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Short-range order diffuse scattering in quasicrystals

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A theory for the diffuse scattering intensity owing to short-range order (SRO) in quasicrystals is given. The diffuse scattering intensity can be calculated based on higher-dimensional cluster models of quasicrystals. It is determined by the overlapped area (or volume) of occupation domains separated from each other by distances up to the correlation length and the SRO correlation functions. It is applied to a random atom distribution in phason flip sites in the Penrose pattern. To confirm the validity of the derived formula, analytical and numerical results for this case have been compared. Both results give similar diffuse scattering intensity, suggesting the validity of the theory.

1. Introduction

X-ray and neutron scattering experiments are standard techniques for investigating the pair correlation of atoms in crystals with some kind of disorder. Scattered intensities of materials can be classified into two terms: the Bragg reflection and diffuse scattering intensities. It is known that the Fourier transform of the pair correlation function of the (electron or nucleus) density of materials gives the total scattering intensity (van Hove, 1954). This general theory is, however, difficult to apply to the analysis of diffuse scattering in materials, so that several approximations have been proposed. When a structure includes some kind of disorder, the Bragg reflection intensity determines its average structure. The deviation (fluctuation) from the average structure causes the diffuse scattering.

There are two kinds of fluctuations which contribute to the diffuse scattering intensity in different ways. They are the fluctuations of atomic positions and the (electron or nucleus) densities of atoms in time and space. The diffuse scattering intensity in crystals is classified into three components: short-range order (SRO), size-effect, and thermal and Huang diffuse scattering. They correspond to zeroth-, first- and second-order terms in a Taylor expansion of the correlation function in terms of the atom displacement parameter (Welberry & Butler, 1994). The thermal diffuse scattering (TDS) and the Huang diffuse scattering (HDS) in crystals are well known; they originate in the thermal excitation of phonons and distortions due to the inclusion of some kind of point defect (Dietrich & Fenzel, 1989; Welberry & Butler, 1994). In TDS and HDS, the correlation length of the atomic displacement parameter is long, while that of the density is in many cases short. Depending on these different natures, different approaches are used in the approximations in the former and latter theories, *i.e.* the reciprocal- and real-space approaches (Welberry & Butler, 1994).

The short-range order (SRO) and/or size effect, which comes from the coupling of the density and displacement fluctuations, give rise to the diffuse intensity that is separate from the Bragg peaks. The theory of SRO diffuse scattering (Cowley, 1950) is extensively applied to the diffuse scattering in alloys and other materials (Welberry & Butler, 1994). In particular, SRO diffuse scattering is often observed in alloys that show an order–disorder-type phase transition.

In quasicrystals the Bragg scattering intensity can be calculated using a higher-dimensional description and this method is extensively used in the structure analysis of quasicrystals (Yamamoto, 1996; Weber & Yamamoto, 1998; Takakura, Yamamoto & Tsai, 2001; Cervellino *et al.*, 2002; Takakura *et al.*, 2007). This description is necessary in the analysis of diffuse scattering intensity, as shown later.

TDS exists in quasicrystals and HDS is expected to exist if quasicrystals include point defects. In addition, phason diffuse scattering (PDS), which is specific to quasicrystals, exists. This is considered to be caused by long-wavelength collective modes of atomic jumps, which are called phason flips. These theories extract the contribution to the diffuse scattering intensity of long-range correlations between atoms, using hydrodynamical approximations, in which a detailed structure of quasicrystals is not taken into account. They contain only some macroscopic constants, like phonon or phason elastic constants (Jarić & Nelson, 1988; Lei *et al.*, 1999; Ishii, 2000). Owing to the macroscopic nature of these theories, they only explain the diffuse scattering around the Bragg peaks. Their characteristic feature is that the diffuse scattering intensity decays as $|\mathbf{q}|^{-2}$, where $\mathbf{q}$ is a vector in reciprocal space from the Bragg reflection (Dietrich & Fenzel, 1989; Jarić & Nelson, 1988; Boissieu *et al.*, 1995).

Since most quasicrystals are alloys (Tsai, 1999) and some quasicrystals show phase transitions between quasicrystalline phases (Ritsch *et al.*, 1998), which are considered to be related to some kind of order–disorder phenomena, SRO diffuse scattering is, as expected, observed in several quasicrystals (Frey & Steurer, 1993; Abe *et al.*, 2000, 2003; Weidner *et al.*, 2004). This has, however, not been analyzed in detail so far, since quasicrystals have no periodicity along at least two directions and therefore the classical theory of SRO diffuse scattering for crystals cannot be applied to quasicrystals.

Recently, the diffuse scattering around the main reflections of the basic Ni-rich phase of a decagonal Al–Ni–Co quasicrystal (d-Al–Ni–Co) has been analyzed based on the hydrodynamical theories of diffuse scattering (Abe *et al.*, 2007) and it was clarified that the application of the theories of TDS and PDS does not explain the diffuse scattering intensity around the Bragg peaks. Monte Carlo simulations of the disorder in Al and the transition metals (TMs) showed that the correlation length of Al–TM extends up to 40–50 Å. This is much longer than the interatomic distance, but shorter than the correlation of PDS. In addition, Kobas *et al.* (2005) showed that the PDS and TDS in the S1 phase of d-Al–Ni–Co can explain the diffuse scattering intensity within the range $|\mathbf{q}| \le (1/60)$ Å^{-1}. They suggest that an interatomic correlation that is greater than 60 Å can be interpreted by PDS. These experiments suggest that a theory of SRO diffuse scattering in quasicrystals is necessary.

An analytical formula for SRO diffuse scattering intensity can be derived by using a higher-dimensional description of quasicrystals, as in the structure-factor calculations. Even if no periodicity exists in quasicrystals, we can calculate the frequency of atom pairs with short interatomic distances. Under appropriate assumptions, the SRO diffuse scattering intensity is determined by the frequency of such pairs and vectors connecting a pair of atoms with a similar local environment. It is known that the frequency is proportional to the overlapped area (volume) of the occupation domains (ODs) for related atoms (Yamamoto, 1996). Therefore, the diffuse scattering intensity can be calculated from the higher-dimensional description of quasicrystals. In a case where longer-range correlation is important, however, this theory will encounter a difficulty, since the number of different environments rapidly increases with increasing distance and this makes calculations difficult.

In the case of the basic Ni-rich phase in d-Al–Ni–Co, we need to consider medium-range order, as mentioned above. Therefore, the theory should be applicable to medium-range order. The direct calculation of diffuse scattering intensity using interatomic correlation functions is difficult in such a case. However, if we can use an inter-cluster correlation function, the calculation will be largely simplified as shown in this paper. The theory of SRO diffuse scattering will be applicable to such a case as long as we need to consider neither shorter nor much longer correlation than the inter-cluster distance. Clusters with a diameter of ~ 20 Å (20 Å clusters) are found in d-Al–Ni–Fe and d-Al–Ni–Co. The correlation lengths in these quasicrystals are therefore not much longer than this inter-cluster distance.

In addition to the lack of theory for SRO diffuse scattering in quasicrystals, there was an experimental difficulty. A decade ago, the measurement of SRO diffuse scattering was not easy, since it appears everywhere in reciprocal space, in contrast to TDS and HDS. The development of two-dimensional X-ray (or neutron) detectors enabled the measurement of diffuse scattering in a wide reciprocal-space region. For example, single-crystal diffraction data measured by CCD cameras usually include intensities from the whole of reciprocal space within a diffraction-angle limit, since more than several hundred frames are measured using a small sample rotation angle (less than 0.5°). This provides the diffuse scattering intensity together with the Bragg intensities. One can easily reconstruct the intensity distribution in reciprocal space from intensities of pixels on the detector by projecting a pixel intensity onto the Ewald sphere. The method is equally applicable to crystals and quasicrystals. Thus, a theory for SRO diffuse scattering in quasicrystals is desired.

In this paper we derive an analytical formula for the SRO diffuse X-ray scattering intensity in quasicrystals. It is applied to the diffuse scattering owing to the phason flip in the Penrose pattern (PP) and the results are compared with the numerical results to confirm the validity of the formula. (A preliminary result of this paper has been published: Yamamoto, 2008.) In order to apply the derived formula to realistic quasicrystals, several approximations are discussed. The extension of the derived formula to neutron magnetic scattering will be given in a separate paper (Yamamoto, 2010).

The arrangement of the paper is as follows. The diffuse scattering intensity calculations are based on higher-dimensional cluster models. The latter are briefly summarized in §2. §3 briefly discusses the interatomic distances in these models. A general formula is derived in §4. This does not include symmetry operations. The formula is rewritten in §5 using the symmetry operations for practical applications. In realistic cases the disorder in quasicrystals will be complicated, so we consider approximations of the general theory. When the diffuse scattering occurs due to the orientational disorder of atom clusters, the expression can be simplified. This is discussed in §6 for several cases. In order to validate the derived diffuse scattering intensity formula, it is applied to the case of phason flips in the PP in §7 and the analytical result is compared with the result of numerical calculations.

2. Higher-dimensional cluster models

It is known that a structure of quasicrystals is obtained from an n-dimensional (nD, $n \ge 5$) periodic structure by taking an intersection of a *three-dimensional* hyperplane parallel to external space. The structure obtained does not depend on the position of the three-dimensional hyperplane in nD space. The structures obtained from different hyperplanes are locally isomorphic to each other. In other words, one structure can be mapped onto another if it is shifted appropriately in external space. In such a description, all atom positions are obtained from ODs in the nD unit cell (Yamamoto, 1996).

For real quasicrystals, it is known that there are several large ODs in which several parts are occupied by different kinds of atoms. It is also known that quasicrystals can be described by several building units, which fill most of the space (Henley & Elser, 1986; Henley, 1991). They are called clusters. In a higher-dimensional cluster model, such large ODs are divided into smaller ones based on the ODs for the cluster centers. Each point in a small OD corresponds to an atom position in a cluster or a position of an interstitial atom, which connects clusters. In the structure analysis of quasicrystals, each small OD plays the role of an independent atom in a unit cell in conventional crystals. The small OD gives an atom position with an almost similar local environment at a short distance.

Since quasicrystals lack periodicity in physical space, if we consider the environment of an atom up to very long distances no atom is equivalent to any other. However, there are many atoms which have almost equal environments in the short range.

In the case of statistically disordered cluster orientations, ODs for all possible clusters with different orientations need to be considered. Let the ith atom of a cluster be located at $\mathbf{x}_i^{\rm e}$ from the cluster center (in external space). When the OD for a cluster center is known, all the atom positions in the cluster can be generated by the ODs which are shifted parallel to external space over $\mathbf{x}_i^{\rm e}$ from the OD position of the cluster center in nD space. That is, when the OD for the cluster center is at $\mathbf{x}_{\rm c}$ in the unit cell of the n-dimensional space, the OD for a constituent atom in the cluster is given by ODs at $\mathbf{x}_{\rm c} + \mathbf{x}_i^{\rm e}$. In order to describe the same quasicrystal structure we can use these small cluster ODs and ODs for interstitial sites rather than using the large ODs mentioned above.

3. Interatomic distances

In the theory of SRO diffuse scattering for crystals the number of atomic pairs with the same interatomic distance needs to be known. The number of pairs is easily calculated since all interatomic distances are calculated from an interatomic vector between two atoms within the unit cell and a lattice vector. It is clear that the same method is not applicable to quasicrystals because of the loss of periodicity. Nevertheless, we can calculate all the necessary interatomic distances in principle based on the nD description of quasicrystals. In this theory, an *average* structure of disordered quasicrystals is described as a periodic structure in n-dimensional space. Each atom is extended in parallel to the $(n-3)$-dimensional internal (complementary) space within a limited area/volume (Yamamoto, 1996). This area is the OD.

In the simplest theory of SRO diffuse scattering, we assume that atomic positions are not disturbed by a change of atomic species on a site (Cowley, 1950; Welberry & Butler, 1994). Therefore, all atoms are assumed to be located at the same positions as in the average structure. In the n-dimensional description all atom positions in the external (physical) space can be given by the location and size of the ODs within the unit cell of n-dimensional space. Using this description, the interatomic distances of all atoms in quasicrystals are calculated by the common area (volume) of ODs which are projected onto the internal (fictitious complementary) space (Yamamoto, 1996). This will be described later.

As an example, an estimation of the frequency of a specified pair in quasicrystals is shown in the case of the one-dimensional section of the PP, which is known as one of the simplest quasiperiodic patterns [Fig. 1; for the PP, see Fig. 2(*a*)]. This is given as a four-dimensional periodic structure. The unit vectors of the four-dimensional reciprocal lattice are given by

$$\mathbf{d}_i^* = \frac{a^*}{5^{1/2}}[c_i\mathbf{a}_1 + s_i\mathbf{a}_2 + c_{2i}\mathbf{a}_3 + s_{2i}\mathbf{a}_4] \quad (i \le 4), \tag{1}$$

where a^* is the reciprocal-lattice constant, $c_i = \cos(2\pi i/5)$, $s_i = \sin(2\pi i/5)$ and $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors in external space, while $\mathbf{a}_3$ and $\mathbf{a}_4$ are those of the internal space. From the relation $\mathbf{d}_i^* \cdot \mathbf{d}_j = \delta_{ij}$, the unit vectors in the direct lattice are

$$\mathbf{d}_i = \frac{2a}{5^{1/2}}[(c_i - 1)\mathbf{a}_1 + s_i\mathbf{a}_2 + (c_{2i} - 1)\mathbf{a}_3 + s_{2i}\mathbf{a}_4] \quad (i \le 4), \tag{2}$$

where a is the lattice constant, that is $a = 1/a^*$. In the following, a vector with $\sum_{i=1}^4 x_i\mathbf{d}_i$ is written as (x_1, x_2, x_3, x_4). In particular $(i, i, i, i)/5$ $(i = 1, 2, 3, 4)$ are written as $\mathbf{x}_i$. Their external and internal space components are denoted by the superscripts e and i.

Real atom positions of the PP are obtained from a periodic structure in four-dimensional space, in which four ODs are located in the unit cell. The ODs at $\mathbf{x}_1$ and $\mathbf{x}_2$ (ODs *A* and *B*, hereafter) are regular pentagons as shown in Figs. 3(*a*) and (*b*), while those at $\mathbf{x}_4$ and $\mathbf{x}_3$ (ODs *C* and *D*) are the pentagons which are obtained from ODs *A* and *B* by the inversion

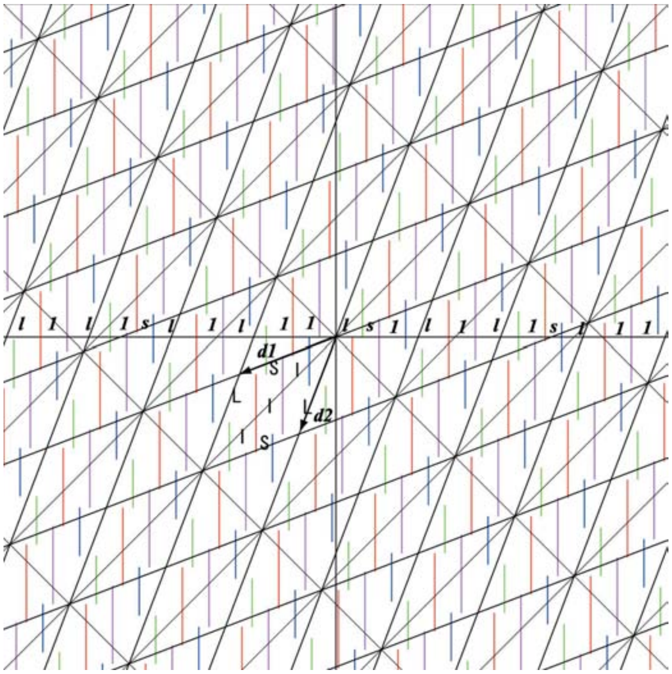

Figure 1
Two-dimensional section of the four-dimensional structure of the Penrose pattern in a subspace spanned by $\mathbf{d}_1 = (0, 1, 1, 0)$ and $\mathbf{d}_2 = (1, 0, 0, 1)$. The thin solid lines show a face-centered lattice in this subspace. At $(i, i, i, i)/5$ $(i = 1, 2, 3, 4)$, there are four occupation domains which are denoted by *A* (blue), *B* (purple), *C* (red) and *D* (green). The external and internal spaces spanned by $\mathbf{a}_1$ and $\mathbf{a}_3$ are parallel to the horizontal and vertical lines. On the external space (the thick horizontal line), there are three interatomic distances with $\tau^{-1}d$, d and τd labeled by s, 1 and l, respectively, where $d = 2a/5^{1/2}$. The interatomic distances just above the horizontal line correspond to those on the horizontal line in Fig. 2(*a*).

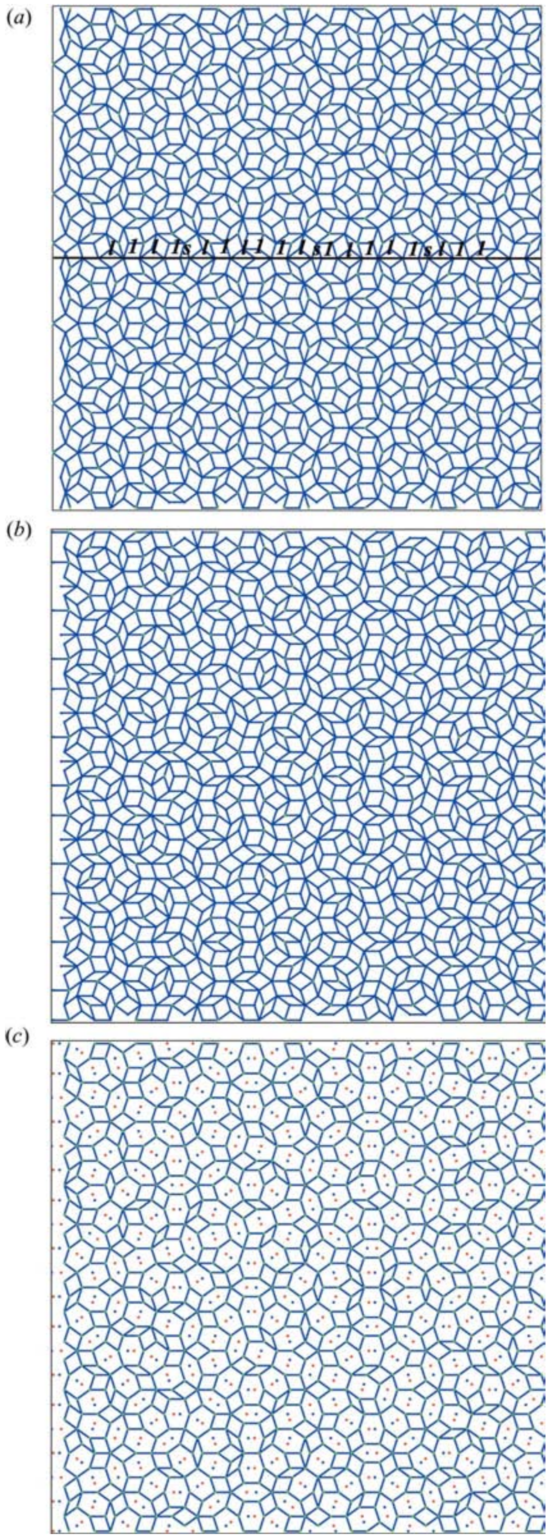

Figure 2
(*a*) Penrose pattern and (*b*) phason-flipped Penrose pattern. They are generated by the occupation domains shown in Fig. 3. Their atom positions flipped by the random phason to each other are shown in hexagons in (*c*). The two-dimensional hyperplanes for all the cases pass through (1, 2, 3, 4)/100. The horizontal line in (*a*) corresponds to the line just above the horizontal line in Fig. 1. Note that the sequence of the interatomic distances on this line (denoted by *s*, 1 and *l*) agrees with that in Fig. 1.

operation. The radius of the corner of OD *A* is $2a/5^{1/2}$, while that of OD *B* is $2\tau a/5^{1/2}$, where τ is the golden mean, $(1+5^{1/2})/2$. The two-dimensional hyperplane spanned by $\mathbf{a}_1$ and $\mathbf{a}_3$ passing through the origin is shown in Fig. 1. A rhombic lattice (thick lines) exists. The unit vectors of this lattice are given by $\mathbf{d}_1' = (0,1,1,0)$ and $\mathbf{d}_2' = (1,0,0,1)$. The external and internal space components of the former are $-2\tau a$ and $-2\tau^{-1}a$, while those of the latter are $-2\tau^{-1}a$ and $-2\tau a$. The internal space component of a lattice point $l_1\mathbf{d}_1'^{\rm i} + l_2\mathbf{d}_2'^{\rm i}$ is, therefore, given by $-2(l_1\tau^{-1} + l_2\tau)a$. The points of all the lattice points projected onto the internal space are then uniformly distributed and this ensures that the point density of the cross points of the ODs with the external space is proportional to the length of the ODs (Elser, 1986). This leads to the property that the frequency of an interatomic distance $\Delta\mathbf{x}^{\rm e}_{ijl} = \mathbf{x}^{\rm e}_i - \mathbf{x}^{\rm e}_j - \mathbf{x}^{\rm e}_l$ between a pair of atom positions generated by ODs at $\mathbf{x}_i$ and $\mathbf{x}_j + \mathbf{x}_l$ is proportional to the overlapped area (length in this case) of these ODs when they are projected onto the internal space (vertical line), where $\mathbf{x}_l$ is a lattice vector (Yamamoto, 1996).

The unit vectors of the rectangular lattice (thin lines) in Fig. 1 are given by $\mathbf{d}_1' - \mathbf{d}_2'$ and $\mathbf{d}_1' + \mathbf{d}_2'$. (Note that in Fig. 3, $\mathbf{a}_3$ and $\mathbf{a}_4$ are parallel to the horizontal and vertical directions, while in Fig. 1, $\mathbf{a}_3$ is parallel to the vertical direction.) Several ODs (vertical bars) cross the external space (the horizontal line) and their cross points give the atom positions in the external space. Three nearest-neighbor distances exist: $d_1 = \tau^{-1}d$, $d_2 = d$ and $d_3 = \tau d$ with $d = 2a/5^{1/2}$. The overlapped areas giving these interatomic distances are denoted in Fig. 1 by the labels *S*, *I* and *L*.

Finally we consider (fictitious) four-dimensional and (real) five-dimensional or six-dimensional quasicrystals. In the PP, which is considered to be a fictitious quasicrystal with two-dimensional external space, the necessary dimension of the external space is 2 and that of the internal space is 2. The overlapped area is then two-dimensional. In real decagonal quasicrystals they are 3 and 2, while for icosahedral ones they

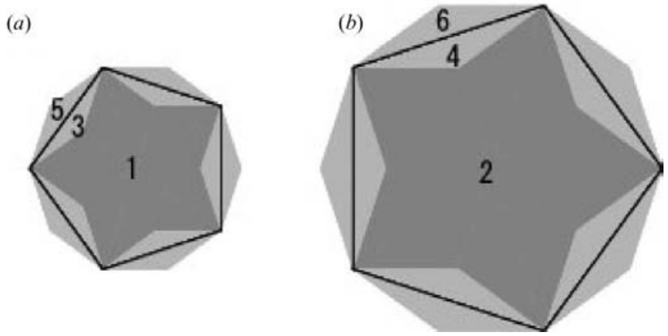

Figure 3
Occupation domains (ODs) of the Penrose pattern and phason-flipped Penrose pattern. The ODs (*a*) and (*b*) are located at (1, 1, 1, 1)/5 and (2, 2, 2, 2)/5 in four-dimensional space. There are two other ODs, which are obtained from these two by the inversion center at the origin. The corresponding inverted domains are represented by a primed number in the text. The former pattern is generated by ODs 1–4, and the latter by ODs 1, 2, 5 and 6.

are 3 and 3, respectively. Similar to the above fictitious two-dimensional quasicrystal, if the internal space is two- or three-dimensional, the interatomic distances between atoms generated by some ODs are proportional to the overlapped area or volume of the ODs.

In a real quasicrystal in which there are several ODs in a unit cell, the position of the ith OD in the unit cell is specified by $\mathbf{x}_i$ and an n-dimensional lattice vector by $\mathbf{x}_l$. The frequency of the interatomic vector, $\Delta\mathbf{x}^{\rm e}_{ijl} = \mathbf{x}^{\rm e}_{jl} - \mathbf{x}^{\rm e}_{i}$, which is the external space component of the difference between $\mathbf{x}_{i0} = \mathbf{x}_i$ and $\mathbf{x}_{jl} = \mathbf{x}_j + \mathbf{x}_l$, is therefore proportional to the overlapped area (volume) of the ODs located at these points when they are projected onto the internal space. As is clear from Fig. 1, for most lattice vectors $\mathbf{x}_l$ the area is zero, but for lattice vectors with a small internal space component the area will have a non-zero value.

4. Short-range order diffuse scattering

In kinematical theory the scattered intensity in quasicrystals can be derived from a general formula (see Appendix *A*). This formula gives both Bragg reflection and diffuse scattering intensities. We treat these two contributions separately. It is well known that the first one can be calculated by an n-dimensional model of quasicrystals, as previously mentioned. This description is applicable to the calculation of the diffuse scattering intensity, but we do not need to consider the scattering vector in n-dimensional space as shown below.

We consider a simple case where one atomic site is occupied by m atomic species and neglect the size effect (Warren *et al.*, 1951). This is extended later to more complicated cases where there are clusters with several different orientations.

We assume that the correlation between atoms decreases rapidly with the interatomic distance. Provided that all atoms generated by the ith small OD have a similar local environment, the correlation between the atoms generated by the ith and jth small ODs will be almost the same. We can calculate the number of pairs of such atoms by the overlapped area (volume), $v_{ijl} \equiv v_{ij}(\Delta\mathbf{x}^{\rm i}_{ijl})$, of the ith and jth ODs when they are projected onto internal space. It is given by Vv_{ijl}/Ω_n, where V is the volume of the quasicrystal (in external space), while Ω_n denotes the unit-cell volume of an n-dimensional lattice. (Note that v_{ijl}/Ω_n gives the number of pairs in a unit volume of external space.) The number of pairs depends on the indices i and j, since the areas of ODs are different in different OD pairs in general. The SRO diffuse scattering intensity is then given by

$$I_{\rm D}(\mathbf{q}) = \frac{V}{\Omega_n}\sum_{l}\sum_{ij\mu\nu}\langle\, \Delta f^{\mu}_{i}\Delta f^{\nu *}_{j}\rangle v_{ijl} \times \exp(2\pi i\mathbf{q}\cdot\Delta\mathbf{x}^{\rm e}_{ijl}), \qquad (3)$$

where $\Delta f^{\mu}_{i} = f^{\mu}_{i}(\mathbf{q}) - \langle f_i(\mathbf{q})\rangle$ is the fluctuation of the atomic scattering factor of the μth atom species of the ith OD from its average, $f^{\mu}_{i}(\mathbf{q})$ is the atomic scattering factor, the expression $\langle x\rangle$ means the statistical average of a quantity x over the quasicrystal and the asterisk stands for the complex conjugate (see Appendix *A*). In the following we simply write f^{μ}_{i} and $\langle f_i\rangle$ rather than $f^{\mu}_{i}(\mathbf{q})$ and $\langle f_i(\mathbf{q})\rangle$.

The atomic fluctuations are expressed by the statistical variables z^{μ}_{il} ($\mu = 1, 2, \ldots, m$), which can assume values of zero and one. A value of one for z^{μ}_{il} indicates that the ith atomic site in the n-dimensional unit cell l is occupied by the μth atom; all other z^{μ}_{il} ($1 \le \mu \le m$) with the same i and l must then have a value of zero. The average of z^{μ}_{il}, $\langle z^{\mu}_{i}\rangle$, is the occupational probability of the μth atom species which occupies the ith OD and is independent of the lattice vector $\mathbf{x}_l$. This means that $\langle z^{\mu}_{i}\rangle$ takes a value between 0 and 1 in general. Its fluctuation, $z^{\mu}_{i0} - \langle z^{\mu}_{i}\rangle$, is denoted by Δz^{μ}_{i0}. Note that the average structure factor $\langle f_i\rangle$ of the ith atomic site located at $\mathbf{x}_{i0}$ is given by $\langle f_i\rangle = \sum_{\mu} f^{\mu}\langle z^{\mu}_{i}\rangle$. Since the structure factor of the ith atom is then given by $f_i = \sum_{\mu} f^{\mu} z^{\mu}_{i} = \sum_{\mu} f^{\mu}(\langle z^{\mu}_{i}\rangle + \Delta z^{\mu}_{i0})$, the fluctuation of the structure factor for the ith site is written as $\Delta f_i = \sum_{\mu} f^{\mu}\Delta z^{\mu}_{i}$. In the same manner, when we consider the atomic site which is generated by the ODs at $\mathbf{x}_{jl}$, the atomic scattering factor in this site is given by $f_j = \sum_{\mu} f^{\mu}(\langle z^{\mu}_{j}\rangle + \Delta z^{\mu}_{jl})$ and its fluctuation by $\Delta f_j = \sum_{\mu} f^{\mu}\Delta z^{\mu}_{jl}$.

We introduce the correlation function $\langle z^{\mu}_{i0} z^{\nu}_{jl}\rangle$, which is the probability of finding the μth atom at $\mathbf{x}_{i0}$ and the νth atom at $\mathbf{x}_{jl}$, and the correlation functions of the fluctuation $\langle \Delta z^{\mu}_{i0}\Delta z^{\nu}_{jl}\rangle$. The latter is equal to $\langle z^{\mu}_{i0} z^{\nu}_{jl}\rangle - \langle z^{\mu}_{i}\rangle\langle z^{\nu}_{j}\rangle$. The average of the fluctuation in the atomic scattering factors is then given by

$$\langle \Delta f_i \Delta f_j\rangle = \sum_{\mu\nu} f^{\mu} f^{\nu} g^{\mu\nu}_{ijl}, \qquad (4)$$

where $g^{\mu\nu}_{ijl} \equiv g^{\mu\nu}_{ij}(\Delta\mathbf{x}^{\rm e}_{ijl}) = \langle \Delta z^{\mu}_{i0}\Delta z^{\nu}_{jl}\rangle = \langle z^{\mu}_{i0} z^{\nu}_{jl}\rangle - \langle z^{\mu}_{i}\rangle\langle z^{\nu}_{j}\rangle$. (We use the latter notation, $g^{\mu\nu}_{ij}(\Delta\mathbf{x}^{\rm e}_{ijl})$, which specifies the interatomic (inter-OD) vector explicitly.)

The correlation function of the fluctuation is related to the SRO parameter (Warren *et al.*, 1951) $\alpha_{ijl} \equiv \alpha^{\mu\nu}_{ij}(\Delta\mathbf{x}^{\rm e}_{ijl})$ by

$$g^{\mu\nu}_{ijl} = -\langle z^{\mu}_{i}\rangle\langle z^{\nu}_{j}\rangle\alpha^{\mu\nu}_{ijl}. \qquad (5)$$

The relation $\sum_{\nu=1}^{m}\langle z^{\mu}_{i0} z^{\nu}_{jl}\rangle = \langle z^{\mu}_{i}\rangle$ leads to the identity

$$g^{\mu\mu}_{ijl} = -\sum_{\mu\neq\nu} g^{\mu\nu}_{ijl}. \qquad (6)$$

Owing to this relation, (3) is rewritten as (Hayakawa & Cohen, 1975)

$$I_{\rm D}(\mathbf{q}) = -\kappa\sum_{ijl}\sum_{\mu>\nu}|f^{\mu} - f^{\nu}|^2 g^{\mu\nu}_{ijl} v_{ijl}\exp(2\pi i\mathbf{q}\cdot\Delta\mathbf{x}^{\rm e}_{ijl}), \qquad (7)$$

where $\kappa = V/\Omega_n$ and the scattering vector $\mathbf{q}$ is a vector in external space. In the summation in (7), i and j only run over ODs in the n-dimensional unit cell, which are statistically occupied, since for the ODs which are fully occupied by a single atomic species the correlation function $g^{\mu\nu}_{ijl}$ is zero. (For such a site, $\Delta f^{\mu}_{i} = 0$ for all μ.) On the other hand, l runs over several lattice points in a quasicrystal, which generate near neighbors of the ith OD, since we assume that the correlation function $g^{\mu\nu}_{ijl}$ rapidly becomes zero when the distance $|\Delta\mathbf{x}^{\rm e}_{ijl}|$ increases.

It should be noted that the above expression is formally different from the corresponding formula in crystals only by the existence of v_{ijl} and the fact that $\Delta\mathbf{x}^{\rm e}_{ijl}$ is a projection of a vector in n-dimensional space onto external space. Thus, if we know v_{ijl}, we can calculate the diffuse scattering intensity owing to SRO occurring in quasicrystals.

5. Symmetry of quasicrystals and diffuse scattering intensity

In the n-dimensional description of quasicrystals, there are several small ODs. They are related by the symmetry operators, $\{R|\tau\}$, of an n-dimensional space group. Consider small ODs located at $\mathbf{x}_i$ and $\mathbf{x}_j$, and their transformed ODs at $\{R|\tau\}\mathbf{x}_i$ and $\{R|\tau\}\mathbf{x}_j$. Since $\{R|\tau\}$ is a symmetry operator, the original and transformed pairs will have identical correlation functions, since the local environments of the original and transformed pairs is the same except for the orientation. Therefore, we assume that they give the same correlation function and overlapped area. Then (7) is rewritten as

$$I_{\rm D}(\mathbf{q}) = -\kappa \sum_{ijl} v_{ijl} \sum_{\mu>\nu R} |Rf^{\mu} - Rf^{\nu}|^2 \times g_{ijl}^{\mu\nu} \exp(2\pi i \mathbf{q} \cdot R\Delta\mathbf{x}_{ijl}^{\rm e}), \tag{8}$$

where $Rf^{\mu} = f^{\mu}(R^{-1}\mathbf{q})$. In this expression, i, j and l run over all values which give rise to independent (statistically occupied) OD pairs, while R runs over all the symmetry operators which generate new but equivalent vectors from $\Delta\mathbf{x}_{ijl}$. Therefore, the summation with respect to R depends on $\mathbf{x}_{ijl}^{\rm e}$. When we use the multiplicities for this vector $a_{ijl} \equiv a_{ij}(\Delta\mathbf{x}_{ijl})$ the above formula is rewritten as

$$I_{\rm D}(\mathbf{q}) = -\kappa \sum_{ijl} v_{ijl} a_{ijl} \sum_{\mu>\nu R} |Rf^{\mu} - Rf^{\nu}|^2 \times g_{ijl}^{\mu\nu} \exp(2\pi i \mathbf{q} \cdot R\Delta\mathbf{x}_{ijl}^{\rm e}), \tag{9}$$

where R runs over all the symmetry operations in the point group. The multiplicity a_{ijl} is determined by the order of the group, which leaves the vector $\Delta\mathbf{x}_{ijl}$ invariant.

6. Orientational disorder of clusters

In some quasicrystals we can simplify the calculation of diffuse scattering more.

There is a case where the disorder occurs in the central part of a cluster. In this case we only need to consider statistically occupied atomic sites located near the cluster center. One important example of this kind of disorder is the orientational disorder of a small cluster at the center of the large cluster. In this case we can expect the situation where the outer shells in each cluster are distorted corresponding to the orientation of the small cluster, but with magnitudes that become smaller with increasing distance from the center. If the distortion of a cluster is negligible in the outermost shell of the cluster, we can consider clusters with almost the same structure but with different orientations. In such a case we can treat the cluster as a rigid cluster. Then the atomic scattering factor f can be replaced by the structure factor of the cluster F in the formulae given in the previous sections. Unlike a spherical atom, a rigid cluster is non-spherical, leading to an anisotropic F. Using F we can calculate the diffuse scattering intensity with medium-range order efficiently.

For example, in the icosahedral Cd–Yb quasicrystal family, a lower-symmetric cluster exists called the Tsai-type cluster, the first shell of which is considered to have a tetrahedral atomic arrangement and is orientationally disordered in a similar way to its 1/1 crystalline approximants (Gomez & Lidin, 2003; Takakura *et al.*, 2007). In this case, the point symmetry of the cluster is 23 and the point group of the quasicrystal is $m\bar{3}\bar{5}$. The orders are 12 and 120, which indicates that ten different orientations of the tetrahedron exist. In the basic Ni-rich phase in Al–Ni–Co quasicrystals, there is one cluster with fivefold symmetry. It takes, however, two orientations. One cluster is related to the other by an 18° rotation (Yamamoto *et al.*, 2005). These two cases have only one rigid cluster but with several different orientations.

In some cases, a quasicrystal can be composed of several different clusters with different orientations. Such a complicated model might be necessary near the phase-transition temperature between b-Ni and S1 phases of d-Al–Ni–Co quasicrystals. In the former, a cluster with a mirror symmetry exists (m cluster), while in the latter the symmetry is fivefold ($5f$ cluster; Takakura, Shiono *et al.*, 2001; Abe *et al.*, 2001). We can consider ten and two different orientations for the former and the latter. Therefore, we need to consider several different clusters and their orientations.

6.1. Orientational disorder of one cluster

We consider a simple case where each site is occupied by one cluster, but with different orientations. In a cluster-based orientational disorder, we can use ODs for the cluster center in the calculation of $v_{ij}(\Delta\mathbf{x}_{ijl})$ rather than the ODs for statistically occupied atoms in the case of atomic disorder. We denote the cluster orientation by μ (or ν). Like the orientational disorder of molecules in crystals (Welberry & Butler, 1994), we can use the structure factor of the cluster with the μth orientation F^{μ} rather than the atomic scattering factor f^{μ} in (9). Then the diffuse scattering intensity is given by

$$I_{\rm D}(\mathbf{q}) = -\kappa \sum_{ijl} v_{ijl} a_{ijl} \sum_{\mu>\nu R} |RF^{\mu} - RF^{\nu}|^2 \times g_{ijl}^{\mu\nu} \exp(2\pi i \mathbf{q} \cdot R\Delta\mathbf{x}_{ijl}^{\rm e}), \tag{10}$$

where F^{μ} is the structure factor of a cluster with the μth orientation, which is located at the ith cluster center, while RF^{μ} denotes the structure factor for a rotated cluster, $F^{\mu}(R^{-1}\mathbf{q})$. (In the calculation of F^{μ}, the atom position of each atom is measured from the cluster center.) In the derivation of this formula we used the fact that the overlapped area for all the atoms within a cluster is equal to that of the cluster center v_{ijl}.

6.2. Disorder of several clusters

We consider a case where one site is occupied by several different clusters and each cluster takes several different orientations. Such a case can be included in the formula described in the previous section as mentioned below. Let the index μ indicate the difference in the cluster orientation and the difference in the kind of clusters. When we denote the structure factor of a cluster with some orientation as F^{μ}, we can use (10) for such a general case since we do not consider the shape of the cluster in the derivation of the formula. For example, in the case of d-Al–Ni–Co, we can specify the five orientations of the m clusters by $1 \leq \mu \leq 5$ and the two orientations of the $5f$ clusters by $6 \leq \mu \leq 7$, when the m and $5f$ clusters occupy one site statistically. We do not need to distinguish the difference of clusters from the difference of orientations. Whenever one site is occupied by clusters with m different structure factors F^{μ} $(1 \leq \mu \leq m)$, we can apply (10). [However, in the practical calculations of the structure factors, the structure factor with a different orientation $F^{\mu}(\mathbf{q})$ can be easily derived from that of the first orientation by applying a symmetry operator R, that is $F^{\mu}(\mathbf{q}) = F^{1}(R^{-1}\mathbf{q})$.]

7. Examples of SRO diffuse scattering in quasicrystals

We consider one simple example, which is a disorder on the atomic level caused by the phason flip in the PP. The diffuse scattering intensity is calculated by (9). The same diffuse scattering intensity can be calculated in a different way using the cluster formula [see (10)], as shown later.

In the following for $a_{ijl} \equiv a_{ij}(\Delta\mathbf{x}_{ijl})$, $v_{ijl} \equiv v_{ij}(\Delta\mathbf{x}^{\rm i}_{ijl})$, $g^{\mu\nu}_{ijl} \equiv g^{\mu\nu}_{ij}(\Delta\mathbf{x}^{\rm e}_{ijl})$ and $\alpha_{ijl} \equiv \alpha^{\mu\nu}_{ij}(\Delta\mathbf{x}^{\rm e}_{ijl})$, the latter notations are used to specify a related interatomic (inter-OD) vector explicitly.

7.1. Random phason flips in the Penrose pattern

It is known that the PP consists of fat and thin rhombi (Fig. 2*a*). This can be described as a four-dimensional periodic structure and it is generated by the occupation domains with four pentagons situated at $(i, i, i, i)/5$ $(i = 1, 2, 3, 4)$. In this fictitious case the external space is two-dimensional. These positions are written as $\mathbf{x}_i$. Their two independent ODs consisting of ODs 1–4 are shown in Fig. 3(*a*). Another pattern consisting of the same rhombi (Fig. 2*b*) is obtained from the ODs 1, 2, 5 and 6. Note that in this case the ODs are decagons with empty parts in the inside. The second one is obtained from the PP by the so-called phason flip. The phason flip positions of the PP are in the two kinds of hexagons shown in Fig. 2(*c*). We call the fat and thin ones hexagons (I) and (II). When one of the phason flip sites is randomly occupied, we have random tiling consisting of the same rhombi. This is a random tiling model due to random phason flip [referred to as model (I) hereafter].

For convenience, we consider two atoms denoted by A and B. When a pair of these two sites are occupied by A (or B) together with other vertices of the PP, we call it an AA (BB) pair. Similarly, when one is occupied by A and the other by B it is called an AB pair. We assume that the first letter denotes the position in the PP shown in blue points in Fig. 2(*c*). If we consider the case where the B atom is a vacancy, we can characterize a model by A and B atom pairs. In model I, there are only AB or BA pairs.

When we allow the same atoms to occupy the two phason flip sites at the same time we obtain two other models. In the second model [model (II)], only AA and BB pairs exist with a probability of 0.5, while in the third one [model (III)] there are AA, BB, AB and BA pairs with a probability of 0.25. In all cases we assume that there is no correlation between phason flip sites located at different hexagons.

For all the cases the average structure can be represented by the ODs shown in Fig. 3 provided that ODs 3, 4, 5 and 6 are occupied with the occupation probability of 0.5, while ODs 1 and 2 are occupied with 1. Therefore, the Bragg reflection intensity is the same for all of them. As shown in the following, however, they give completely different diffuse scattering. As stated previously, the sites fully occupied by a single atom do not contribute to the diffuse scattering intensity, so we can neglect the sites generated by ODs 1 and 2 in the diffuse scattering intensity calculations. The ODs 3 and 5 generate the phason flip sites in hexagon (I), while the ODs 4 and 6 generate those in hexagon (II). The area of ODs 4 and 6 is τ^2 times larger than that of ODs 3 and 5. The vectors between the two phason flip sites are given by $\Delta\mathbf{x}_1 = (1, 1, 0, 1)$ and $\Delta\mathbf{x}_2 = (-1, 1, -1, 0)$ and equivalent ones which are related to these by the fivefold rotation and inversion operations.

Before discussing the correlation functions of the three models, we first consider the self-correlation functions $g^{\mu\mu}_{ii}(\mathbf{0})$ which are 1/4 for $i = 3, 4, 5, 6$, where $\mathbf{0}$ is the zero vector. This gives the so-called Laue monotonic diffuse scattering, which is given by [using the relations $v_{33}(\mathbf{0}) = v_{55}(\mathbf{0})$, $v_{44}(\mathbf{0}) = v_{66}(\mathbf{0}) = \tau^2 v_{33}(\mathbf{0})$ *etc*, see Appendix *B*]

$$I_L(\mathbf{q}) = \frac{\kappa|f^A|^2}{2} v_{33}(\mathbf{0})(1 + \tau^2). \qquad (11)$$

This does not depend on the three models.

The other correlation functions for these three models are different. From this assumption, the non-zero correlation functions of the models (except for the self correlation) are $g^{\mu\nu}_{ij}(R^n_5\Delta\mathbf{x}^{\rm e}_1)$, $g^{\mu\nu}_{ij}(R^n_5\Delta\mathbf{x}^{\rm e}_2)$, $g^{\mu\nu}_{ij}(IR^n_5\Delta\mathbf{x}^{\rm e}_1)$ and $g^{\mu\nu}_{ij}(IR^n_5\Delta\mathbf{x}^{\rm e}_2)$ for $(i, j) = (3, 5')$ and $(4, 6')$ and $n = 0, 1, 2, 3, 4$. (I and R_5 are the inversion and the fivefold rotation.) They are equal to $g^{\mu\nu}_{ij}(\Delta\mathbf{x}^{\rm e}_1)$, $g^{\mu\nu}_{ij}(\Delta\mathbf{x}^{\rm e}_2)$, $g^{\mu\nu}_{ij}(\Delta\mathbf{x}^{\rm e}_1)$ and $g^{\mu\nu}_{ij}(\Delta\mathbf{x}^{\rm e}_2)$, respectively. The overlapped area of ODs for these pairs are the same as the summation of areas of ODs 3 and 5′ and that of ODs 4 and 6′. (For the meaning of a primed letter, see the caption of Fig. 3.) From $g^{\mu\nu}_{ijl} = \langle z^{\mu}_{i0} z^{\nu}_{jl}\rangle - \langle z^{\mu}_{i}\rangle\langle z^{\nu}_{j}\rangle$ and $\langle z^{\mu}_{i}\rangle = 1/2$ for $3 \leq i, j \leq 6$, we have $g^{AB}_{35'}(\Delta\mathbf{x}^{\rm e}_1) = g^{BA}_{35'}(\Delta\mathbf{x}^{\rm e}_1) = g^{AB}_{46'}(\Delta\mathbf{x}^{\rm e}_2) = g^{BA}_{46'}(\Delta\mathbf{x}^{\rm e}_2) = 1/4$ in model I. [Note that $\langle z^{\mu}_{i0} z^{\nu}_{jl}\rangle / \langle z^{\mu}_{i}\rangle$ is the conditional probability of the νth atom found at $\mathbf{x}_{jl}$ when the μth atom is at $\mathbf{x}_{i0}$. When OD 3 is occupied by the A (or B) atom, OD 5 is always occupied by B (or A).] In contrast, in model (II) they are $-1/4$, while in model (III) they are all zero since $\langle z^{\mu}_{i0} z^{\nu}_{jl}\rangle$ for $\mathbf{x}_{ijl} = \mathbf{x}_1$ and $\mathbf{x}_2$ are 1/4 for any μ and ν. (Note that AA, AB, BA and BB pairs exist with the occupation probability of 1/4 in this case.)

From equation (9), the additional diffuse scattering intensity of these three cases is given by

$$
\begin{aligned}
I_{\rm D}(\mathbf{q}) - I_{\rm L}(\mathbf{q})
&= -\frac{\kappa|f^A|^2}{4} v_{35'}(\Delta\mathbf{x}_1^{\rm i})\Big[\sum_R g_{35'}^{AB}(\Delta\mathbf{x}_1^{\rm e})\exp(2\pi i\mathbf{q}\cdot R\Delta\mathbf{x}_1^{\rm e}) \\
&\quad + \tau^2 \sum_R g_{46'}^{AB}(\Delta\mathbf{x}_2^{\rm e})\exp(2\pi i\mathbf{q}\cdot R\Delta\mathbf{x}_2^{\rm e})\Big] + \text{c.c.}, \qquad (12)
\end{aligned}
$$

(where c.c. is complex conjugate) since the B atom is a vacancy, so that $f^B = 0$ and R runs over five rotation operators that rotate by $2\pi j/5$ $(j = 0, 1, 2, 3, 4)$. For simplicity, we assumed that the A atom is spherically symmetric, so that $Rf^A = f^A$. The correlation functions for models (I) and (II) lead to

$$
\begin{aligned}
I_{\rm D}(\mathbf{q}) - I_{\rm L}(\mathbf{q}) &= \frac{\kappa|f^A|^2}{4} v_{35'}(\Delta\mathbf{x}_1^{\rm i})\Big[\mp\sum_R \exp(2\pi i\mathbf{q}\cdot R\Delta\mathbf{x}_1^{\rm e}) \\
&\quad \mp \tau^2 \sum_R \exp(2\pi i\mathbf{q}\cdot R\Delta\mathbf{x}_2^{\rm e})\Big] + \text{c.c.}, \qquad (13)
\end{aligned}
$$

where the upper and lower signs correspond to models (I) and (II). Therefore, a hump of the diffuse scattering intensity in model (I) corresponds to a dip in model (II) and *vice versa*. Note that at $\mathbf{q} = 0$ the total intensity $I_{\rm D}(\mathbf{q})$ of model (I) is zero since the two exponential functions are 1, while it takes the maximum value in model (II).

Models (I) or (II) have a dip or hump at the strong Bragg reflection positions, as shown below. In such a position the vector $\mathbf{q}$ is given as the projection of a lattice vector in four-dimensional space onto the external space. Let the four-dimensional lattice vector be $\mathbf{q}'$. Then $\mathbf{q}'^{\rm e} = \mathbf{q}$. Strong Bragg reflections appear at the position $\mathbf{q}$ when the internal space component of the corresponding $\mathbf{q}'$ is small. Since the vectors $\Delta\mathbf{x}_1$ and $\Delta\mathbf{x}_2$ are lattice vectors in four-dimensional space, it means that for such a $\mathbf{q}'$, $\mathbf{q}\cdot\Delta\mathbf{x}_i^{\rm e} \simeq \mathbf{q}'\cdot\Delta\mathbf{x}_i \simeq 0$ mod 1, $(i = 1, 2)$. Thus, for a similar reason as for the case of $\mathbf{q} = 0$, the diffuse scattering intensity around such $\mathbf{q}$ has a dip in model (I) and a hump in model (II) as mentioned above. Equations (11) and (13) give the diffuse scattering intensity shown in Figs. 4(*a*) and 5(*a*). For simplicity, we used a point atom, for which the atomic scattering factor has no $\mathbf{q}$ dependence.

The diffuse scattering intensity can be calculated directly by numerical calculations (Welberry, 1991). For a given atom arrangement, its Fourier amplitude at the diffraction vector $\mathbf{q}$ can be obtained by a numerical Fourier transformation. Using the Fourier amplitude $F(\mathbf{q})$ of a given atom distribution, the total scattered intensity is given by $|F(\mathbf{q})|^2$ (except for the scaling factor). This includes Bragg intensity, which is much stronger than the diffuse scattering intensity. The contribution to the Bragg scattering can be removed by using the fluctuation of the occupation probability for each atomic site instead of the occupation probability itself (Yamamoto, 2008). The calculated diffuse scattering intensity distribution, however, shows strong so-called speckle noise, since no ensemble average was taken into account in contrast to the analytical one. This noise can be reduced by taking an ensemble average. The patterns of models (I) and (II) after taking a 1000 ensemble average are shown in Figs. 4(*b*) and 5(*b*). It is evident that the analytical and numerical results are quite similar, suggesting the validity of the analytical intensity formula.

7.2. Random phason flips as cluster disorder

The case of the phason flips mentioned above [model (I)] can be regarded as cluster disorder. The cluster in this case is

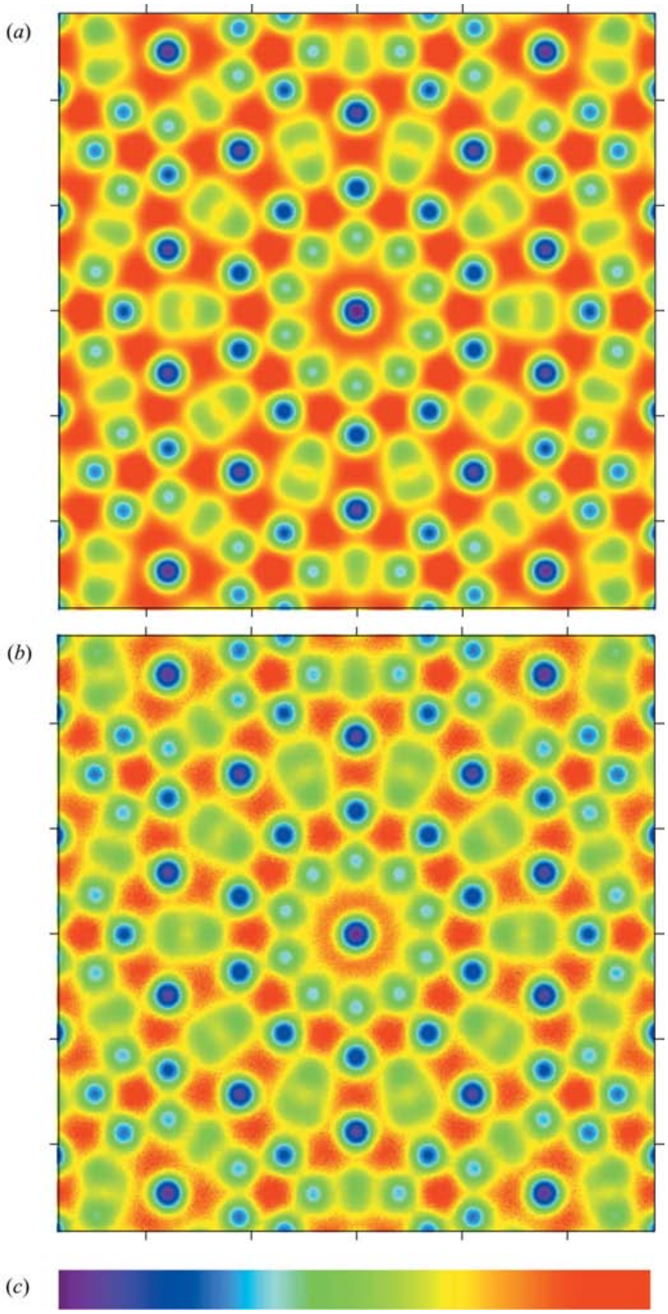

Figure 4
Diffuse scattering intensities of model (I) calculated analytically (*a*) and numerically (*b*), where one of the phason flip sites shown in Fig. 2(*c*) is occupied randomly. The intensity is denoted by the rainbow colors shown in (*c*), blue being the lowest and red the highest. In the numerical calculation, a 1000 ensemble average is taken to reduce the speckle noise. The interval of the scale is $5a^*$ [$a^* = 2/(5^{1/2}a_{\rm r})$, where $a_{\rm r}$ is the edge length of the Penrose pattern shown in Fig. 2].

an AB atom pair in the hexagons in Fig. 2(c). The cluster center is at the midpoint of A and B atomic sites. Then there are two possible orientations for each cluster. We will refer to them as up and down orientations. Note that there are five AB atom-pair directions which are related by fivefold rotations. Their cluster centers are generated by the OD having the same rhombus with ODs 3 and 5, or 4 and 6 at $\mathbf{x}_1 + \Delta\mathbf{x}_1^{\rm e}/2$ or $\mathbf{x}_2 + \Delta\mathbf{x}_2^{\rm e}/2$. The clusters located at these two centers are denoted by $n = 1$ and 2. Then the structure factors of the clusters for the up orientation are $F^1 = f^A\exp(\pi i\mathbf{q}\cdot\Delta\mathbf{x}_1^{\rm e})$ and $F^2 = f^A\exp(\pi i\mathbf{q}\cdot\Delta\mathbf{x}_2^{\rm e})$, while those for the down orientation are F^{1*} and F^{2*}. Denoting the two orientations in cluster 1 by $\mu = 1, 2$ and those of cluster 2 with $\mu = 3, 4$, the diffuse scattering intensity is given as

$$I_{\rm D}(\mathbf{q}) = -\kappa\Big[v_{33}(\mathbf{0})\sum_R |RF^1 - RF^{1*}|^2 g_{11}^{12}(\mathbf{0}) + v_{44}(\mathbf{0})\sum_R |RF^2 - RF^{2*}|^2 g_{22}^{34}(\mathbf{0})\Big]. \qquad (14)$$

This leads to the same total diffuse scattering intensity [the sum of equation (11) and the upper sign part of equation (13); see Appendix B].

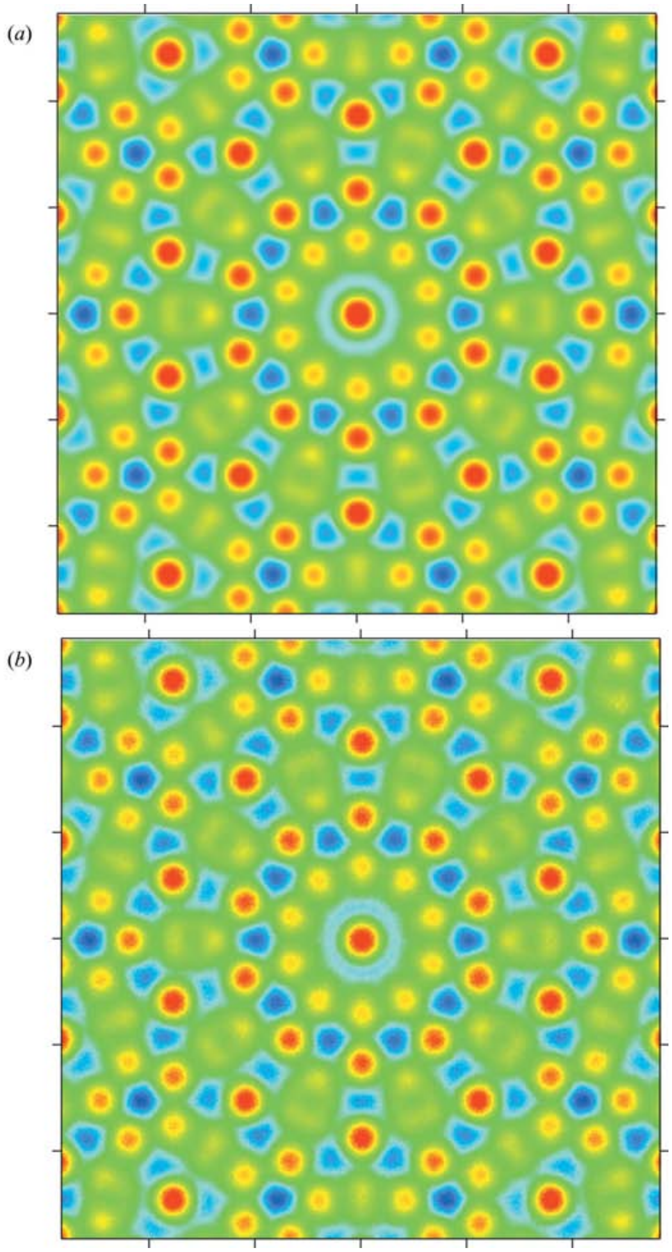

Figure 5
Diffuse scattering intensities of model (II), which are calculated analytically (a) and numerically (b), where the two phason flip sites in Fig. 2(c) are occupied or both empty. The intensity is denoted by the same rainbow colors as in Fig. 4(c). In the numerical calculation, a 1000 ensemble average is taken to reduce the speckle noise. The scale interval is the same as in Fig. 4.

8. Discussion

The scattered intensity of SRO diffuse scattering in crystals is obtained from equation (9) by setting $v_{ijl} = v_{ij}(\Delta\mathbf{x}_{ijl}^{\rm i})$ to 1 for all interatomic vectors $\Delta\mathbf{x}_{ijl}$ in three-dimensional space and Ω_n to the volume of the unit cell of a crystal Ω,

$$I_{\rm D}(\mathbf{q}) = -N\sum_{ijl} a_{ijl}\sum_{\mu>\nu R}|Rf^{\mu} - Rf^{\nu}|^2 \times g_{ijl}^{\mu\nu}\exp(2\pi i\mathbf{q}\cdot R\Delta\mathbf{x}_{ijl}), \qquad (15)$$

where $N = V/\Omega$ is the number of unit cells in a crystal; the superscript e is dropped, since the vector $\mathbf{x}$ indicates a vector in three-dimensional physical space. In this expression, f^{μ} is the atomic scattering factor of the μth atom or the structure factor of the μth cluster (molecule) in the (three-dimensional) unit cell. It is noted that the essential difference between a crystal and a quasicrystal exists in the calculation of the frequency $v_{ij}(\mathbf{x}_{ijl}^{i})$ of atom pairs distant from each other by $\mathbf{x}_{ijl}$. This is given by the overlapped area (volume) of ODs in quasicrystals, while it is always 1 in crystals (except for the multiplicity a_{ijl}).

It can be shown that equation (15) is equivalent to a classic formula for binary crystals with only one atomic site in the unit cell ($m = 2$ and $n = 1$). We drop the indices i and j for simplicity since they are always 1; $g_l^{\mu\nu} \equiv g_{11l}^{\mu\nu}$. In this case, provided that the atom is located at the origin, the above equation becomes

$$I_{\rm D}(\mathbf{q}) = -N\sum_l a_l\sum_R |f^1 - f^2|^2 g_l^{12} \times \exp(2\pi i\mathbf{q}\cdot R\mathbf{x}_l). \qquad (16)$$

The multiplicity $a_l \equiv a(\mathbf{x}_l)$ is determined by the order of the group, which is a subgroup of a point group and leaves the lattice vector $\mathbf{x}_l$ invariant. From the definition, we have $g_l^{12} = \langle z_0^1 z_l^2\rangle - \langle z_0^1\rangle\langle z_l^2\rangle$ in this simple case. For Cu_3Au, $\langle z^1\rangle = \sigma = 3/4$ and $\langle z^2\rangle = \sigma' = 1/4$ provided that the first and second atoms are Cu and Au. When $\langle z_0^1 z_l^2\rangle = \langle z_0^2 z_l^1\rangle = \xi(l)$ we obtain $g_l^{12} = g_l^{21} = -\sigma\sigma' + \xi(l)$. Thus, (16) is expressed by

$$I_{\rm D}(\mathbf{q}) = N\sum_l\sum_R a_l|\Delta f|^2[\sigma\sigma' - \xi(l)] \times \exp(2\pi i\mathbf{q}\cdot R\mathbf{x}_l), \qquad (17)$$

where $\xi(0) = 0$ and $\Delta f = f^1 - f^2$.

The value of $\xi(l)$ is limited within $0 \le \xi(l) \le \sigma'$. When $\xi(l) = \sigma'$, we have $[\sigma\sigma' - \xi(l)] = -\sigma'^2$. In the completely ordered superstructure with body-centered cubic lattice, $\xi(l)$ is 0 or σ' depending on the lattice vector $\mathbf{x}_l$. Then $-g_l^{12} = [\sigma\sigma' - \xi(l)]$ is 3/16 or −1/16. The correlation function g_l^{12} is related to the α parameter by $g_l^{12} = -\sigma\sigma'\alpha_l^{12}$, as mentioned previously, so that these correlation functions correspond to 1 and −1/3 of the α parameters, in agreement with the values shown by Cowley (1950).

A general formula for the orientational disorder in rigid clusters [see (10)] is applicable to the case where clusters with mirror symmetry (*m* clusters) are located in five different orientations at the cluster sites in the S1 phase. Kobas *et al.* (2005) analyzed the diffuse scattering intensity of the S1 phase under the assumption that the five *m* clusters are randomly distributed over their cluster centers. In this special case, (10) is proportional to $\sum_\mu |F^\mu - \langle F\rangle|^2$, where F^μ is the structure factor of the *m* cluster with μth orientation and $\langle F\rangle \equiv (1/10)\sum_{\mu=1}^{10} F^\mu$ is the average structure factor of all the *m* clusters with different orientations (see Appendix *C*). It was shown that such a simple model explains the diffuse scattering intensity distribution qualitatively.

It is known that the S1 phase consists of pentagonal clusters (5*f* clusters) with two different orientations and the b-Ni phase consists of *m* clusters (Yamamoto *et al.*, 2005). Since the b-Ni phase is the high-temperature phase of the S1 phase, it is expected that a part of the 5*f* clusters is transformed into *m* clusters near the transition temperature to the b-Ni phase. Then the probability of 5*f* clusters at each cluster center will not be one in the S1 phase. Therefore, we can expect that the diffuse scattering intensity is also related to the structure factors of the 5*f* clusters. The analysis mentioned above suggests that this contribution is small. If this is negligible, it means that some sites are completely occupied by a 5*f* cluster and others are occupied only by *m* clusters randomly, since five different cluster centers exist in the S1 phase (Yamamoto *et al.*, 2005) and the site completely occupied by a single cluster does not contribute to the diffuse scattering intensity. Thus, the sites occupied by the *m* clusters will be some specific sites, but where such sites are is not known.

It is also known that the b-Ni phase shows broad peaks at the satellite positions in the S1 phase (Abe *et al.*, 2003). This implies that 5*f* clusters exist with non-zero inter-cluster correlation in the b-Ni phase. Therefore, we need to consider a case where the *m* clusters and the 5*f* clusters coexist near the phase-transition temperature in both phases. The present diffuse scattering intensity formula is applicable to such a complicated but more realistic model as mentioned in §6. The model building of such a model is, however, beyond the scope of this paper.

9. Summary and concluding remarks

An analytical expression has been derived for the diffuse scattering intensity owing to the short-range order of atoms or clusters in quasicrystals. The formula is similar to that for conventional crystals except for the factors giving the frequencies of the interatomic (inter-cluster) vectors. In quasicrystals, they are calculated by using the overlapped area (volume) of the occupation domains in their *n*-dimensional description. The diffuse scattering intensity calculation using this formula is demonstrated for phason flip disorder in the Penrose pattern. The validity of the formula was confirmed by comparing it with results from numerical calculations. The derived formula is general and includes symmetry. Therefore, the diffuse scattering intensity of quasicrystals can be calculated efficiently owing to their high symmetries.

APPENDIX *A*
Derivation of a diffuse scattering intensity formula

For simplicity, we consider a fictitious quasicrystal composed of a single atom. Then in the kinematical theory of X-ray scattering, the scattered intensity of X-rays with the scattering vector $\mathbf{q}$ is proportional to (van Hove, 1954)

$$I(\mathbf{q}) = \int_V \mathrm{d}\mathbf{x}^{\rm e} \int_V \mathrm{d}\mathbf{x}'^{\rm e} \left\langle \rho(\mathbf{x}^{\rm e})\rho(\mathbf{x}'^{\rm e})\right\rangle \exp[2\pi i\mathbf{q}\cdot(\mathbf{x}^{\rm e} - \mathbf{x}'^{\rm e})], \qquad (18)$$

where V is the volume of a quasicrystal. The integrals over $\mathbf{x}^{\rm e}$ and $\mathbf{x}'^{\rm e}$ are taken over the volume of the material. In quasicrystals it is known that the atomic structure is given by an *n*-dimensional description, and the three-dimensional structure is obtained from its *n*-dimensional model by taking a three-dimensional intersection (Yamamoto, 1996). The electron density in the *n*-dimensional space is continuously extended within an OD. The position of each atom in the three-dimensional external space is obtained as the intersection of an OD with three-dimensional space, so that electron density in the external space is described by

$$\rho(\mathbf{x}^{\rm e}) = \sum_l \sum_i \rho_i(\mathbf{x}^{\rm e} - \mathbf{x}_{il}^{\rm e}) D_i(-\mathbf{x}_{il}^{\rm i}), \qquad (19)$$

where $\rho_i(\mathbf{x}^{\rm e})$ is the electron density of the *i*th atom located at the origin, and $\mathbf{x}_{il}^{\rm e}$ and $\mathbf{x}_{il}^{\rm i}$ are the external and internal space components of the positional vector of the center of the *i*th OD in the *l*th unit cell of an *n*-dimensional lattice, $\mathbf{x}_i + \mathbf{x}_l$. The function $D_i(\mathbf{x}^{\rm i})$ is the occupation probability and it is one when $\mathbf{x}^{\rm i}$ is within the *i*th OD located at the origin, otherwise it is zero. The index *l* runs over all the lattice points in the *n*-dimensional lattice, while *i* runs over all the ODs in the unit cell. Owing to $D(-\mathbf{x}_{il}^{\rm i})$, only ODs near the three-dimensional external space (hyperplane) give the atom position. Using the above expression, (18) is rewritten as

$$\begin{aligned} I(\mathbf{q}) &= \int_V \mathrm{d}\mathbf{x}^{\rm e} \int_V \mathrm{d}\mathbf{x}'^{\rm e} \sum_{lm} \sum_{ij} \exp[2\pi i\mathbf{q}\cdot(\mathbf{x}^{\rm e} - \mathbf{x}^{\rm e\prime})] \\ &\quad \times \left\langle \rho_i(\mathbf{x}^{\rm e} - \mathbf{x}_{il}^{\rm e})\rho_i(\mathbf{x}'^{\rm e} - \mathbf{x}_{jm}^{\rm e})\right\rangle D_i(-\mathbf{x}_{il}^{\rm i}) D_j(-\mathbf{x}_{jm}^{\rm i}) \\ &= \sum_{lm} \sum_{ij} \langle f_i f_j^*\rangle D_i(-\mathbf{x}_{il}^{\rm i}) D_j(-\mathbf{x}_{jm}^{\rm i}) \exp(2\pi i\mathbf{q}\cdot\Delta\mathbf{x}_{iljm}^{\rm e}), \end{aligned} \qquad (20)$$

where $f_i \equiv f_i(\mathbf{q}) = \int_V \mathrm{d}\mathbf{x}^{\rm e} \exp(2\pi i\mathbf{q}\cdot\mathbf{x}^{\rm e})\rho(\mathbf{x}^{\rm e})$ is the atomic scattering factor of atoms which occupy the *i*th OD in the unit cell of the *n*-dimensional lattice, while $\Delta\mathbf{x}_{iljm}^{\rm e} = \mathbf{x}_{il}^{\rm e} - \mathbf{x}_{jm}^{\rm e}$. (We assume that $\langle f_i\rangle$ is independent of *l*.) This expression includes the Bragg intensity in addition to the diffuse scattering intensity. The former and the latter are from the first and second terms of $\langle f_i f_j^*\rangle = \langle f_i\rangle\langle f_j^*\rangle + \langle\Delta f_i \Delta f_j^*\rangle$, where $\Delta f_i =$

$f_i - \langle f_i \rangle$ and $\Delta f_j = f_j - \langle f_j \rangle$. The Bragg intensity, $I_{\rm B}(\mathbf{q})$, is given by

$$I_{\rm B}(\mathbf{q}) = \left| \sum_{li} \langle f_i \rangle D_i(-\mathbf{x}^{\rm i}_{il}) \exp(2\pi i \mathbf{q} \cdot \mathbf{x}^{\rm e}_{il}) \right|^2. \tag{21}$$

Using $D_i(\mathbf{x}^{\rm i}_{il}) = \int {\rm d}\mathbf{q}^{\rm i}\, D_i(\mathbf{q}^{\rm i}) \exp(-2\pi i \mathbf{q}^{\rm i} \cdot \mathbf{x}^{\rm i}_{il})$ [or $D_i(\mathbf{q}^{\rm i}) = (2\pi)^{-d/2} \int {\rm d}\mathbf{x}^{\rm i}\, D_i(\mathbf{x}^{\rm i}) \exp(2\pi i \mathbf{q}^{\rm i} \cdot \mathbf{x}^{\rm i}_{il})$ $(d = n - 3)$], this is rewritten as

$$I_{\rm B}(\mathbf{q}) = \left| \int {\rm d}\mathbf{q}^{\rm i}\, L(\mathbf{q}_n) F(\mathbf{q}_n) \right|^2, \tag{22}$$

where $L(\mathbf{q}_n) = \sum_l \exp(2\pi i \mathbf{q}_n \cdot \mathbf{x}_l)$ is the periodic delta function (the Laue function) in n-dimensional space and $F(\mathbf{q}_n)$ is the structure factor. The latter is given by

$$F(\mathbf{q}_n) = \sum_i \langle f_i \rangle D_i(\mathbf{q}^{\rm i}) \exp(2\pi i \mathbf{q}_n \cdot \mathbf{x}_i) \tag{23}$$

with the n-dimensional vectors $\mathbf{q}_n = \mathbf{q} + \mathbf{q}^{\rm i}$ and $\mathbf{x}_i = \mathbf{x}^{\rm e}_i + \mathbf{x}^{\rm i}_i$. Equation (22) implies that the Bragg intensity can be obtained by the projection of the structure factor in n-dimensional space onto the external space.

On the other hand, the diffuse scattering intensity is given by

$$\begin{aligned} I_{\rm D}(\mathbf{q}) &= \sum_{lm} \sum_{ij} \langle \Delta f_{il} \Delta f^*_{jm} \rangle D_i(-\mathbf{x}^{\rm i}_{jm}) D_j(-\mathbf{x}^{\rm i}_{il}) \\ &\quad \times \exp(2\pi i \mathbf{q} \cdot \Delta\mathbf{x}^{\rm e}_{iljm}) \\ &= \frac{V}{\Omega_n} \sum_l \sum_{ij} \langle \Delta f_{i0} \Delta f^*_{jl} \rangle v_{ij}(\Delta\mathbf{x}^{\rm i}_{ijl}) \\ &\quad \times \exp(2\pi i \mathbf{q} \cdot \Delta\mathbf{x}^{\rm e}_{ijl}), \end{aligned} \tag{24}$$

where Ω_n is the volume of the unit cell of the n-dimensional lattice, while $v_{ij}(\Delta\mathbf{x}^{\rm i}_{ijl})$ is the overlapped areas (volume) of the ith and jth ODs located at $\mathbf{x}_{i0}$ and $\mathbf{x}_{jl}$. In a higher-dimensional model a large OD is subdivided into several smaller ones, so that each small OD gives a similar local atom environment. Provided that all the large ODs are subdivided into such small ODs, $\langle \Delta f_{i0} \Delta f^*_{jl} \rangle$ is almost independent of the lattice vector l.

When the ith and jth sites are occupied by m different atom species, f_i and f_j are replaced by f^μ_i and f^ν_i in the above equation and the summation with respect to ij is replaced by that of $ij\mu\nu$. Thus, equation (3) is obtained.

APPENDIX *B*
Phason flips and cluster disorder

In case of the phason flip in the PP we can use a fictitious cluster consisting of one atom with the structure factor $F^{\rm i} = f^A \exp(2\pi \mathbf{q} \cdot R\Delta\mathbf{x}^{\rm e}_i/2)$, as described in the text, so that $RF^{\rm i} - RF^{{\rm i}*} = 2f^A \sin(2\pi \mathbf{q} \cdot R\Delta\mathbf{x}^{\rm e}_i/2)$. This leads to $|RF^{\rm i} - RF^{{\rm i}*}|^2 = (2|f^A|^2)[1 - \cos(2\pi \mathbf{q} \cdot R\Delta\mathbf{x}^{\rm e}_i)]$. On the other hand, from the overlapped area of the ODs we have $(1/5)v_{33}(\mathbf{0}) = v_{35'}(\Delta\mathbf{x}^{\rm i}_1)$, $(1/5)v_{44}(\mathbf{0}) = v_{46'}(\Delta\mathbf{x}^{\rm i}_2)$, $v_{44}(\mathbf{0}) = \tau^2 v_{33}(\mathbf{0})$, $g^{12}_{35'}(\mathbf{0}) = g^{12}_{46'}(\mathbf{0}) = -1/4$. Therefore, equation (14) is equal to the sum of (11) and the upper sign part of (13).

APPENDIX *C*
Diffuse scattering intensity for clusters with no inter-cluster correlations

We consider a case where a cluster has m different orientations and there is no correlation between clusters located at different sites. Then the non-zero correlation function components are only $g^{\mu\mu}(\mathbf{0}) = (\langle z^\mu \rangle - 1)/\langle z^\mu \rangle^2$ and $g^{\mu\nu}(\mathbf{0}) = -\langle z^\mu \rangle \langle z^\nu \rangle$ $(\nu \neq \nu)$. In such a simple case, equation (10) is reduced (except for the scale factor) to

$$\begin{aligned} &\sum_{\mu > \nu} |F^\mu - F^\nu|^2 \langle z^\mu \rangle \langle z^\nu \rangle \\ &= \frac{1}{2} \sum_{\mu,\nu} |F^\mu - F^\nu|^2 \langle z^\mu \rangle \langle z^\nu \rangle \\ &= \frac{1}{2} \sum_{\mu,\nu} \left[|F^\mu|^2 - 2Re(F^\mu F^{\nu*}) + |F^\nu|^2 \right] \\ &\quad \times \langle z^\mu \rangle \langle z^\nu \rangle \\ &= \sum_\mu \left[|F^\mu|^2 - |\langle F \rangle|^2 \right] \langle z^\mu \rangle, \end{aligned} \tag{25}$$

where $\langle F \rangle = \sum_\mu F^\mu \langle z^\mu \rangle$. (Note that $\langle F \rangle$ does not depend on μ, so that $\sum_\mu \langle F \rangle \langle z^\mu \rangle = \langle F \rangle$ since $\sum_\mu \langle z^\mu \rangle = 1$.) This is equal to the average of the squared deviation of the structure factor of the μth orientation from the average structure factor,

$$\sum_\mu |F^\mu - \langle F \rangle|^2 \langle z^\mu \rangle, \tag{26}$$

since this gives

$$\begin{aligned} &\sum_\mu \left[|F^\mu|^2 - 2ReF^\mu \langle F^* \rangle + |\langle F \rangle|^2 \right] \\ &\quad \times \langle z^\mu \rangle, \end{aligned} \tag{27}$$

and (27) is equal to (25). (Note that $Re \sum_\mu F^\mu \langle z^\mu \rangle \langle F^* \rangle = |\langle F \rangle|^2$.) Equation (26) ensures the non-negativity of the diffuse scattering intensity and it is reduced to the formula used by Kobas *et al.* (2005) when $\langle z^\mu \rangle = (1/m)$.

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