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Random stacking model applied to tetrahedrally bonded amorphous semiconductors: The scattering intensity*

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In this work we present the results of a careful analysis of a random stacking, or stacking fault, model for tetrahedrally bonded amorphous semiconductors. In this model due originally to Wilson, the structure is characterized by the probability of faulting α $(0 \leq \alpha \leq 1)$ when close-packed pairs of planes (double layers) are stacked in the direction perpendicular to the planes: adjacent planes are relatively displaced, occupying positions A or B or C; complete randomness is achieved for $\alpha = 1/2$, and a wurtzite or diamond structure for $\alpha = 0$ or 1, respectively. We modified Wilson's earlier results by taking the limit of an infinite stacking sequence and by separating discrete and continuous parts of the scattering: this facilitates the analytical and numerical application of the model for structures with arbitrary fault probability α. In the course of our analysis we carefully examined some other recent and more restricted treatments of the random stacking model. We find that the "invariant vectors" whose existence was pointed out by Betteridge are a consequence only of the relative displacement of adjacent planes and of the maintenance of any fixed interlayer spacing and do not result from the existence of perfect tetrahedral bonds as Betteridge and Heine asserted. Perfect tetrahedral bonding occurs for only one particular ratio of interplane spacing to in-plane spacing: $c/a = \sqrt{2/3}$. Hodges' assertion that the scattering from a completely random stacking structure $(\alpha = 1/2)$ is closer to wurtzite scattering is irrelevant because of his omission of one of the two equivalent three layer sequences from consideration: when both sequences are included the asserted connection disappears. We also give some preliminary results of a numerical calculation of the scattering intensity for various fault probabilities.

I. INTRODUCTION

The present investigation was originally motivated by some work on a random stacking model[1-4] of a tetrahedrally bonded amorphous semiconductor. The model system is described as a close-packed structure which is constructed by randomly stacking close-packed two-dimensionally perfect layers of unit cells in three different relative positions. Each unit cell contains two atoms in the direction of stacking, perpendicular to the planes. As a result, bonds in adjacent layers are in either diamondlike (staggered) or wurtzitelike (eclipsed) configurations while maintaining perfect lattice spacing and perfect tetrahedral bonding. Although this is a newly proposed structural model for amorphous group-IV semiconductors (Si, Ge) and some other tetrahedrally coordinated III-V semiconductors (such as GaP, GaAs, GaSb, etc.), the problem of stacking faults in close-packed structures has a long history[5-10] of hexagonal cobalt, SiC, etc. Theories developed for the latter problem of stacking faults are expected to be useful for treating the former problem of a structural model for those amorphous semiconductors if suitably modified. This attempt to apply the methods of the latter problem to the study of the former problem is the main theme of the present paper. To be more precise, the purpose of the present paper is twofold. First, we briefly review earlier work of Wilson on the x-ray scattering intensity of materials with stacking faults, rewrite Wilson's result in a simplified form and analyze some characteristic features of the result. This analysis itself is interesting and significant in its own right. Second, we apply Wilson's theory to the study of a structural model for tetrahedrally bonded amorphous semiconductors and give some discussion of the properties of the model.

In the course of this, we examine the origin of the "invariant vectors" which were first pointed out by Betteridge.[1] We find that these vectors are correlated with maintaining fixed interplanar spacing and the existence of only two possible relative displacements of adjacent two dimensionally perfect layers rather than with perfect tetrahedral coordination as suggested by Betteridge and Heine.[2, 3]

In order to explain the x-ray scattering intensity of hexagonal cobalt, Wilson[5] developed a formalism which was applied to close-packed structures made by piling up close-packed planes of atoms in three different relative positions. For treating the effects of stacking faults, Wilson introduced the probability α of each added plane being a fault in a structure which should otherwise be proper hexagonal. The system with $\alpha = 0$ corresponds to a hexagonal close-packed structure, while one with $\alpha = 1$ to a cubic close-packed structure (fcc). His formalism covers the whole range of values of

α, i.e., $0 \leq \alpha \leq 1$. In Sec. II, we review his formalism. In Sec. III, we modify his result and evaluate a simplified form for an infinite system. We also discuss the behavior of the obtained structure intensity in the limit of $\alpha = 0$ and $\alpha = 1$ as well as for the specific value of $\alpha = \frac{1}{2}$ which corresponds to a completely random stacking sequence.

Armed with the formalism as described above, we then turn to the second point of our theme concerning tetrahedrally bonded amorphous semiconductors. It seems to be appropriate at this stage to give a picture of the present situation of research in the field of these fourfold coordinated amorphous semiconductors. The radial distribution function (RDF) as obtained from experimental data of the structure factor indicates that all near-neighbor coordinates are very similar to that of the perfect tetrahedrally bonded diamond structure crystal.[11] Since improvements of experimental techniques producing more information on the structure are in the future, recent progress in this field has to a great extent depended on new approaches in modeling. Structural models proposed so far may be classified into three categories: i.e.; (i) the microcrystal or cluster approach[12,13]; (ii) the perturbed crystal approach; and (iii) the continuous network approach. In the first approach, the amorphous solid is assumed to consist of crystallites of one or a mixture of the real or hypothetical polymorphs of the same element or compound. In the second approach, the amorphous material is treated as a heavily distorted crystal containing a large number of structural defects such as mono- and divacancies. In the third approach, the amorphous and semiconductor is supposed to consist of an infinite nonperiodic three-dimensional array of interlinked atoms in which the perfect tetrahedral bonding around each atom is retained, but fluctuations of about 10% or 15% in bond angles and bond lengths are allowed.

Each approach has merits and drawbacks. The microcrystal approach can take full advantage of knowledge and methods provided by traditional crystallography. Accordingly, the formalisms are well known and enable us to make various trial and error attempts. Shortcomings are that unrealistic crystallites or clusters have to be included to achieve acceptable fits between model and experiment, and that the random orientation of the crystallites causes high-angle boundaries which yield much higher volume fraction of void-rich disordered regions than expected. Some of the perturbed crystal models are comparatively easy to treat because several methods developed for substitutionally disordered systems are applicable to these models *mutatis mutandis*. The models, however, have been criticized as lacking firm physical grounding. The random network models are considered to simulate real systems fairly well in the sense that short-range order is satisfied throughout the material. In addition, there have been reports that quantitative agreement has been obtained between model and experiment concerning some physical properties such as the RDF. A difficulty lies in the construction of a continuous network which is big enough to be free from size effects. Another difficulty is that, even if such a network is constructed, a powerful standard method to treat a big network has not yet been established.

In this way, approaches in modeling are still tentative, and accordingly, improvements in models are topics of great interest. A random stacking model proposed by Betteridge[1] is an attempt towards this goal. This model has the merits of some of the above described models. Namely, for this model, the background provided by traditional crystallography can be used. Moreover, the idealized, chemically satisfied short-range order is guaranteed around each atom.

The random stacking model is thought to be most appropriate in application to carefully prepared amorphous films which have been evaporated slowly onto warmed substrates. More ideal, voidless films are expected to form using a recently developed technique using a glow discharge decomposition. Thus, physically speaking, we have good grounds for believing that the random stacking model serves as the best approach to these nearly ideal films, although a fair judgement on this point must be delayed until more experimental information regarding ideal films is obtained and more detailed and comprehensive investigation of the model is accomplished.

In the present paper, we are going to discuss the scattering intensity of this model of a random stacking sequence, while in the succeeding papers we intend to treat some other properties such as the electronic density of states, etc. It is important to note that the study of the scattering intensity or the structure factor alone is not enough to judge the validity of a model. This is because the structure factor or the RDF does not define the structure uniquely.

In Sec. IV, we examine Hodge's example[4] of a completely random case, and we comment on one of his conclusions. In Sec. V, we give further analysis of invariant vectors discussed by Betteridge and Heine.[1,2] Section VI is devoted to discussion.

II. WILSON'S FORMALISM

The basic idea of Wilson's formalism is to carry out a calculation of the structure intensity of a random stacking structure in two stages. The first stage introduces a perfect mathematical lattice. The second stage introduces the structure factor as a random variable. The average value of this random variable can be obtained by determining the probability distribution of this variable, which is the needed weight function.

First, a perfect mathematical lattice is introduced with lattice points located at positions

$$\vec{r}_j = j_1\vec{a}_1 + j_2\vec{a}_2 + j_3\vec{a}_3\,, \tag{2.1}$$

where j_1, j_2, j_3 are integers and $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are primitive translation vectors.

The structure factor for this lattice is defined by

$$S(\vec{s}) = \sum_j F_j(\vec{s}) \exp(-i\vec{s}\cdot\vec{r}_j) \tag{2.2}$$

as a function of s, with $s\equiv|\vec{s}|=4\pi\sin\theta/\lambda$, θ being a scattering angle, and λ the wavelength. The vector $\vec{s}$ is parallel to $\vec{k}'-\vec{k}$, where $\vec{k}$ and $\vec{k}'$ are, respectively, the wave vectors of the incident and scattered waves. The structure factor $F_j(\vec{s})$ of the unit cell located at $\vec{r}_j$ is given by

$$F_j(\vec{s}) = \sum_g f_{gj}(\vec{s}) \exp(-i\vec{s}\cdot\vec{u}_{gj})\,, \tag{2.3}$$

in which $f_{gj}(\vec{s})$ and $\vec{u}_{gj}$ are the form factor and the position vector of the gth atom in the jth unit cell, respectively. The scattering intensity is

$$I(\vec{s}) \equiv |S(\vec{s})|^2 = \sum_{ij} F_i^* F_j \exp(-i\vec{s}\cdot\vec{r}_{ij})\,, \tag{2.4}$$

$\vec{r}_{ij}$ being $\vec{r}_j-\vec{r}_i$.

If we put $i_1=j_1+m_1$, $i_2=j_2+m_2$, $i_3=j_3+m_3$, then Eq. (2.3) is rewritten as

$$I(\vec{s}) = \sum_m \left(\sum_j F^*_{j+m} F_j \right) \exp(i\vec{s}\cdot\vec{r}_m)\,. \tag{2.5}$$

In a structure with a perfect space group $F_j\equiv F_{j+m}$ and, therefore, $\sum_j F^*_{j+m}F_j$ would become

$$(n_1-|m_1|)(n_2-|m_2|)(n_3-|m_3|)|F|^2\,, \tag{2.6}$$

where n_1, n_2, n_3 are the numbers of unit cells in the crystal in the direction of the respective axes.

Second, a type of compositional disorder is introduced in this lattice. In a structure where F_j is a random variable, F_j and F_{j+m} are not necessarily equal, and the problem of calculating the scattering intensity becomes that of finding the average value of $F^*_{j+m}F_j$. Let $\langle F^*_{j+m}F_j\rangle\equiv J_m$. Then the scattering intensity is

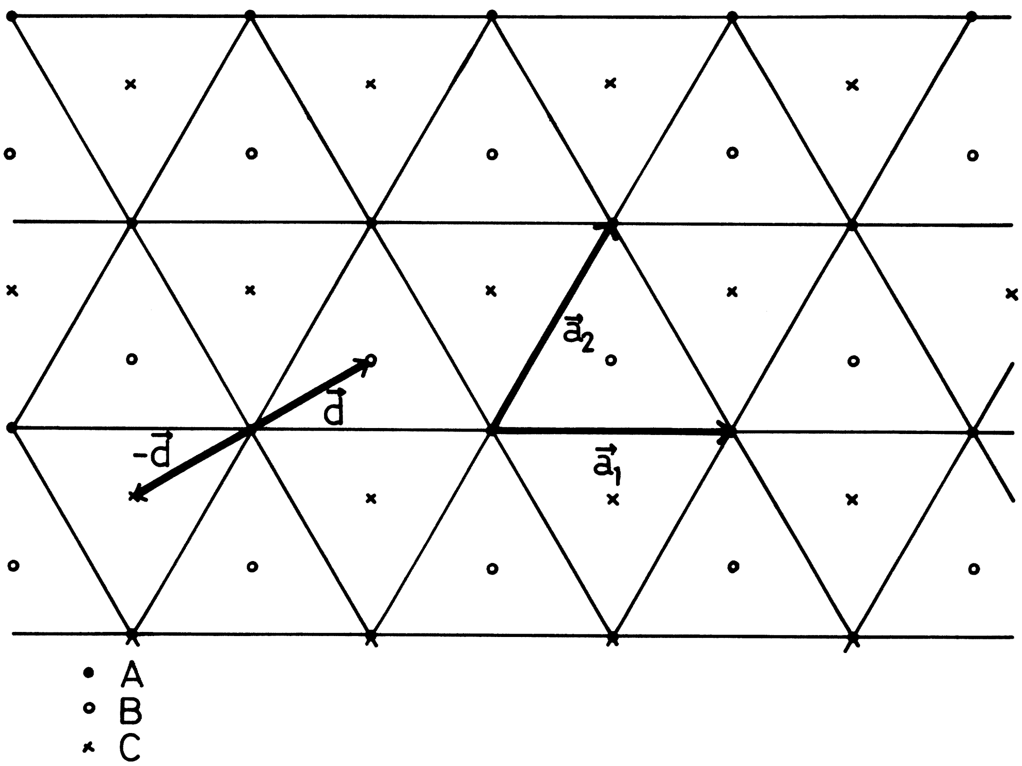


FIG. 1. Vectors $\vec{a}_1$ and $\vec{a}_2$ are primitive translation vectors in the close-packed plane chosen to include an angle $\frac{1}{3}\pi$. In a plane of type A, atoms occupy lattice sites of a triangular lattice indicated by small circles. In a plane of type B, atoms occupy sites denoted by crosses while in a plane of type C, atoms occupy sites denoted by triangles.

$$I(\vec{s})=\sum_m J_m(n_1-|m_1|)(n_2-|m_2|)\times(n_2-|m_3|)\exp(i\vec{s}\cdot\vec{r}_m)\,. \tag{2.7}$$

Now we consider a random stacking sequence which is made by piling up close-packed planes of unit cells in three different relative positions A, B, and C as shown in Fig. 1. The vectors $\vec{a}_1$ and $\vec{a}_2$ are primitive translation vectors in the close-packed plane chosen to include an angle of $\frac{1}{3}\pi$, and $|\vec{a}_1|=|\vec{a}_2|$. The vector $\vec{a}_3$ is parallel to the stacking direction with magnitude equal to a constant interplanar distance. Adjacent planes are displaced relative to each other by $\vec{d}=\frac{1}{3}(\vec{a}_1+\vec{a}_2)$ or $-\vec{d}$. The possible values of F_j are expressed as $F_X=\exp(-i\vec{s}\cdot\vec{d}\,\xi_X)f(\vec{s})$, where $\xi_X=0, 1$ or -1, according as $X=A$, B, or C respectively. The factor $f(\vec{s})$ is 1 when each unit cell contains one atom only as is the case for hexagonal cobalt. When this arrangement of planes is used as a model of a tetrahedrally bonded amorphous semiconductor, a basis has two atoms at $\pm\frac{3}{8}\vec{a}_3$ about each site and we have

$$f(\vec{s})=\tfrac{1}{2}[\exp(\tfrac{3}{8}i\vec{s}\cdot\vec{a}_3)+\exp(-\tfrac{3}{8}i\vec{s}\cdot\vec{a}_3)]=\cos(\tfrac{3}{8}\vec{s}\cdot\vec{a}_3)\,. \tag{2.8}$$

Now let us return to Eq. (2.2) in which $\vec{u}_{\vec{\ell}j}$ should be now regarded as a random variable, determined by which of the three possible positions A, B, or C, an atom or set of atoms, occupies in the plane. The latter are found following Wilson, who evaluated the probability P_m of the $(j+m)$th plane being like the jth. The structure is proper hexagonal if there are no faults at all, but because of occasional faults, the stacking sequence is disordered. Suppose that the chance of there being a fault at the $(j+m)$th plane is α. Then we have the probability of the $(j+m)$th being like the $(j+m-1)$th is 0; the probability of the $(j+m)$th being like the $(j+m-2)$th is $1-\alpha$; the probability of the $(j+m)$th being neither is α; so that

$$P_m=P_{m-1}\times 0+P_{m-2}(1-\alpha)+(1-P_{m-1}-P_{m-2})\alpha$$

or

$$P_m+\alpha P_{m-1}-(1-2\alpha)P_{m-2}=\alpha\,. \tag{2.9}$$

The solution of this equation is

$$P_m=\tfrac{1}{3}+Q_e\rho_e^m+Q_0\rho_0^m\,, \tag{2.10}$$

where

$$\rho_e=\tfrac{1}{2}(-\alpha+D^{1/2})\,, \tag{2.11a}$$

$$\rho_0=-\tfrac{1}{2}(\alpha+D^{1/2})\,, \tag{2.11b}$$

with $D=4-8\alpha+\alpha^2$, and Q_e and Q_0 are arbitrary constants. They must be chosen so that $P_0=1$ and $P_1=0$, and it is easy to obtain

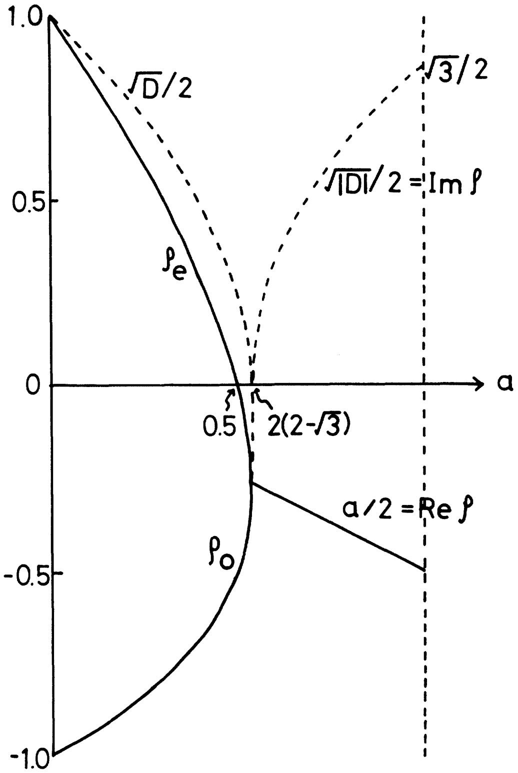


FIG. 2. ρ_e and ρ_0 as a function of α.

$$Q_e=\tfrac{1}{3}[1-(1-\alpha)/D^{1/2}]\,, \tag{2.12a}$$

$$Q_0=\tfrac{1}{3}[1+(1-\alpha)/D^{1/2}]\,. \tag{2.12b}$$

Equation (2.10) has been derived for m positive. It is clear however that the chance of the $(j+m)$th being like the jth must be the same as the chance of the jth being like the $(j+m)$th: i.e., $P_{-m}=P_m$. The values ρ_e and ρ_0 as functions of α are shown in Fig. 2. Since $|\rho_e|<1$, and $|\rho_0|<1$, except for cases where $\alpha=1$ and $\alpha=0$, then $P_m\to\frac{1}{3}$ when $m\to\infty$.

Using P_m, one can calculate J_m as

$$\begin{aligned}J_m&\equiv\langle F^*_{j+m}F_j\rangle\\&=[P_mF_A^*+(1-P_m)(F_B^*+F_C^*)/2]\tfrac{1}{3}F_A\\&\quad+[P_mF_B^*+(1-P_m)(F_C^*+F_A^*)/2]\tfrac{1}{3}F_B\\&\quad+[P_mF_C^*+(1-P_m)(F_A^*+F_B^*)/2]\tfrac{1}{3}F_C\\&=[P_m+(1-P_m)K]\,|f(\vec{s})|^2\\&\quad+[\tfrac{1}{3}(1+2K)+(1-K)(Q_e\rho_e^m+Q_0\rho_0^m)]|f(\vec{s})|^2\,,\end{aligned} \tag{2.13}$$

where

$$\begin{aligned}K&=\tfrac{1}{6}[(F_B^*+F_C^*)F_A+(F_C^*+F_A^*)F_B+(F_A^*+F_B^*)F_C]\\&=\tfrac{1}{3}[\cos(2\vec{s}\cdot\vec{d})+2\cos(\vec{s}\cdot\vec{d})]\,.\end{aligned} \tag{2.14}$$

Substituting Eq. (2.13) in Eq. (2.7), Wilson obtained

$$I(\vec{s}) = \frac{\sin^2(\frac{1}{2}n_1\vec{a}_1\cdot\vec{s})}{\sin^2(\frac{1}{2}\vec{a}_1\cdot\vec{s})}\,\frac{\sin^2(\frac{1}{2}n_2\vec{a}_2\cdot\vec{s})}{\sin^2(\frac{1}{2}\vec{a}_2\cdot\vec{s})}\,I_3(\vec{s})\,, \tag{2.15}$$

with

$$I_3(\vec{s}) = \left(\frac{1+2K}{3}\,\frac{\sin^2(\frac{1}{2}n_3\vec{a}_3\cdot\vec{s})}{\sin^2(\frac{1}{2}\vec{a}\cdot\vec{s})} + (1-K)(Q_e I_e + Q_0 I_0)\right)|f(\vec{s})|^2\,, \tag{2.16}$$

where

$$I_x = \frac{n_3(1-\rho_x^2)}{1-2\rho_x\cos(\vec{s}\cdot\vec{a}_3)+\rho_x^2} + \frac{2\{2\rho_x^2-\rho_x(1+\rho_x^2)\cos(\vec{s}\cdot\vec{a}_3)+\rho_x^{n_3+1}\cos[(n_3+1)\vec{s}\cdot\vec{a}_3]-2\rho_x^{n_3+2}\cos(n_3\vec{s}\cdot\vec{a}_3)+\rho_x^{n_3+3}\cos[(n_3-1)\vec{s}\cdot\vec{a}_3]\}}{[1-2\rho_x\cos(\vec{s}\cdot\vec{a}_3)+\rho_x^2]^2}\,, \tag{2.17}$$

x being either e or 0 in Eq. (2.17).

III. MODIFICATION OF WILSON'S FORMALISM

The purpose of this section is to rewrite the scattering intensity (2.16) for the third axis in a more compact form when the system is infinite. To begin with, it is easy to see that when n_1 and n_2 become infinite, those factors in Eq. (2.15) that concern the first and second axis reduce to sums of sequences of δ functions at $\frac{1}{2}\vec{a}_1\cdot\vec{s}=h\pi$, and $\frac{1}{2}\vec{a}_2\cdot\vec{s}=k\pi$, where h and k are integers. Then it follows directly that K defined by Eq. (2.14) becomes

$$K = \cos[\tfrac{2}{3}\pi(h+k)] = \begin{cases} 1, & h+k=0 \pmod 3), \\ -\frac{1}{2}, & h+k\neq 0 \pmod 3). \end{cases} \tag{3.1}$$

This yields the result that, when $h+k=0$ (mod 3), we have $\frac{1}{3}(1+2K)=1$, and $1-K=0$, while, for $h+k\neq 0$ (mod 3), $\frac{1}{3}(1+2K)=0$, and $1-K=\frac{3}{2}$. This indicates that the first term of Eq. (2.16) is nonvanishing only when $h+k=0$ (mod 3), while the second term differs from zero only when $h+k\neq 0$ (mod 3).

When n_3 approaches infinity, the first term of Eq. (2.16) turns out to be a sum of δ functions at $\frac{1}{2}\vec{a}_3\cdot\vec{s}=l\pi$ with l being an integer. On the other hand, the second term of Eq. (2.16) is a continuous function of $\vec{s}\cdot\vec{a}_3\equiv\eta$. The behavior of this term is given by Eq. (2.17), from which it is readily seen that the first term I_x increases proportionally to n_3 in the limit of n_3 infinite while the second term of I_x is at most of the order of magnitude 1, when α is neither 0 nor 1. Therefore, it is appropriate to define the continuous part of $I_3(\vec{s})$ by

$$\lim_{n_3\to\infty} n_3^{-1}\,\tfrac{3}{2}(Q_e I_e + Q_0 I_0)|f(\vec{s})|^2\,.$$

Combining the above arguments, we obtain the following expression for $I(\vec{s})$ of an infinite system:

$$I(\vec{s}) = \sum_{h,\,k;\,\text{integer}} \delta_{\vec{s}\cdot\vec{a}_1/2-h\pi,0}\,\delta_{\vec{s}\cdot\vec{a}_2/2-k\pi,0}\,\mathcal{I}_3(\vec{s};h,k)\,, \tag{3.2}$$

where $\mathcal{I}_3(\vec{s};h,k)$ has both a discrete part and a continuous part. The discrete part is written

$$\mathcal{I}_3^D(\vec{s};h+k=0(\text{mod }3)) = \sum_{l;\,\text{integer}} \delta_{\vec{s}\cdot\vec{a}_3/2-l\pi,0}|f(\vec{s})|^2\,, \tag{3.3}$$

where the δ functions are expressed in arbitrary normalization. The continuous part is described as

$$\mathcal{I}_3^C(\vec{s};h+k\neq 0(\text{mod }3)) = \lim_{n_3\to\infty}\frac{1}{n_3}\,\frac{3}{2}\,(Q_e I_e + Q_0 I_0)|f(\vec{s})|^2 \tag{3.4}$$

which is cast in a more compact form as

$$\mathcal{I}_3^C(\vec{s};h+k\neq 0(\text{mod }3)) = \frac{3\alpha(1-\alpha)}{\frac{1}{4}(5\alpha^2-8\alpha+4)+\alpha^2\cos\eta+(2\alpha-1)\cos^2\eta}\,. \tag{3.5}$$

Before we discuss the behavior of $\mathcal{I}_3^C$, it is useful for later reference to touch upon the scattering intensities of perfect fcc (or diamond) and hexagonal (or wurtzitelike) structures. Whether we are referring to fcc or diamond will be clear in the context from the use of a cell structure factor containing one or two atoms, respectively. This is also the case in deciding whether we are discussing a hexagonal or a wurtzitelike structure. For an infinite fcc (or diamond) crystal based on the sequence *ABC*, we have

$$I^{ABC}(\vec{s}) = \sum_{h+k+l'=0\,(\mathrm{mod}\ 3)} \delta_{\vec{s}\cdot\vec{a}_1/2-h\pi,\,0}\,\delta_{\vec{s}\cdot\vec{a}_2/2-k,\,0} \times \delta_{3\vec{s}\cdot\vec{a}_3/2-l'\pi,\,0}\,|f(\vec{s})|^2\,, \tag{3.6a}$$

while for the repeat *ACB* we have

$$I^{ACB}(\vec{s}) = \sum_{h+k-l'=0\,(\mathrm{mod}\ 3)} \delta_{\vec{s}\cdot\vec{a}_1/2-h\pi,\,0}\,\delta_{\vec{s}\cdot\vec{a}_2/2-k\pi,\,0} \times \delta_{3\vec{s}\cdot\vec{a}_3/2-l'\pi,\,0}\,|f(\vec{s})|^2. \tag{3.6b}$$

Now it is easy to see that

$$I^{ABC}(s) = I^{ACB}(-s)\,. \tag{3.6c}$$

Generally, the quantity of physical interest, especially in connection with x-ray experiments, is the scattering intensity as a function of $s = |\vec{s}|$. A theoretical value for this quantity is obtained by taking the average over angles of $I(\vec{s})$ with vector $\vec{s}$ satisfying $|\vec{s}| = s$. Therefore, both Eqs. (3.6a) and (3.6b) yield the same mean value and it does not matter whether we take *ABC* or *ACB*. For later convenience, it is useful to rearrange Eqs. (3.6a) and (3.6b) in the following way:

$$I^{ABC}(\vec{s}) = \sum_{h+k=0\,(\mathrm{mod}\ 3)}\ \sum_{l'=0\,(\mathrm{mod}\ 3)} W^f(\vec{s}) + \sum_{h+k=1\,(\mathrm{mod}\ 3)}\ \sum_{l'=-1\,(\mathrm{mod}\ 3)} W^f(\vec{s}) + \sum_{h+k=-1\,(\mathrm{mod}\ 3)}\ \sum_{l'=1\,(\mathrm{mod}\ 3)} W^f(\vec{s})\,, \tag{3.7a}$$

$$I^{ACB}(\vec{s}) = \sum_{h+k=0\,(\mathrm{mod}\ 3)}\ \sum_{l'=0\,(\mathrm{mod}\ 3)} W^f(\vec{s}) + \sum_{h+k=1\,(\mathrm{mod}\ 3)}\ \sum_{l'=1\,(\mathrm{mod}\ 3)} W^f(\vec{s}) + \sum_{h+k=-1\,(\mathrm{mod}\ 3)}\ \sum_{l'=-1\,(\mathrm{mod}\ 3)} W^f(\vec{s})\,, \tag{3.7b}$$

where

$$W^f(\vec{s}) = \delta_{\vec{s}\cdot\vec{a}_1/2-h\pi,\,0}\,\delta_{\vec{s}\cdot\vec{a}_2/2-k\pi,\,0}\,\delta_{3\vec{s}\cdot\vec{a}_3/2-l'\pi,\,0}\,|f(\vec{s})|^2\,. \tag{3.8}$$

The scattering intensity of a hexagonal (or wurtzitelike) structure (repeat sequence *AB*) is described as

$$I^{AB}(\vec{s}) = \sum_{h+k=0\,(\mathrm{mod}\ 3)}\ \sum_{l'';\ \mathrm{even}} W^h(\vec{s}) + \sum_{h+k\neq 0\,(\mathrm{mod}\ 3)} \left(\frac{1}{4}\sum_{l'';\ \mathrm{even}} W^h(\vec{s}) + \frac{3}{4}\sum_{l'';\ \mathrm{odd}} W^h(\vec{s})\right) \tag{3.9}$$

where

$$W^h(\vec{s}) = \delta_{\vec{s}\cdot\vec{a}_1/2-h\pi,\,0}\,\delta_{\vec{s}\cdot\vec{a}_2/2-k\pi,\,0}\,\delta_{\vec{s}\cdot\vec{a}_3-l''\pi\,0}\,|f(\vec{s})|^2\,. \tag{3.10}$$

All possible repeat sequences such as (*BCBC*... and *ACAC*) for this structure give the same expression for the scattering intensity as given in Eq. (3.10).

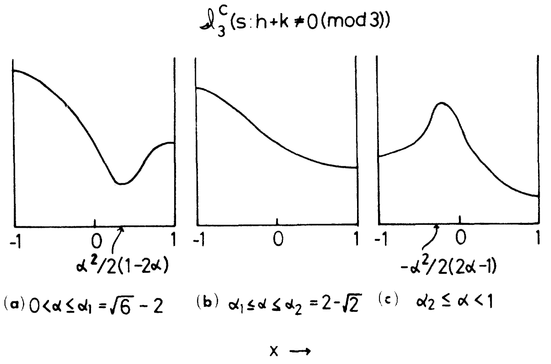
Now let us turn to the general expression (2.16) due to Wilson and evaluate the intensities for $\alpha = 0$, and $\alpha = 1$. Substitution of $\alpha = 0$ into Eqs. (2.16) and (2.17) yields the identical form as Eq. (3.10). On the other hand, the case $\alpha = 1$ reduces to

$$I^{\alpha=1}(\vec{s}) = \sum_{h+k=0\,(\mathrm{mod}\ 3)}\ \sum_{l'=0\,(\mathrm{mod}\ 3)} W^f(\vec{s}) + \frac{1}{2}\sum_{h+k\neq 0\,(\mathrm{mod}\ 3)} \left(\sum_{l'=-1\,(\mathrm{mod}\ 3)} W^f(\vec{s}) + \sum_{l'=1\,(\mathrm{mod}\ 3)} W^f(\vec{s})\right) \tag{3.11}$$

which is the arithmetic mean of Eqs. (3.7a) and (3.7b). This is an expected result since Wilson's general formalism for $\alpha = 1$ allows the two possible fcc structures *ABCABC* ⋯ and *ACBACB* ⋯ with the same weight of 50:50.

In the next place, we study the behavior of s_3^C as given by Eq. (3.5). Using notation $x = \cos\eta$, we analyze s_3^C as a function of x. Since $|x| \leq 1$, we only have to study this function for this region of variable x. It is a straightforward task to derive the following conclusion. As shown in Fig. 3, the behavior of s_3^C is different for different ranges of α. For $0 < \alpha \leq \alpha_1 \equiv \sqrt{6} - 2$, s_3^C has an absolute maximum at $x = -1$, decreases as x increases, has a minimum at $x = \alpha^2/2(1-2\alpha)$, then increases again until x becomes 1, where s_3^C has a relative maximum. For $\alpha_1 \leq \alpha \leq \alpha_2 \equiv 2 - \sqrt{2}$, s_3^C is a monotonically decreasing function of x between $-1 \leq x \leq 1$. For $\alpha_2 \leq \alpha < 1$, s_3^C has a relative minimum at $x = -1$, increases with increasing x until it reaches a maximum at $x = -\alpha^2(2\alpha - 1)$, then monotonically decreases and has an absolute minimum at $x = 1$.

Then, it is easy to see the asymptotic behavior of s_3^C in the limits of $\alpha = \delta \equiv 0_+$ and $\alpha = 1 - \delta$. When $\alpha = \delta$, s_3^C has an absolute maximum at $x = -1$ or



(a) $0<\alpha\leq\alpha_1=\sqrt{6}-2$ (b) $\alpha_1\leq\alpha\leq\alpha_2=2-\sqrt{2}$ (c) $\alpha_2\leq\alpha<1$

FIG. 3. g_3^C vs x for different values of α.

equivalently at $\eta\equiv\vec{s}\cdot\vec{a}_3=(2\nu+1)\pi$, with ν being an integer and a relative maximum at $x=1$ or equivalently at $\eta=2\eta\pi$. On the other hand, when $\alpha=1-\delta$, g_3^C has a maximum at $x=-\frac{1}{2}$ or, equivalently, at $\eta=(\frac{2}{3}\nu)(3\nu\pm1)$. In both cases, i.e., for both $\alpha=\delta$, and $\alpha=1-\delta$, the maximum behaves like $1/\delta$, while, at values of η other than those giving maxima, g_3^C approaches zero like δ. Apparently these results are consistent with Eqs. (3.10) and (3.11).

Equation (3.5) shows that g_3^C is a periodic function of η with periodicity 2π. The calculated values of g_3^C for various α are given in Figs. 4 and 5 where $0\leq\eta\leq2\pi$.

IV. COMPLETELY RANDOM STACKING

Hodges[4] has treated an infinite random stacking sequence where stacking is completely random. For this case, the probability of finding a layer B or a layer C on top of a layer A is 50:50. Since the relative translations of the added layer are $\vec{d}$ and $-\vec{d}$, respectively, $\vec{d}$ being $\frac{1}{3}(\vec{a}_1\pm\vec{a}_2)$, we have $\vec{r}_{j+m}-\vec{r}_j=m_3\vec{a}_3\pm\vec{d}\pm\vec{d}\pm\vec{d}\pm\cdots$. Accordingly the average $J_m\equiv\langle F_{j+m}^*F_j\rangle$ in this case is written

$$J_m=\{\tfrac{1}{2}[\exp(i\vec{s}\cdot\vec{d})+\exp(-i\vec{s}\cdot\vec{d})]\}^{|m_3|}\ . \qquad (4.1)$$

Inserting this into Eq. (2.7) and taking the limit of an infinite system, we obtain the scattering intensity of the form expressed by Eq. (3.2) where $g_3(\vec{s};h,k)$ is given by

$$g_3(\vec{s};h,k)=(\{1-\cos(\vec{s}\cdot\vec{d})\exp[i(\vec{s}\cdot\vec{a}_3+i\delta)]\}^{-1}$$
$$-\{1-\cos(\vec{s}\cdot\vec{d})\exp[i(\vec{s}\cdot\vec{a}_3-i\delta)]\}^{-1})$$
$$\times|f(\vec{s})|^2\ . \qquad (4.2)$$

Note that a convergence factor $\exp(-\delta|m_3|)$, $\delta\rightarrow0_+$, has been included in the summation of the geometric series. As shown in Eq. (3.2), h and k are integers, and therefore, $\cos(\vec{s}\cdot\vec{d})$ is 1 or $-\frac{1}{2}$ depending whether $h+k=0(\text{mod }3)$ is satisfied or not, respectively. When $\cos(\vec{s}\cdot\vec{d})=1$, i.e., when $h+k=0(\text{mod }3)$, Eq. (4.2) reduces to a series of δ functions at values $\frac{1}{2}\vec{s}\cdot\vec{a}_3=l\pi$, where l are integers. The second case ($h+k\neq0$ (mod 3)) yields $\cos(\vec{s}\cdot\vec{d})=-\frac{1}{2}$, and Eq. (4.2) reduces to

$$g_3^C(\vec{s};h+k\neq0\ (\text{mod }3))$$
$$=\{3/[4+5\cos(\vec{s}\cdot\vec{a}_3)]\}\,|f(\vec{s})|^2\ . \qquad (4.3)$$

This is equivalent to Eq. (3.5) with $\alpha=\frac{1}{2}$ and this guarantees that the modified formalism (3.5) covers the completely random case which is described by taking α to be $\frac{1}{2}$.

We now mention that one of Hodge's arguments is not correct. The discussion due to Hodges is summarized as follows. He has given a figure

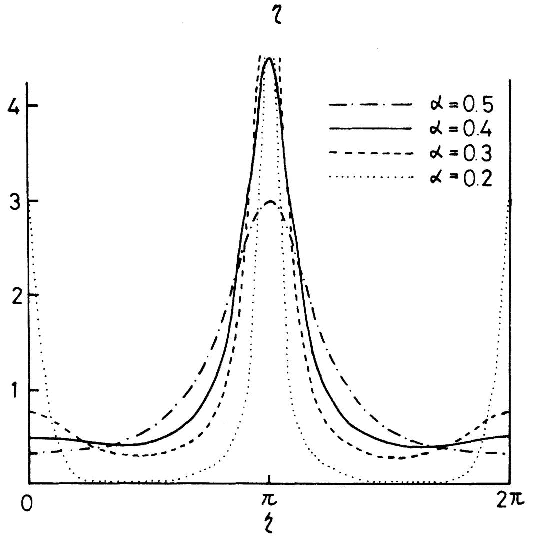


FIG. 4. Structural weight g_3^C (s_3; $h+k+1$(mod 3), α) as a function of $\eta=\vec{s}\cdot\vec{a}_3\equiv s_3\vec{e}_3\cdot\vec{a}_3$ for $\alpha=0.2.3$, 0.4, and 0.5.

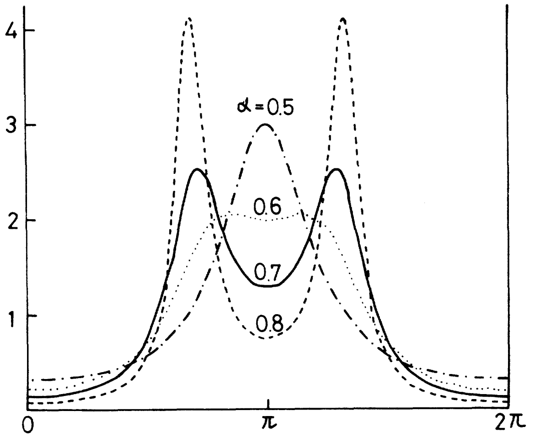


FIG. 5. The structural weight g_3^C (s_3; $h+k=1$(mod 3), α) for $\alpha=0.6$, 0.7, and 0.8.

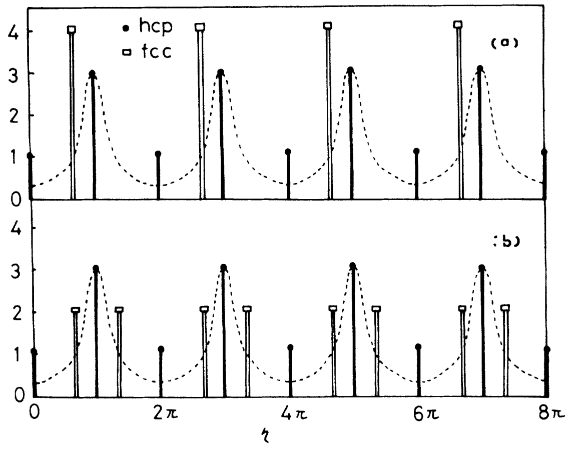


FIG. 6. (a) Continuous part of the structural weight in the third axis for $\alpha=0.5$ is denoted by a dotted curve as a function of $\eta=\vec{s}\cdot\vec{a}_3$. The structural weight for hcp and fcc is also shown for the case where $h+k=-1$ (mod 3). (For detail see text.) The periodic lattice structure weight has been arbitrarily normalized so that the height of the random stacking peak is the same as that of the hcp at that point. (b) The same figure as Fig. 6(a) except for the structural weight for fcc which in the present figure is shown for the cases where $h+k=\pm 1$(mod 3). The spikes are normalized in the same way as in Fig. 6(a).

(dotted curve in our Fig. 6) for Eq. (4.3) as a function of $\eta=\vec{s}\cdot\vec{a}_3$, where he has implicitly assumed that $h+k=-1$ (mod 3), and compared this figure with the structural weights in the third axis for fcc and hcp. Note that here $|f(\vec{s})|^2$ is taken to be 1. For fcc, he has considered only one of the possible sequences, i.e., *ABCABC*$\cdots$. Because $h+k=-1$ (mod 3) must be satisfied, the δ-function-like spikes are defined by the third term of Eq. (3.7a) [spikes as denoted by small squares in our Fig. 6(a)]. The corresponding term for hcp is given by the second term in Eq. (3.9) [spikes as denoted by small circles in Fig. 6(a)]. He argues that, as shown in Fig. 6(a), the continuous part $\mathcal{G}_3^C(\vec{s};h+k=-1\ (\mathrm{mod}\ 3))$ of the random stacking sequence behaves to a remarkable extent as if the hcp reciprocal-lattice vectors of large structural weight (at η an odd integer multiple of π) have simply been smeared with a Lorentzian convolution. Even if we also take into account the hcp vectors of small structural weight (at η, an even integer multiple of π) the whole series of δ functions for hcp has the same symmetry as the structural weight of the random stacking layers. On the other hand, the structural weight of fcc is nonzero only when $\eta=(\frac{2}{3}\pi)(3\nu+1)$ for integer ν, and has a different symmetry from that of Eq. (4.3). This tendency is emphasized when $|f(\vec{s})|^2=\cos^2(\frac{3}{8}\vec{s}\cdot\vec{a}_3)$ is included.

Hodges therefore has concluded that the results for the random stacking must look very similar to the wurtzite microcrystallite model, thus supporting the structural model due to Rudee and Howie[2] of 14 Å randomly oriented microcrystallites, all of the wurtzitelike structure.

Careful consideration shows that this conclusion by Hodges is not appropriate. There is no reason why we should pick only one of the two possible configurations for fcc, consequently both cases *ABCABC*$\cdots$ and *ACBACB*$\cdots$ must be taken into account. This indicates that Eq. (4.3) must be compared to the second term in Eq. (3.11) rather than to the third term of Eq. (3.7a). As clearly shown in Fig. 6(b), the second term in Eq. (3.11) has the same symmetry as that of the random stacking sequence. Actually, as we have presented in Figs. 4 and 5, the continuous part $\mathcal{G}_3^C(s;h+k=-1\ (\mathrm{mod}\ 3))$ changes from the wurtzitelike limit to the diamond limit when α is changed from 0 to 1.

V. INVARIANT VECTORS

In his paper on a random stacking model for *a*-Ge and *a*-Si, Betteridge[1] has placed emphasis on those reciprocal-lattice vectors that are invariant for all stacking sequences. By invariant, he means two things: (a) these vectors occur for all stacking sequences, that is, all tetrahedrally bonded structures; and (b) each invariant vector always occurs with the same structure factor. In a later paper, Betteridge and Heine[2] attributed these invariant vectors to the short-range order, that is, to the perfect tetrahedral coordination, and they argue that the separation of the set of reciprocal-lattice vectors into those which are invariant and those which vary with the stacking sequence (long-range order) provides a method of distinguishing the contributions of short- and long-range order in a reciprocal-space description.

We would like to show here that these invariant vectors are not the consequences of the short-range order alone. Actually they can be understood as a kind of mean effect of the random stacking sequence, and tetrahedral bonding is not essential to obtain them.

The invariant vectors which Betteridge has found correspond to the reciprocal vectors which give the discrete part of the scattering intensity as defined by Eqs. (3.2) and (3.3). As can be seen from Eqs. (3.2) to (3.5) this discrete part is unaffected by the stacking sequence while the continuous part is dependent on α, the parameter concerning the random sequence. The reciprocal-lattice vectors $\vec{s}_0$ at which the discrete δ functions occur are defined as follows. When we write $\vec{s}_0$ as

$$\vec{s}_0\cdot\vec{a}_1=2h\pi\ ,\quad \vec{s}_0\cdot\vec{a}_2=2k\pi,\quad \vec{s}_0\cdot\vec{a}_3=2l\pi, \qquad (5.1)$$

then h, k, and l must satisfy

$$h+k=0 \pmod 3), \tag{5.2a}$$

$$l: \text{ integer }. \tag{5.2b}$$

This definition applies to the general random stacking model for, e.g., hexagonal cobalt, SiC. Thus, the invariant vectors as determined by Eq. (5.2) have essentially no connection with the perfect tetrahedral bonding. The important factors which give rise to these invariant vectors are the following facts: (i) that the relative translations of perfect layers are strictly given by $\vec{d}$ or $-\vec{d}$ $[\vec{d}=\frac{1}{3}(\vec{a}_1+\vec{a}_2)]$ throughout the material; and (ii) that the interlayer distance is constant. The former factor leads to condition (5.2a), while the latter to (5.2b). The long-range order in the sense stated in (i) and (ii) in the above is of course based upon perfect short-range order. This short-range order, however, does by no means imply *perfect* tetrahedral bonds. We note that not only is this so, but even the short-range order does not have to be in the sense of close-packed nearest-neighbor arrangements, because all the mathematical steps and arguments so far in the present paper have not required any special value for the interlayer distance. In other words, we did not need to define the magnitude of the primitive translation vector $\vec{a}_3$ for our formalism and discussion. The only requirement is that $\vec{a}_3$ must be perpendicular to two-dimensional ordered layers. When the model is extended to tetrahedrally bonded amorphous semiconductors, the scattering intensity of a unit cell, i.e., $|f(\vec{s})|^2 = \cos^2(\frac{3}{8}\vec{s}\cdot\vec{a}_3)$ [Eq. (2.8)], must be included. The requirement that this factor be nonzero introduces an additional condition that

$$l \neq 2 \pmod 4). \tag{5.3}$$

The close-packed structures for monatomic lattice or the perfect tetrahedral bonding for diatomic lattices are realized only when

$$|\vec{a}_3| = \sqrt{2/3}\ |\vec{a}_1| = \sqrt{2/3}\ |\vec{a}_2|\ . \tag{5.4}$$

Physically, the invariant vectors can be understood as the mean effect of the random stacking sequence. This may be seen as follows. We introduce a "virtually-crystal model" which is defined by a set of primitive vectors $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ as given in Sec. II and by a unit cell whose structure factor is equal to the average of the structure factors of unit cells in layers type A, B, and C; i.e.,

$$F_{\text{v.c.}}(\vec{s}) = \tfrac{1}{3}(F_A + F_B + F_C)\ , \tag{5.5}$$

where F_A, F_B, and F_C are defined in Sec. II. Namely the virtual crystal thus defined corresponds to a regular stacking of two-dimensionally ordered layers where the latter are specified by translation vectors $\vec{a}_1$ and $\vec{a}_2$ while the regular stacking is determined by $\vec{a}_3$. From Eqs. (2.5) and (5.4), the scattering intensity for this virtual crystal is calculated as

$$\begin{aligned} I_{\text{v.c.}}(\vec{s}) &= \sum_m |[\tfrac{1}{3}(F_A+F_B+F_C)]|^2 \exp(i\vec{s}\cdot\vec{r}_m)(\eta_1-|m_1|)(n_2-|m_2|)(n_3-|m_3|) \\ &= \tfrac{1}{3}(1+2K) \sum_{h;\,\text{integer}} \sum_{k;\,\text{integer}} \sum_{l;\,\text{integer}} \delta_{\vec{s}\cdot\vec{a}_1/2-h\pi,\,0}\, \delta_{\vec{s}\cdot\vec{a}_2/2-k\pi,\,0}\, \delta_{\vec{s}\cdot\vec{a}_3/2-l\pi,\,0} \cos^2(\tfrac{3}{4}l\pi)\ , \end{aligned} \tag{5.6}$$

where $n=n(n_1, n_2, n_3)$ are allowed to become infinite and K is given in Eq. (3.1). Following the discussion of Sec. III, we can conclude that Eq. (5.6) is exactly the same as the discrete part of the scattering intensity for a random stacking model which is shown in Eqs. (3.2) and (3.3). This indicates that the invariant vectors correspond to the average effect of the random stacking sequence while the continuous part in Eq. (3.5) reflects the effect of randomness or fluctuations.

VI. DISCUSSION

As an extension of Wilson's formalism, we have evaluated the modified expression for the scattered intensity of a random stacking model. The scattered intensity so obtained consists of two parts, one being a discrete part and another a continuous part. The discrete part is described by a series of δ functions and is independent of the scattering sequence. The reciprocal lattice vectors at which these δ functions occur correspond to the invariant vectors proposed by Betteridge.[1] Although Betteridge and Heine[2] have concluded that these invariant vectors arise from the perfect tetrahedral coordination, we have shown that their conclusion is not correct. We have also shown that the discrete part of the scattering intensity which is nonvanishing at these invariant vectors represents the average effects of the random stacking while the continuous part represents the effects of fluctuations. The average effects reflect the ordered aspects of the structure. More precisely, these invariant vectors appear as a result of the long-range order in the sense that the relative translations of perfect layers are always strictly $\vec{d}$ or $-\vec{d}$ and that the interlayer distance is constant. Therefore, although these invariant vectors might play an important role in materials which satisfy the above described two conditions for the appearance of these invariant vectors, they are rather spurious in amorphous systems where no such long-range order is expected.

The continuous part changes from the hcp limit (or the wurtzitelike limit) to the fcc limit (or the diamond limit) according to the change of the parameter which describes the random sequence.

In this paper, we have confined ourselves to the analysis of the model. In a succeeding paper, we will present some numerical results for the scattering intensity and compare the calculated results to the experimental data of the diffraction pattern. In our further papers, we will also treat the electronic density of states and the optical properties of tetrahedrally bonded amorphous semiconductors on the basis of the random stacking model.

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