

Symmetry analysis of extinction rules in diffuse-scattering experiments

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Structured diffuse-scattering intensities, whether of compositional or of pure displacive origin, static or dynamic, contain important information about the symmetry of the individual compositional and/or displacive modes responsible for the observed intensities. However, the interpretation of the experimental data is very often impeded by the lack of a symmetry-based approach to the analysis of the structured diffuse-scattering distributions. Recently, we have demonstrated the existence of systematic phonon selection rules for diffuse scattering that depend on the symmetries of the mode and the scattering vector, and not on the specific structure. Here, we show that such symmetry analysis can be successfully extended and also applied to structure-dependent diffuse scattering associated with 'disordered' materials: the combination of theoretically determined, diffuse-scattering extinction conditions with the concept of non-characteristic orbits proves to be very useful in the interpretation of the observed diffuse-scattering extinctions. The utility of this approach is illustrated by the analysis of diffuse-scattering data from ThAsSe, FeOF and FeF₂. The essential part of the associated calculations are performed by the computer programs *NEUTRON* (systematic phonon extinction rules in inelastic scattering) and *NONCHAR* (non-characteristic orbits of space groups) that are available on the Bilbao crystallographic server (<http://www.cryst.ehu.es>).

1. Introduction

There is currently no systematic group-theory-based approach to the interpretation of the structured diffuse scattering (DS) characteristic of the reciprocal spaces of many 'disordered' materials. In particular, there is no systematic symmetry-based approach to the interpretation of real, or pseudo (apparent), 'extinction conditions' in experimentally observed structured diffuse intensity distributions (Brink *et al.*, 2000, 2001; Withers *et al.*, 2004, 2006; Liu *et al.*, 2005; Withers, 2005). Fig. 1, for example, shows (a) close to [001], (b) (01 $\bar{4}$) and (c) (110) zone-axis electron-diffraction patterns (EDP's) of the $P4_2/mnm$ rutile type, 'disordered' transition metal oxyfluoride, FeOF (Brink *et al.*, 2000). The structured diffuse scattering characteristic of this particular 'disordered' material takes the form of rods of diffuse intensity running through the $\mathbf{H} \pm \epsilon(110)^*$ positions of reciprocal space. Here, $\mathbf{H} = (h, k, l)$ is a parent or average structure Bragg reflection (*i.e.* \mathbf{H} is a vector of the reciprocal lattice \mathbf{L}^* , $\mathbf{H} \in \mathbf{L}^*$), and ϵ represents a continuous variable, see also Brink *et al.* (2000). Given the $P4_2/mnm$ average structure space-group symmetry, why, however, does this diffuse streaking appear to only run through the $h + k + l$ odd, but not the $h + k + l$ even, parent

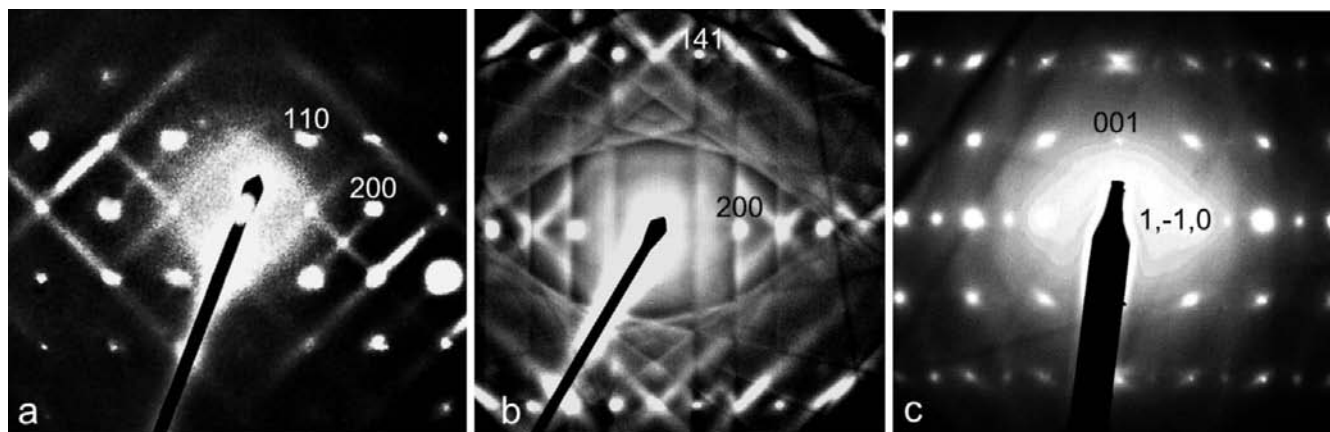


Figure 1 Close to [001], (b) $\langle 01\bar{4} \rangle$ and (c) $\langle 110 \rangle$ zone-axis electron-diffraction patterns of the $P4_2/mnm$ rutile type, ‘disordered’ transition metal oxyfluoride, FeOF (see Brink *et al.*, 2000, for details). Note that the diffuse streaking of $\mathbf{H} \pm \epsilon \langle 110 \rangle^*$ type runs through the $h + k + l$ odd, but not the $h + k + l$ even, parent reflections in (a) and (b), but is missing altogether in (c).

reflections (see Figs. 1a and b)? Likewise, why is there no diffuse streaking of $\mathbf{H} \pm \epsilon \langle 1\bar{1}0 \rangle^*$ type apparent in Fig. 1(c)?

The purpose of the current contribution is to use a group-theoretical approach to explain in formal symmetry terms why such ‘extinction conditions’ in diffuse distributions can and do occur and what can be learnt about the nature of the real-space ‘disorder’ in materials of this type from such symmetry information. Example disordered materials will be used throughout to illustrate the symmetry in real space that is responsible for the ‘extinction conditions’ observed in reciprocal space. We begin with a formal introduction to the symmetry analysis of the possible extinction conditions that can be expected for the characteristic DS associated with disordered materials.

2. Extinction conditions in structured diffuse distributions

Structured DS (at the $\mathbf{H} \pm \mathbf{q}$ positions of reciprocal space), whether of compositional and induced displacive or of pure displacive origin, whether static or dynamic, contains important information about the symmetry of the individual compositional and/or displacive modes (associated with the modulation wavevectors \mathbf{q}) responsible. In general, the analysis of this structured DS is hampered by the (often) essentially continuous nature of the scattering (see *e.g.* Fig. 1): there are usually a large number of wavevectors \mathbf{q} distributed throughout the first Brillouin zone of the average structure which contribute to the observed structured diffuse-intensity distribution. Whether intensity is observed at a particular $\mathbf{H} - \mathbf{q}$ position in reciprocal space, however, formally depends on the symmetry/symmetries of the compositional and/or displacive modulation waves associated with the individual modulation wavevector \mathbf{q} .

We have previously demonstrated the existence of systematic extinction rules for experimental (displacive) DS data, additional to the obvious ones coming from the transverse or longitudinal character of the individual mode polar-

ization vectors (Perez-Mato *et al.*, 1998; Aroyo *et al.*, 2002). The method for the derivation of these extinction conditions is a straightforward extension of the procedure developed for the calculation of phonon selection rules for inelastic neutron scattering (Perez-Mato *et al.*, 1998) and is now briefly outlined.

2.1. Extinction rules in DS

The displacement of the α th atom in the primitive unit cell \mathbf{t} away from its average structure position at $(\mathbf{r}_\alpha + \mathbf{t})$ owing to a static displacive mode of symmetry j can be written in the form

$$\mathbf{u}_{\alpha,j}(\mathbf{r}_\alpha + \mathbf{t}) = \sum_{\mathbf{q}} Q(\mathbf{q}, j) \mathbf{e}(\alpha|\mathbf{q}, j) \exp[2\pi i \mathbf{q} \cdot (\mathbf{r}_\alpha + \mathbf{t})], \quad (1)$$

where $\mathbf{e}(\alpha|\mathbf{q}, j)$ represents the complex displacement polarization vector particularized for the α th atom associated with the modulation wavevector \mathbf{q} and mode symmetry j with the property that $\mathbf{e}(\alpha|-\mathbf{q}, j) = \mathbf{e}(\alpha|\mathbf{q}, j)^*$, and $Q(\mathbf{q}, j)$ is the related amplitude. The sum is over all \mathbf{q} vectors of the wavevector star \mathbf{q}^* (or over \mathbf{q}^* and $(-\mathbf{q})^*$ if \mathbf{q} and $-\mathbf{q}$ do not belong to the same star).¹

Likewise, a compositional modulation associated with a mode of the same symmetry j describing the deviation of the scattering factor of the α th atom in the primitive average structure unit cell \mathbf{t} away from its average value can be written in the form

$$\delta f_{\alpha,j}(\mathbf{r}_\alpha + \mathbf{t}) = \sum_{\mathbf{q}} A(\mathbf{q}, j) a(\alpha|\mathbf{q}, j) \exp[2\pi i \mathbf{q} \cdot (\mathbf{r}_\alpha + \mathbf{t})], \quad (2)$$

where the scalars $a(\alpha|-\mathbf{q}, j) = a(\alpha|\mathbf{q}, j)^*$ are the amplitudes of the compositional modulations. The set $\{a(\alpha|-\mathbf{q}, j)\}$ for all α form a mathematical vector, also called the polarization vector of the compositional modulation associated with the modulation wavevector \mathbf{q} and mode symmetry j . $A(\mathbf{q}, j)$ is the global amplitude of this modulation. Any arbitrary atomic

¹ For the term ‘wavevector star’ and other terms of representation theory of space groups the reader is referred to Cracknell *et al.* (1979) and references therein.

ordering arrangement and/or atomic displacement pattern can then be described in terms of an appropriate summation (over modulation wavevectors within or on the first Brillouin zone of the underlying average structure and of all possible mode symmetries j) of such compositional and displacive modulation waves.

Whether such modes contribute to the observed diffuse intensity at a particular $\mathbf{Q} = \mathbf{H} - \mathbf{q}$ position in reciprocal space then depends on the symmetry of the mode eigenvectors. The compositional and displacive polarization vectors $a(\alpha|\mathbf{q}, j)$ and $\mathbf{e}(\alpha|\mathbf{q}, j)$ associated with the mode wavevector \mathbf{q} and symmetry j transform according to irreducible representations (irreps) $\mathbf{D}^{\mathbf{q},j}$ of the so-called little group $\mathcal{G}^{\mathbf{q}}$, which is a subgroup of the space group $\mathcal{G} = \{(\mathbf{W}, \mathbf{w})\}$. The elements of the little group $(\mathbf{W}^{\mathbf{q}}, \mathbf{w}^{\mathbf{q}})$ are determined by the conditions: $\mathcal{G}^{\mathbf{q}} = \{(\mathbf{W}^{\mathbf{q}}, \mathbf{w}^{\mathbf{q}}) \in \mathcal{G} | \mathbf{q}\mathbf{W}^{\mathbf{q}} = \mathbf{q} + \mathbf{H}, \mathbf{H} \in \mathbf{L}^*\}$. The irreps of the little group, also called *small* or *little-group* irreps are discussed in many books on representation theory (here we use the notation of Cracknell *et al.*, 1979).

For a given modulation wavevector \mathbf{q} , the set of all possible scattering vectors $\mathbf{Q} = \mathbf{H} - \mathbf{q}, \mathbf{H} \in \mathbf{L}^*$ forms an infinite set. The action of the elements $\mathbf{W}^{\mathbf{q}} \in \overline{\mathcal{G}}^{\mathbf{q}}$ (where $\overline{\mathcal{G}}^{\mathbf{q}}$ is the point group of $\mathcal{G}^{\mathbf{q}}$, known as the *little co-group*) on the \mathbf{Q} vectors results in the distribution of the \mathbf{Q} set into orbits. The elements $\mathbf{W}^{\mathbf{q}}$ satisfying the condition $\mathbf{Q}\mathbf{W}^{\mathbf{q}} = \mathbf{Q}$ form the so-called *strict point group* $\overline{\mathcal{G}}^{\mathbf{Q}}$ of the scattering vector \mathbf{Q} . One can distinguish general \mathbf{Q} vector orbits characterized by a strict point group consisting of the identity element only, $\overline{\mathcal{G}}^{\mathbf{Q}} = \mathcal{I}$, and special \mathbf{Q} vector orbits with $\overline{\mathcal{G}}^{\mathbf{Q}} > \mathcal{I}$. Grouping together the \mathbf{Q} orbits with the same set of strict point groups results in the partition of the \mathbf{Q} set into classes of \mathbf{Q} vectors characterized by the same set of selection rules.

The selection rules are derived from the transformation properties of the structure factor (whether static or dynamic) under the elements $\mathbf{W}^{\mathbf{q}} = (\mathbf{W}^{\mathbf{q}}, \mathbf{w}^{\mathbf{q}})$ of the little group $\mathcal{G}^{\mathbf{q}}$ of the wavevector \mathbf{q} . The reformulation of the theorem on inelastic scattering phonon activity (Perez-Mato *et al.*, 1998) for the case of DS is straightforward. The main result is: *all phonon modes of wavevector \mathbf{q} and symmetry given by the little-group irrep $\mathbf{D}^{\mathbf{q},j}$ are DS-inactive at a scattering vector $\mathbf{Q} = \mathbf{H} - \mathbf{q}, \mathbf{H} \in \mathbf{L}^*$ if:*

$$\sum_{\mathbf{w}^{\mathbf{q}} \in \overline{\mathcal{G}}^{\mathbf{Q}}} \chi^{\mathbf{q},j}(\mathbf{W}^{\mathbf{q}}, \mathbf{w}^{\mathbf{q}}) \exp(-i\mathbf{Q} \cdot \mathbf{w}^{\mathbf{q}}) = 0 \quad (3)$$

where $\chi^{\mathbf{q},j}(\mathbf{W}^{\mathbf{q}}, \mathbf{w}^{\mathbf{q}})$ is the character of the small irrep $\mathbf{D}^{\mathbf{q},j}$, and $\overline{\mathcal{G}}^{\mathbf{Q}}$ is the strict point group of \mathbf{Q} .

If for a given wavevector, the scattering \mathbf{Q} vector is of a general type, $\overline{\mathcal{G}}^{\mathbf{Q}} = \mathcal{I}$, then all types of symmetry modes associated with the wavevector \mathbf{q} are allowed, *i.e.* there are non-trivial symmetry restrictions on the DS phonon activity only for special \mathbf{Q} vectors. These basic results have been developed in a step-wise procedure for the calculation of the DS extinction rules for a modulation wavevector \mathbf{q} , and a scattering vector \mathbf{Q} (*cf.* Kirov *et al.*, 2003, for more details on the procedure). Note that this procedure is valid whether the mode is dynamic or static. An algorithm based on this

procedure serves as a basis for the computer program *NEUTRON* (Kirov *et al.*, 2003). Given the space group and the wavevector, the program examines the scattering activity of the corresponding modes for all possible types of scattering vectors. *NEUTRON* forms part of the Bilbao Crystallographic server (<http://www.cryst.ehu.es>) and can be used *via* the Internet from any computer with a web browser; Aroyo *et al.* (2006).

These extinction rules are of considerable help in the identification of the symmetry of the \mathbf{q} modes responsible for the measured DS at a given \mathbf{Q} vector. This identification proves to be very useful, *e.g.* in understanding the phase-transition behavior of K_2SnCl_6 (Aroyo *et al.*, 2002). In that case, it was possible to characterize symmetrically not only the mode driving the phase transition, but also a low lying dispersion branch whose symmetry is compatible with that of the critical mode.

2.2. Non-characteristic orbits

The theoretically determined systematic extinction rules discussed above depend only on mode symmetry and scattering vector, and hence are independent of the symmetry of specific atomic positions in the average crystal structure. Experimentally, however, the local crystal chemistry underlying the observed DS in a significant number of ‘disordered’ materials (see *e.g.* Brink *et al.*, 2000; Withers *et al.*, 2004; Liu *et al.*, 2005; Withers, 2005) ensures that the observed, or apparent, extinction rules (see *e.g.* Fig. 1) depend on the local symmetry of the atoms or group of atoms primarily contributing to the observed DS. Very often it is a specific orbit of atoms or group of atoms (with higher symmetry than that of the average structure) that are responsible for the observed DS and its associated extinction rules. In the case of the $\mathbf{H} \pm \epsilon(110)^*$ diffuse scattering characteristic of FeOF shown in Fig. 1, for example, the observed diffuse scattering is overwhelmingly dominated by the displacive shifts of the Fe atoms and not by the compositional ordering of the O and F atoms (see *e.g.* Brink *et al.*, 2000). Likewise, the sheets of diffuse scattering observed perpendicular to the $\langle 110 \rangle$ directions in the case of ThAsSe (see Fig. 2) and UAsSe (see Withers *et al.*, 2006) are due to local dimerization of As atoms along the $\langle 110 \rangle$ real-space directions (Withers *et al.*, 2004). In both these cases, the symmetry of the Fe and As atoms responsible for the observed structured DS is higher than of the average structure. In order to understand the observed extinction conditions in such cases, it is thus necessary to extend the above theory.

In general, the study of diffraction data that are clearly dependent on specific groups of atoms should involve the so-called *inherent* or *eigensymmetry* of the occupied atomic orbits of the crystal structure, *e.g.* see Engel *et al.* (1984) and references therein. If the inherent symmetry space group \mathcal{E} of an orbit of a space group \mathcal{G} (known as the *generating* space group) coincides with the group \mathcal{G} , $\mathcal{E} = \mathcal{G}$, the crystallographic orbit is called *characteristic*. In many crystal structures, however, one or several kinds of atoms form substructures with higher

symmetry than the space group \mathcal{G} of the crystal structure. In these cases, the inherent symmetries of the occupied orbits are described by space groups that are supergroups of the crystal-structure space group, $\mathcal{E} > \mathcal{G}$, and the crystallographic orbits are called *non-characteristic*. A simple example is that of sphalerite ZnS with space-group symmetry $\mathcal{G} = F\bar{4}3m$, while both atoms occupy non-characteristic orbits with eigensymmetry $\mathcal{E} = Fm\bar{3}m$. Another well known example is that of the fluorite CaF₂ structure of space-group symmetry $\mathcal{G} = Fm\bar{3}m$. The Ca position $4a\ 000$ is characteristic as its eigensymmetry $\mathcal{E}_{Ca} = \mathcal{G} = Fm\bar{3}m$. However, the F atoms, occupying the position $8c\ \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, form a primitive cubic close-packed array with a cell parameter one half that of fluorite, *i.e.* the F orbit is non-characteristic as its eigensymmetry $\mathcal{E}_F = Pm\bar{3}m$ is a supergroup of \mathcal{G} , $Pm\bar{3}m(\frac{1}{2}a) > Fm\bar{3}m(a)$. Such non-characteristic orbits whose eigensymmetry groups \mathcal{E} are *klassengleiche* supergroups of \mathcal{G} , *i.e.* their eigensymmetry groups have addi-

tional translations with respect to \mathcal{G} , are called *extraordinary* crystallographic orbits.

The symmetry of the diffraction pattern of atoms occupying non-characteristic orbits is determined not by the symmetry group of the crystal \mathcal{G} , but by the corresponding eigensymmetry groups $\mathcal{E} > \mathcal{G}$ as atoms occupying non-characteristic orbits contribute to a diffraction pattern with symmetry \mathcal{E} . For example, atoms occupying extraordinary orbits do not contribute to some classes of reflections. This is indicated under the *special reflection conditions* tabulated in *International Tables for Crystallography*, Vol. A (2002), although the data are incomplete: the cases of extraordinary orbits due to special values of the variable parameters of the representatives of the crystallographic orbits or due to metric specialization are not taken into account (for more details, *e.g.* see Engel *et al.*, 1984).

The underlying idea of our approach to the analysis of structure-dependent DS data is that such an analysis should be based on the above-discussed extinction conditions, but calculated with respect to the eigensymmetry group of the corresponding occupied orbits. The following statement by Matsumoto & Wondratschek (1987) supports our reasoning: If a physical interaction (magnetic, electric *etc.*) is restricted to a \mathcal{G} orbit of one kind of atoms or group of atoms, then the symmetry of the corresponding effect will be determined by the eigensymmetry of the orbit and not by \mathcal{G} . This is illustrated below in three separate cases. Both theoretical discussions and tabulations of non-crystallographic orbits of the space groups and their eigensymmetry groups can be found in the literature (*cf.* Engel *et al.*, 1984). Recently, we have developed an algorithmic procedure for the determination of the non-characteristic orbits of the space groups and their eigensymmetry groups (Aroyo *et al.*, 2009). The algorithm is implemented in the computer program *NONCHAR* that is available on the Bilbao Crystallographic Server (<http://www.cryst.ehu.es>).

The theoretically determined DS extinction conditions combined with the concept of non-characteristic orbits can be very useful in the interpretation of experimentally observed structure-dependent systematic DS extinctions. The utility of this approach for the case of extraordinary orbits is demonstrated below by the analysis of DS data from ThAsSe, FeOF and FeF₂.

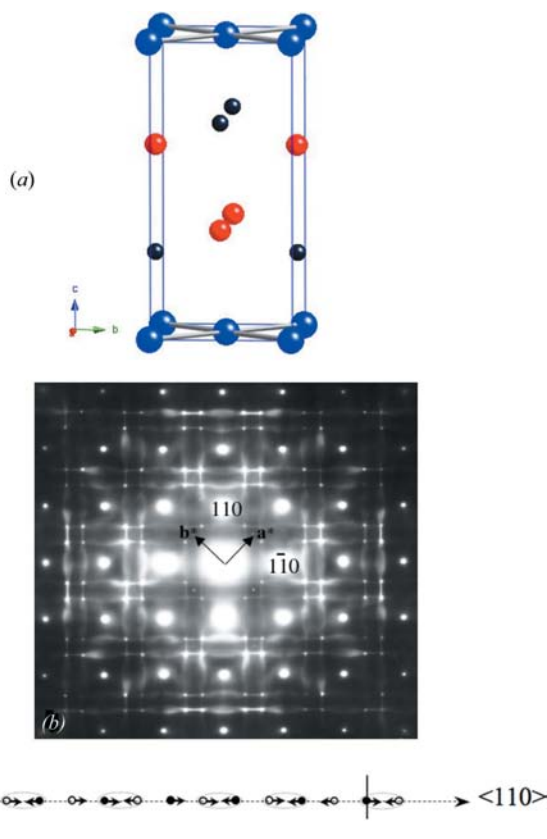


Figure 2

(a) A close to [100] projection of the $P4/nmm$ (*origin choice 2*), ZrSiS-type average structure of ThAsSe. The As atoms are represented by large blue balls, Th atoms by small black balls and Se atoms by medium-sized red balls. The covalent bonding between the As atoms is represented by the grey rods. (b) A typical [001] zone-axis EDP of ThAsSe taken at 100 K. In addition to the strong Bragg reflections of the underlying $P4/nmm$ average structure, note the presence of characteristic diffuse streaking running along the $H_{\pm} \sim 0.14(110)^* + \epsilon(110)^*$ ($\epsilon \sim \frac{1}{2}$) positions of reciprocal space around the nominally n -glide forbidden $hk0$, $h+k$ odd reflections. (c) The resultant predicted one-dimensional AsAs dimerization pattern responsible for the observed sheets of diffuse intensity running perpendicular to the $\langle 110 \rangle$ directions of real space (for details, see Withers *et al.*, 2004).

3. Examples

3.1. Diffuse scattering in ThAsSe

The room-temperature average structure of ThAsSe (see Fig. 2a) is of ZrSiS type with space group $P4/nmm$ (No. 129). The As atoms occupy a fixed high-symmetry $2a$ position, while the Th and Se atoms lie on a symmetry line with one free parameter belonging to the Wyckoff position position $2c$ of $P4/nmm$. Normally the valence state of the Th, As and Se atoms is taken as +4, -3 and -2, respectively. From a charge-balance point of view, there is thus one additional electron per formula unit on the As atoms which delocalizes and, at room temperature, makes ThAsSe a metal. On cooling, however, the

resistivity increases dramatically, suggesting some sort of localization of these itinerant electrons. Experimentally, on cooling a characteristic, highly structured diffuse intensity distribution becomes more and more apparent. This diffuse distribution takes the form of two orthogonal $\mathbf{H}_{\pm} \sim 0.14(110)^* \pm \beta(1\bar{1}0)^* \pm \gamma[001]^*$ (β, γ essentially continuous) planes of diffuse scattering (see *e.g.* Fig. 2*b* and Withers *et al.*, 2004). Note that the \mathbf{q} vectors associated with this diffuse distribution are thus of general type, and therefore all symmetry types of \mathbf{q} modes can be DS-active and could be observed at any lattice vector $\mathbf{H} = (h, k, l)$ of the reciprocal lattice of $P4/nmm$. Nonetheless, there is a clear systematic extinction condition associated with this diffuse distribution, *i.e.* the diffuse occurs only around the parent $\mathbf{H} = (h, k, l)$ with $h + k = 2n + 1$ (odd) Bragg reflections. This is an interesting and important example in that despite the fact that the \mathbf{q} vectors are of general type there is nonetheless still a clear systematic extinction condition. The reason is that the displacements responsible for the observed diffuse distribution come only from displacements of the As atoms (see Withers *et al.*, 2004), which lie on a non-characteristic orbit.

Analysis of the eigensymmetry groups of the occupied orbits of ThAsSe by the program NONCHAR indicates that the As atoms (in Wyckoff position 2*a*) occupy a non-characteristic orbit while the 2*c* orbits of Th and Se atoms are characteristic. (The 2*c* orbits of $P4/nmm$ become non-characteristic for special values of a free parameter that do not correspond to the specific values for Th and Se atoms in the ThAsSe structure.) The eigensymmetry group of the As orbit is the klassengleiche supergroup $C4/mmm$ of the crystal space group $P4/nmm$ with no change in the lattice parameters, *i.e.* the orbit 2*a* of $P4/nmm$ is *extraordinary*.

The group–subgroup relation in direct space between the crystal space group $\mathcal{G} = P4/nmm$ and the klassengleiche supergroup $\mathcal{E} = C4/mmm$, $C4/mmm(\mathbf{a}, \mathbf{b}, \mathbf{c}) > P4/nmm(\mathbf{a}, \mathbf{b}, \mathbf{c})$ implies the inverse relationship between the corresponding reciprocal space groups² $\mathcal{E}^* < \mathcal{G}^*$, *i.e.* $(C4/mmm)^* < (P4/nmm)^*$. Note that the group–subgroup relation is again of klassengleiche type, *i.e.* the group \mathcal{E}^* has half as many translations as \mathcal{G}^* . In terms of wavevectors, this indicates that certain wavevectors that were equivalent under \mathcal{G}^* (*e.g.* related by a reciprocal lattice translation) become non-equivalent under \mathcal{E}^* . In other words, the orbit of the wavevector \mathbf{q} of \mathcal{G}^* splits into orbits with respect to \mathcal{E}^* . In the special case of ThAsSe, the $(P4/nmm)^*$ orbit of the general wavevector \mathbf{q} splits in two $(C4/mmm)^*$ orbits of general wavevectors with representatives: $\mathbf{q}_1 = \mathbf{q} = (q_x, q_y, q_z)$ and $\mathbf{q}_2 = (q_x + 1, q_y, q_z)$.

The wavevectors \mathbf{q}_1 and \mathbf{q}_2 , having no special symmetry with respect to the eigensymmetry group of the As atoms, do not exhibit any specific extinction conditions: all symmetry types of \mathbf{q}_1 and \mathbf{q}_2 modes can be DS active and can be observed at scattering vectors $\mathbf{Q}_1 = \mathbf{H} - \mathbf{q}_1$ and $\mathbf{Q}_2 = \mathbf{H} - \mathbf{q}_2$, where \mathbf{H} is

any reciprocal lattice vector of $(C4/mmm)^*$ (*i.e.* $\mathbf{H} = (h, k, l)$, with $h + k = \text{even}$). Depending whether the active modes correspond to \mathbf{q}_1 or \mathbf{q}_2 , the following apparent extinction conditions appear:

(i) Modes of wavevector $\mathbf{q}_1 = (q_x, q_y, q_z)$ can be observed at $\mathbf{Q}_1 = \mathbf{H} - \mathbf{q}_1 = (h - q_x, k - q_y, l - q_z)$, and where $h + k = \text{even}$.

(ii) Modes of wavevector $\mathbf{q}_2 = (q_x + 1, q_y, q_z)$ can be observed at $\mathbf{Q}_2 = \mathbf{H} - \mathbf{q}_2 = (h - q_x - 1, k - q_y, l - q_z)$, with $h + k = \text{even}$.

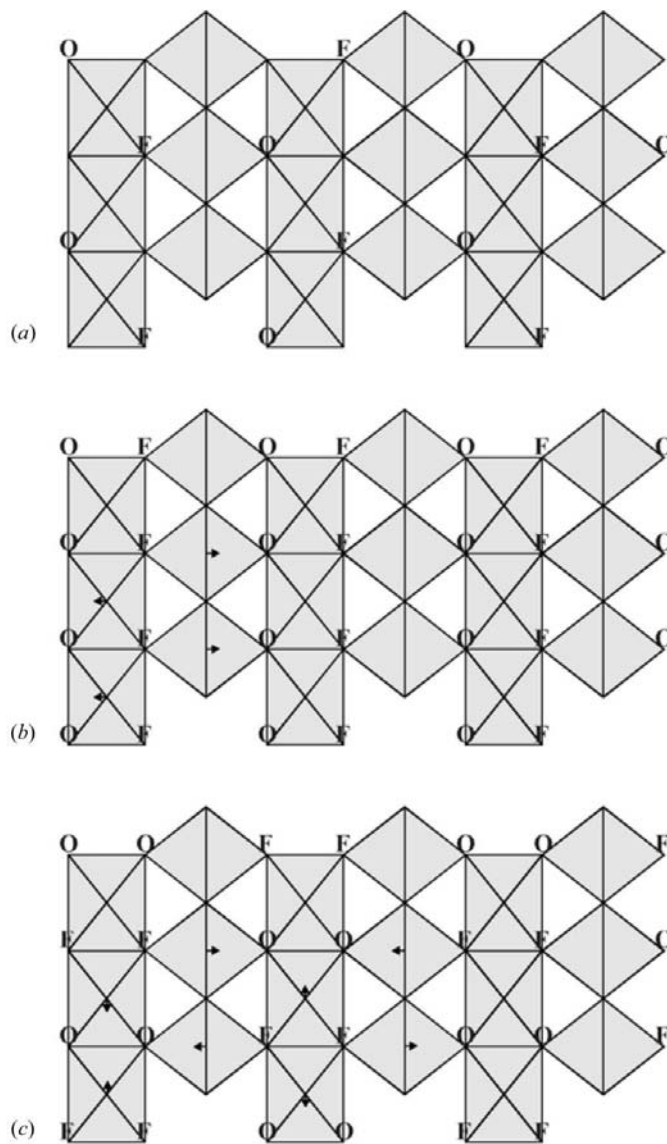


Figure 3

(*a*) A (110) plane of the rutile-type average structure of FeOF. The Fe-centred $\text{Fe}(\text{O},\text{F})_6$ octahedra are clearly apparent in projection. Note that opposite vertices in each octahedra are shown as never being occupied by the same anion, consistent with bond-valence sum considerations which require this constraint in order that the centering Fe ion can then displace away from the F atoms and towards the O atoms in each octahedra to remedy the local over- and under-bonding of the O and F atoms (see Brink *et al.*, 2000, for details). (*b*) and (*c*) show the two ordered O/F distributions and associated Fe displacement patterns possible within any one (110) plane compatible with the above constraint.

² The group \mathcal{G}^* , which is a semi-direct product of the point group $\mathcal{P}_{\mathcal{G}}$ of the space group \mathcal{G} and the translation group of the reciprocal lattice \mathbf{L}^* of \mathcal{G} , is called *reciprocal space group* of \mathcal{G} . For more details see Aroyo & Wondratschek (1995).

Table 1

Little co-group irreps of the space group $I4/mmm$ for wavevectors belonging to the $\Delta(\mathbf{Y})$ line.

The irrep matrices (which coincide with the characters, as all irreps are one-dimensional) are listed for the elements of the little co-group $\mathcal{G}^{\Delta}(\mathcal{G}^{\mathbf{Y}})$

Irreps	1	2_{xx0}	m_z	m_{xz}
$\Delta 1(\mathbf{Y}1)$	1	1	1	1
$\Delta 2(\mathbf{Y}2)$	1	1	-1	-1
$\Delta 3(\mathbf{Y}3)$	1	-1	1	-1
$\Delta 4(\mathbf{Y}4)$	1	-1	-1	1

In the interpretation of the above results one should take into account that the indexing of the experimental data in Fig. 2(b) is done with respect to the reciprocal basis of the crystal space group $P4/nmm$. Also as $(1, 0, 0)$ is a reciprocal lattice vector of $(P4/mmm)^*$, then the modes of wavevector \mathbf{q}_2 will be observed at $\mathbf{Q}_2 = (h' - q_x, k - q_y, l - q_z)$ with $h' + k = \text{odd}$.

The symmetry conditions observed in the case of ThAsSe are clearly related to modes of wavevector \mathbf{q}_2 . In real space they imply that neighboring As atoms along the modulated $\langle 110 \rangle$ directions tend to displace out of phase. Note that the observed $\mathbf{H}\pm \sim 0.14\langle 110 \rangle^* \pm \beta\langle \bar{1}\bar{1}0 \rangle^* \pm \gamma[001]^*$ (β, γ essentially continuous) planes of diffuse scattering imply the existence of one-dimensional correlated chains of As atoms along the modulated $\langle 110 \rangle$ directions of real space. The knowledge that the wavevector is of type 2, of the two possibilities above, associated with the observed diffuse scattering enables the pattern of As displacements responsible for the observed structured diffuse scattering to be derived, as shown in Fig. 2(c) (for details on how this can be achieved, see Brink *et al.*, 2000; Withers *et al.*, 2004). The increase in this As–As dimerization on lowering the temperature then explains the increase in resistivity on lowering of temperature.

3.2. Oxygen/fluorine ordering in FeOF

In the case of the transition metal oxyfluoride FeOF, the observed $\mathbf{H} \pm \epsilon\langle \bar{1}\bar{1}0 \rangle^*$ diffuse scattering (see Fig. 1) requires long-range ordering in $\{1\bar{1}0\}$ planes, but with no correlation from one such plane to the next while the transverse polarized nature of the observed structured diffuse scattering implies that correlated displacements within these $\{1\bar{1}0\}$ planes must be responsible. Fig. 3(a) shows one such $\{1\bar{1}0\}$ plane of the $P4_2/mnm$ rutile type, average structure. The Fe-centered $\text{Fe}(\text{O,F})_6$ octahedra characteristic of the average structure type are clearly apparent in projection. Bond-valence sum calculations using the average crystal structure reported by Vlasse *et al.* (1973) show clearly that oxygen and fluorine are respectively under- and over-bonded in the FeOF average structure and that therefore O and F atoms must occupy opposite vertices in the local FeO_3F_3 octahedra (as shown in Fig. 3a; see Brink *et al.*, 2000 for details).

The centering Fe atom can then displace away from the F atoms and towards the O atoms in each octahedra to remedy the local over- and under-bonding of the O and F atoms. Note, however, that there are two distinct possible patterns of O/F ordering and induced Fe displacements possible, as shown in

Table 2

Selection rules for $\Delta = (q_x, -q_x, 0)$ modes, space group $I4/mmm$.

The symmetry types (irreps) of modes which can be DS-active (allowed) are listed for a representative $\mathbf{Q} = \mathbf{H} - \Delta = (h - q_x, k + q_x, l)$ of a \mathbf{Q} orbit. The groups $\mathcal{G}^{\mathbf{Q}}$ are given as oriented site-symmetry symbols. For the irrep labels, see Table 1.

$\mathbf{Q} = \mathbf{H} - \Delta$ $\mathbf{H}(h, k, l); h + k + l = 2n$	$\mathcal{G}^{\mathbf{Q}}$	DS-active modes
$\mathbf{Q}(-h - q_x, h + q_x, 0)$	$m.2m$	$\Delta 1$
$\mathbf{Q}(h - q_x, k + q_x, 0)$	$m..$	$\Delta 1, \Delta 3$
$\mathbf{Q}(-h - q_x, h + q_x, l)$	$..m$	$\Delta 1, \Delta 4$
$\mathbf{Q}(h - q_x, k + q_x, l)$	1	$\Delta 1, \Delta 2, \Delta 3, \Delta 4$

Figs. 3(b) and (c). It will be shown below that a characteristic diffuse extinction condition apparent in Fig. 1(c) can be used to distinguish between these two possibilities. Note that O and F neighbor each other in the periodic table and hence there is very little contrast in electron-diffraction patterns associated with O/F ordering. It is not therefore surprising that the displacements of the Fe atoms induced by the O/F ordering dominate the observed structured diffuse scattering.

The scattering vectors of the observed diffuse distribution can be described as $\mathbf{Q} = \mathbf{H} - \mathbf{q}$, where the modulation wavevectors \mathbf{q} are of two types: $\mathbf{q}_- = (q_x, -q_x, 0)$ and $\mathbf{q}_+ = (q_x, q_x, 0)$. In the following we present an analysis of one of these two types of wavevector, namely $\mathbf{q} = \mathbf{q}_-$. The results for \mathbf{q}_+ are analogous due to the symmetry equivalence of \mathbf{q}_- and \mathbf{q}_+ (\mathbf{q}_- and \mathbf{q}_+ belong to the same wavevector star).

The crystal-chemical considerations described above (see also Brink *et al.*, 2000) show that the induced Fe displacements are primarily responsible for the observed DS shown in Fig. 1. At this stage, it is important to realise that the Fe atoms occupy an orbit that belongs to the special $2a$ Wyckoff position of $P4_2/mnm$. This orbit is extraordinary as its eigensymmetry group $\mathcal{E} = I4/mmm$ is a klassengleiche supergroup of index 2 of $P4_2/mnm$ with no change of the lattice parameters.

Similar to the case of ThAsSe, the reciprocal space group \mathcal{E}^* is a klassengleiche subgroup of index 2 of \mathcal{G}^* , *i.e.* the translations of \mathcal{E}^* are just half of the translations of \mathcal{G}^* . As a consequence, the orbit of the wavevector \mathbf{q} of \mathcal{G}^* splits into two orbits of wavevectors of \mathcal{E}^* with representatives $(q_x, -q_x, 0)$ and $(q_x, -q_x, 1)$. According to the notation of Cracknell *et al.* (1979) $(q_x, -q_x, 0)$ corresponds to a special Δ line while $(q_x, -q_x, 1)$ is a special \mathbf{Y} line. The little co-groups \mathcal{G}^{Δ} and $\mathcal{G}^{\mathbf{Y}}$ coincide: they are of the crystal class $mm2$, with the following symmetry operations $\{1 = (x, y, z), 2_{xx0} = (-y, -x, -z), m_{xy0} = (x, y, -z), m_{xz} = (-y, -x, z)\}$. [For clarity, the point-group symmetry operations are identified by their action on a point (x, y, z) .] There are four one-dimensional small irreps of the little group $\mathcal{G}^{\Delta}(\mathcal{G}^{\mathbf{Y}})$ and the corresponding characters for the little co-group elements are listed in Table 1.

The DS selection rules calculated by *NEUTRON* for the eigensymmetry group $\mathcal{E} = I4/mmm$ and wavevectors along the lines $\Delta = (q_x, -q_x, 0)$ and $\mathbf{Y} = (q_x, -q_x, 1)$ are displayed in Tables 2 and 3. The infinite set of scattering vectors $\mathbf{Q} = \mathbf{H} - \mathbf{q}$ are distributed into several \mathbf{Q} -vector types, and the DS selection rules are the same for all scattering vectors

Table 3

 Selection rules for $\mathbf{Y} = (q_x, -q_x, 1)$ modes, space group $I4/mmm$.

 The symmetry types (irreps) of modes which can be DS-active (allowed) are listed for a representative $\mathbf{Q} = \mathbf{H} - \mathbf{Y} = (h - q_x, k + q_x, l - 1)$ of a \mathbf{Q} orbit. The groups $\overline{\mathcal{G}}^{\mathbf{Q}}$ are given as oriented site-symmetry symbols. For the irrep labels, see Table 1.

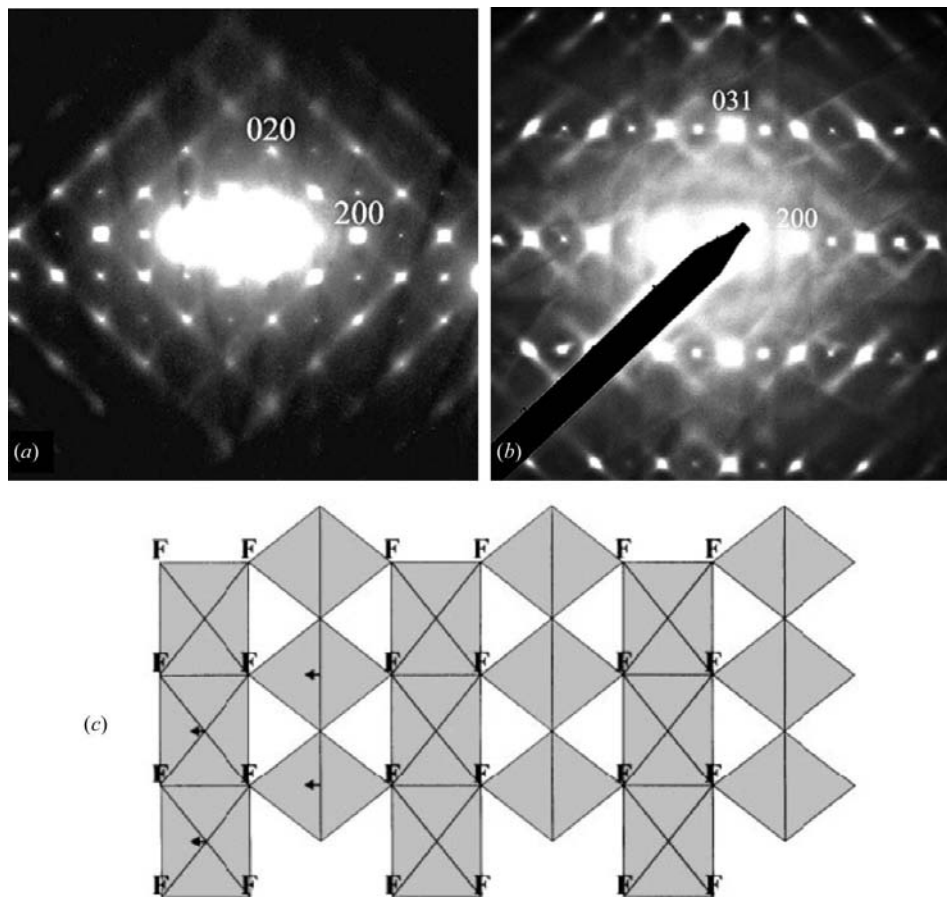
$\mathbf{Q} = \mathbf{H} - \mathbf{Y}$ $\mathbf{H}(h, k, l): h + k + l = 2n$	$\overline{\mathcal{G}}^{\mathbf{Q}}$	DS-active modes
$\mathbf{Q}(h - q_x, k + q_x, 0)$	$m..$	Y1, Y3
$\mathbf{Q}(-h - q_x, h + q_x, l - 1)$	$..m$	Y1, Y4
$\mathbf{Q}(h - q_x, k + q_x, l - 1)$	1	Y1, Y2, Y3, Y4

belonging to the same vector type. The strict point groups $\overline{\mathcal{G}}^{\mathbf{Q}}$, characterizing the \mathbf{Q} -vector types are specified by oriented site-symmetry symbols. The components of the scattering vectors \mathbf{Q} are given with respect to the basis of \mathcal{E}^* but their transformation to the basis of \mathcal{G}^* is trivial as the corresponding transformation matrix is the identity.

Symmetry modes of any irrep type are DS active at scattering vectors of the general type (last rows of Tables 2 and 3). The form of the general \mathbf{Q} vectors for the wavevectors Δ and \mathbf{Y} imply that only displacements of the modulation vector of

the type $\mathbf{Y} = (q_x, -q_x, 1)$ could be responsible for the experimentally observed continuous rods of diffuse scattering along $[110]^*$ and $[\bar{1}\bar{1}0]^*$ running only through the $(h + k + l) = \text{odd}$ reflections of the parent rutile structure (see *e.g.* Fig. 1*b*). Symmetry modes of wavevector \mathbf{Y} are observed at scattering vectors $\mathbf{Q}(h - q_x, k + q_x, l - 1)$ with $(h + k + l) = 2n$, *i.e.* at $(h + k + l - 1) = 2n - 1$ odd parent reflections. Note from Table 3 that Y3 modes associated with the $\mathbf{Y} = (q_x, -q_x, 1)$ -type modulation wavevector are DS-active when looking down the $[001]$ orientation, as observed experimentally (see Fig. 1*a*). By contrast, Y4 modes are DS-inactive at this orientation. Likewise, Y3 modes are DS-inactive when looking down a $[110]$ direction explaining the absence of diffuse streaking along the $[\bar{1}\bar{1}0]$ direction, as also observed experimentally (see Fig. 1*c*). Finally, Y3 modes are DS-active in general provided $(h + k + l) = \text{odd}$ (see Fig. 1*b*).

The presented symmetry analysis of the extinction rules in DS experimental data of FeOF permits the identification of the symmetry modes of the type Y3 as responsible for the observed structured DS. This conclusion agrees with the symmetry identification carried out in Brink *et al.* (2000) using crystal-chemistry arguments.


Figure 4

(*a*) Close to $[001]$ and (*b*) $[\bar{0}1\bar{3}]$ zone-axis electron-diffraction patterns of FeF_2 . This time the $\mathbf{H} \pm \epsilon(110)^*$ diffuse streaking runs through the $h + k + l$ even, but not the $h + k + l$ odd, parent reflections of the $P4_2/mnm$ rutile type, average structure (see Brink *et al.*, 2001, for details). (*c*) shows a $\langle 110 \rangle$ plane of the rutile-type average structure of FeF_2 and the pattern of Fe displacements within this plane responsible for the observed $\mathbf{H} \pm \epsilon(110)^*$ diffuse distribution.

3.3. The case of FeF_2

As a final example, consider the case of FeF_2 (see Brink *et al.*, 2001 for details). Similarly to FeOF, it also crystallizes in the rutile average structure type but with a distinctly larger c axis. This material also shows transverse polarized $\mathbf{H} \pm \epsilon(\bar{1}\bar{1}0)^*$ diffuse scattering [see *e.g.* the (*a*) close to $[001]$ and (*b*) $[01\bar{3}]$ zone-axis electron-diffraction patterns shown in Fig. 4] again requiring long-range ordering in $\{1\bar{1}0\}$ planes, but with no correlation from one such plane to the next. The transverse polarized nature of the observed structured diffuse scattering again implies that correlated displacements within these $\{1\bar{1}0\}$ planes must be responsible. This time, however, the $\mathbf{H} \pm \epsilon(\bar{1}\bar{1}0)^*$ diffuse streaking runs through the $(h + k + l) = \text{even}$ rather than odd average structure Bragg reflections. Clearly the observed DS must again arise from correlated Fe displacements within the relevant $\{1\bar{1}0\}$ plane (see Fig. 4*c*), but this time the relevant modulation wavevector must be of the type $\Delta = (q_x, -q_x, 0)$ (as shown in Fig. 4*c*). Likewise, the mode symmetry

associated with these modulated wavevectors must again be of $\Delta 3$ mode symmetry type. The modes of symmetry $\Delta 3$ are DS-active in general provided $(h + k + l) = \text{even}$ as required (see Figs. 4*a* and *b*). They are also observed at the [001] zone-axis orientation, again as required (see Fig. 4*a*).

4. Conclusions

Three different ‘disordered’ systems, ThAsSe, FeOF and FeF₂, have been used to illustrate the point that initially unexpected extinction conditions with respect to the average structure space-group symmetry (see *e.g.* Figs. 1, 2 and 4) can arise in structured diffuse distributions if the atom, or group of atoms, giving rise to the structured DS fall on sites with higher space-group symmetry than the average structure space-group symmetry. Knowledge of the relevant supergroup symmetry enables the real space structural origin of the observed ‘extinction conditions’ to be understood as well as giving great insight into the real space structural disorder responsible. In addition to these unexpected ‘extinction conditions’, it has also been demonstrated that additional extinction conditions can arise at special zone-axis orientations as a result of the symmetry of the modes responsible for the observed structured diffuse scattering.

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