crystallogr.* **23** 549

Kuźma Yu B and Bilonizhbo N S 1975 *Dopov. Akad. Nauk. Ukr. RSR Ser.* A **3** 275

Parthé E and Chabot B 1984 *Handbook on the Physics and Chemistry of Rare Earths* vol 6, ed K A Gschneider Jr and L Eyring (Amsterdam: Elsevier) p 249

Tian J, Liang J, Fan H and Li F 1988 *Phys. Status Solidi* a **107** 45

Völlenkle H, Wittmann A and Nowotny H 1967 *Mh. Chem.* **98** 2174
Zhao Z B and Ma R Z 1988 *Acta Phys. Sinica* **37** 1940
—— 1989 *Acta Phys. Sinica* **38** 1687
Zhao Z B, Ma R Z and Miao B H 1989a *Scr. Metall.* **23** 743
Zhao Z B, Xia S K, Ma R Z and Pan S M 1989b *J. Less-Common Met.* **155** 75
Zhao Z B, Xia S K, Ma R Z, Ping J Y, Miao B H and Pan S M 1989c *Solid State Commun.* **69** 1011
Zhao Z B, Xia S K, Wang C R and Ma R Z 1989d *J. Phys.: Condens. Matter* **1** 7503