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Interpretation of X-ray Scattering Patterns due to Periodic Structural Fluctuations. I. The Case of Transverse Modulation of Positional Parameters in Primitive Lattices

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This paper deals with transverse periodic fluctuations of atomic positions. The coherently scattered X-ray intensity is calculated for two types of modulating functions. 1. A rectangular wave: This type of modulation may be conceived for structures with domain-like antiparallel shifts of atomic positions (*e.g.* in antiferroelectics). 2. A triangular wave: Some type of micro-twinning can be described as a transverse triangular modulation of the structure. For these two types of lattice modulations the characteristic features of scattering patterns are discussed so as to determine the type of the modulating function and its parameters (wavelength, amplitude). These results are compared with those published by Korekawa [*Theorie der Satellitenreflexe* (1967). Habilitationschrift der Ludwig-Maximilian-Universität München] for sinusoidal type modulations.

Introduction

On single-crystal X-ray photographs groups of reflexions, which are called 'satellites', are sometimes observed close to the main reflexions. Often, the intensity of the satellite reflexions is weak enough to be neglected in a first approximation, and the structure may be described by a unit cell which is defined by the main reflexions only. Thus, with the satellites neglected an average picture of the structure is obtained. The real structure, however, is determined by both the main and the satellite reflexions. The real unit cell defined by the distance between main and satellite reflexions is larger than the cell given by the main reflexions only. The latter will be referred to as the subcell hereafter. A structure which gives rise to a scattering pattern of main and satellite reflexions can be conceived as being made up of subcells; their spatial arrangement is given by a periodic function, the 'modulating function'. The size of the unit cell is given by the period M of the modulating function. A lattice which is defined in such a way is shown in Fig. 1(*a*). In Fig. 1(*b*) the amplitude of the modulating function has vanished to zero, leading to a structure called the 'idealized structure'. In this case the subcell has become the unit cell.

In the example given in Fig. 1(*a*) the spatial positions of subcells follow a transverse modulation function, which is periodic in only one dimension. This paper is restricted to this type of lattice modulation only. However, other types are conceivable:

1. The positional parameters of subcells may be modulated in a longitudinal mode.

2. The scattering factors, rather than the positional parameters, are affected by a periodic function, giving rise to density fluctuations.

In the real case the modulated structure may be a combination of these fundamental types of modulations, and the modulation function may be periodic in more than one dimension.

The phenomenon of satellite reflexions – known in light scattering for a long time – was first applied to problems of X-ray scattering by Dehlinger (1927) who described the line broadening of powder lines. A first theoretical approach was given by Kochendörfer (1939) who used the concept of sinusoidal lattice modulations. Daniel & Lipson (1943, 1944) calculated the scattered amplitudes for the two types of lattice modulations: a sinusoidal modulation of scattering power and a sinusoidal modulation of spacing, which in our terminology is a longitudinal modulation of positional parameters. Hargreaves (1951) tried to introduce a square-wave modulation of positional parameters; however, because of the approximations used he ob-

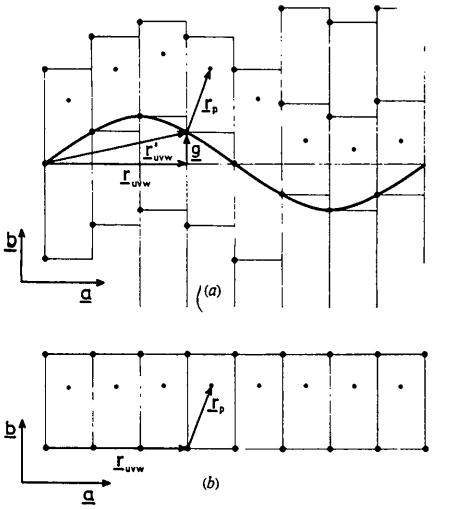

Fig. 1. (*a*) A modulated structure given by a periodic shift function. (*b*) The corresponding structure without the modulation.

tained substantially the same result as for a sinusoidal modulation. He also proposed a model in which lamellae, modulated in a longitudinal mode, are separated by volumes of unchanged matrix. By this model he was able to obtain reasonable agreement between theory and experiment for the Cu–Ni–Fe alloys. Guinier (1955) proposed a model consisting of isolated, randomly distributed composition fluctuations. By the random character of the model the diffuse broadening of satellite peaks can be accounted for. De Fontaine (1966) studied the combined case of modulation of scattering power and of spacing. The modulation functions for the scattering power and for the positional parameters are represented by a Fourier series in his approach. He also proposed a model of a 'quasi periodic modulated structure', in which the scattering power is modulated by a sine wave with the sine wave itself frequency modulated by a cosine wave of much longer period. The resulting scattering pattern consists of sharp Bragg peaks flanked by diffuse satellite envelopes. Korekawa (1967) was the first to give a systematic review on satellite theory and to discuss the 'pure' as well as the combined cases of modulation of scattering power and of positional parameters in both longitudinal and transverse modes. For modulation functions other than sinusoidal he also used the approach of Fourier series expansion which (except for the case of pure density fluctuations) yields lengthy and rather complex expressions for the scattered amplitudes. Therefore his results are practically applicable only for sinusoidal type modulations. In this paper a theoretical approach is given by which modulations also other than sinusoidal can be described to yield simple analytical expressions for the amplitude of coherently scattered X-rays. The intent is to give simple and exact solutions for cases of modulation functions where by the conventional method only very complex analytical expressions are obtained. As an example, lattices modulated by a triangular or a rectangular wave (transverse mode) will be discussed and rules will be given to interpret the scattering patterns.

Theoretical

The total (complex) amptitude of X-rays which are diffracted from a periodic structure, as shown in Fig. 1(*b*). is given by:

$$A=\sum_{u,v,w}\exp\left[2\pi i(\xi u+\eta v+\xi w)\right]\sum_{p=1}^{j}f_p\exp\left[2\pi i(\mathbf{r}_p\,.\,\mathbf{r}^*)\right]. \tag{1}$$

(u,v,w) and (ξ,η,ζ) represent vectors of the lattice and the reciprocal lattice, respectively:

$$\mathbf{r}^*=\xi\mathbf{a}^*+\eta\mathbf{b}^*+\zeta\mathbf{c}^*$$
$$\mathbf{r}_{uvw}=u\mathbf{a}+v\mathbf{b}+w\mathbf{c}\,.$$

The sum over all atoms j within the cell is the structure factor F of a unit cell; the sum over u (or v, or w) is known to be the Laue function $G(\zeta)$:

$$G(\zeta)=\sum_{u=0}^{N_1-1}\exp\left(2\pi i\xi u\right) \tag{2}$$

$$G(\xi)=\exp\left[\pi i(N_1-1)\xi\right]\frac{\sin\pi N_1\xi}{\sin\pi\xi}\,. \tag{3}$$

If the number of unit cells N_1 is large enough, it is safe to set

$$G(\xi)=\begin{cases}N_1 \text{ for } \xi=h\ (h=0,\pm1,\pm2\ldots)\\ 0\quad\text{otherwise}\,.\end{cases} \tag{4}$$

Therefore the total amplitude A is proportional to the structure factor F:

$$A=N_1N_2N_3F\,. \tag{5}$$

This is the well known equation on which the structure determination by diffraction methods is based.

The modulated lattice of Fig. 1(*a*) arises from the idealized lattice of Fig. 1(*b*) by substituting $\mathbf{r}'_{uvw}$ for $\mathbf{r}_{uvw}$:

$$\mathbf{r}'_{uvw}=\mathbf{r}_{uvw}+\mathbf{g}(u,v,w)\,. \tag{6}$$

The discussion in this paper will be restricted to problems where the vector $\mathbf{g}$ depends only on u and where $\mathbf{g}$ is parallel to $\mathbf{b}$:

$$\mathbf{g}=\mathbf{b}\,g(u)\,. \tag{7}$$

If applied to the problem of Fig. 1(*a*) equation (1) takes the following form:

$$A=G(\eta)G(\zeta)F\sum_{u=0}^{N_1-1}\exp 2\pi i[\xi u+\eta g(u)]\,. \tag{8}$$

This can be broken up into two sums by the following substitution

$$u=qM+s \tag{9}$$

with

$$q=0,1,2\ldots[N_1/M]$$
$$s=0,1,2\ldots M-1,$$

M = period of the modulation function in units of subcells.

$[N_1/(M)]$ is the largest integer of which the magnitude does not exceed the magnitude of N_1/M. Since $g(u)$ is a periodic function, the following relation must hold

$$g(u)=g(qM+s)=g(s)\,.$$

With this relation for $g(u)$, equation (8) can be written

$$A=G(\eta)G(\zeta)F\sum_{q=0}^{[N_1/M]-1}\exp\left(2\pi i\xi qM\right)\times\sum_{s=0}^{M-1}\exp\left\{2\pi i[\xi s+\eta g(s)]\right\}+\varepsilon\,. \tag{10}$$

ε is a correction term if N_1 is not an integral multiple of M. ε is negligibly small if the magnitude of $[N_1/M]$ is large enough. The first sum is a summation over all

unit cells (superstructure), the index of the second sum refers to the subcells.

If the approximation for the Laue function given by equation (4) is accounted for, we obtain

$$A(P/M,k,1)=N_1N_2N_3F\frac{1}{M}\times\sum_{s=0}^{M-1}\exp\{2\pi i[\frac{P}{M}s+k\,.\,g(s)]\}$$
$$\text{with } p=0,1,2\ldots. \qquad (11)$$

The total amplitude A can be normalized to the structure factor of the idealized structure which is given by equation (5). This leads to the basic equation which describes the satellite problem for modulated structures of the type shown in Fig. 1(*a*) and for any kind of modulation function which is defined for $0\leq s\leq M$:

$$\tilde{A}(P/M,k,1)=\frac{1}{M}\sum_{s=0}^{M-1}\exp\{2\pi i[\frac{P}{M}s+k\,.\,g(s)]\}\,. \qquad (12)$$

$\tilde{A}$ is the normalized geometrical structure factor of the unit cell (superstructure).

Apparently, scattered X-ray intensity is to be expected only at positions $\xi=1/M,2/M,3/M\ldots$ and $k,1$ integers. These are the positions of the satellite reflexions; except for $\xi=h$(*i.e.* $P=M,2M,\ldots$). The latter are the positions of the main reflexions. The approach given here is different from the ones used by other authors. The basic difference is that equation (8) is split into two sums, which leads to equation (10). This approach is therefore only exact in cases where the period M is a multiple integer of subcells, a condition which is experimentally found in many superstructures. The results which can be derived from equation (12) are exact in the sense that the Laue approximation can be accepted as being valid in the kinematic theory. Because of this approximation the number M is limited. If N_1 is of the order of 10^4 for crystals of standard quality, M is restricted between 2 and, say, 50. These, however, are the most relevant cases for application.

Rectangular wave

Two examples will be given, for which equation (12) will be evaluated. The first one is a lattice modulated by a rectangular wave. This type of modulation may be conceived for structures with domain-like antiparallel shifts of atomic positions. The period of the modulation has to be much below the range of coherence. In some antiferroelectrics such microdomains may be expected in which the antiparallel shifts of atoms give rise to the antiparallel orientation of the dielectric polarization vector. An asymmetric structure of rectangular modulation is shown in Fig. 2. The width of the domains is D_1 and $M-D_1$. The function $g(s)$ can be defined by:

$$g(s)=\begin{cases} b & 0\leq s<D_1 \\ -b & D_1\leq s<M\,. \end{cases} \qquad (13)$$

Substitution of equation (13) into equation (12) will give

$$\tilde{A}=1/M[\sum_{s=0}^{D_1-1}\exp\{2\pi i(P/Ms+kb)\}+\sum_{s=D_1}^{M-1}\exp\{2\pi i(P/Ms-kb)\}]\,. \qquad (14)$$

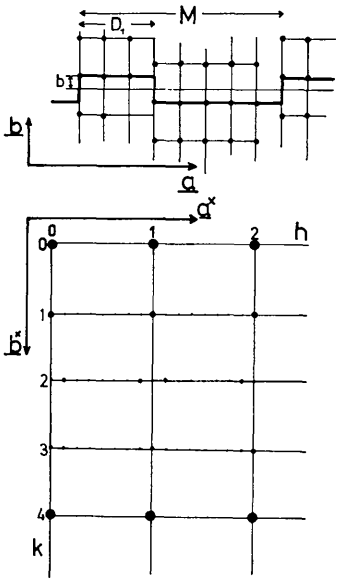

Fig. 2. Lattice modulated by a rectangular modulation function and the corresponding diffraction pattern (for $b=0{\cdot}125$, $D_1=3$, $M=8$). The value of b is exaggerated in the drawing.

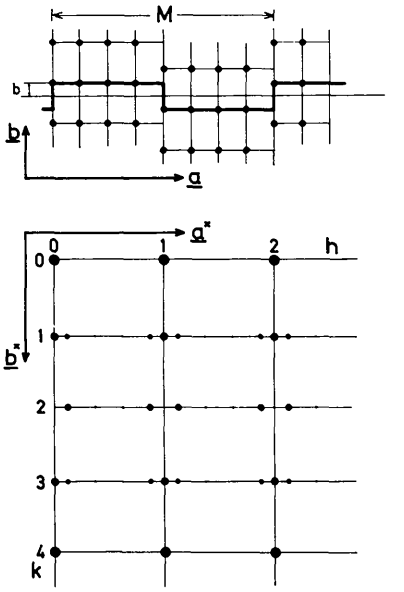

Fig. 3. Lattice modulated by a symmetric rectangular modulation function and the corresponding diffraction pattern (for $b=0{\cdot}125$). The value of b is exaggerated in the drawing.

This can be simplified by the use of the trigonometric identities to yield the magnitudes of the amplitudes of the main reflexions and of the satellites:

$$|\tilde{A}| = \{1 + 4D_1/M(D_1/M - 1)\sin^2(2\pi kb)\}^{1/2} \quad (15a)$$

for main reflexions,

$$|\tilde{A}| = \left|\frac{2\sin(2\pi kb)\sin(\pi n D_1/M)}{M\sin(\pi n/M)}\right| \quad (15b)$$

for satellites; $n = 1, 2, 3, \ldots$.

The index P in equation (14) counts the reflexions in the **a*** direction. It has been substituted by

$$P = Mh + n$$
$$h = \text{integer}; \quad -M/2 \leq n \leq M/2 \,. \quad (16)$$

n refers to the order of satellites between two main reflexions.

Two features can be derived from equation (15):

(1) All satellites have a zero at $k_0 = 1/(2b)$. For this value of k the structure factor becomes zero. By finding the zeros of the satellites b can be determined. If b is known, the zero of the main reflexions [equation (15*a*)] can be used to determine M_1.

(2) If $M/D_1 = q$ (q integer), systematic extinctions are found for the satellites: all satellites are extinct with $n = qm; m = 1, 2, 3, \ldots$.

One special case of $g(s)$ will be discussed further: the case where $g(s)$ is a symmetric function: $D_1 = M/2$. An example for $M = 8$ is shown in Fig. 3. For this symmetric case equations (15*a*) and (15*b*) can be reduced to yield the simple result:

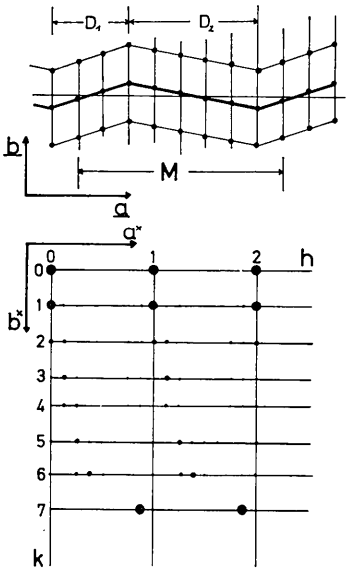

Fig. 4. Lattice modulated by a triangular modulation function and the corresponding diffraction pattern (for $b = 0{\cdot}125$, $D_1 = 3$, $D_2 = 5$). The value of b is exaggerated in the drawing.

$$|\tilde{A}| = |\cos(2\pi kb)| \quad \text{(main reflexions)} \quad (17a)$$

$$|\tilde{A}| = 2/M\left|\frac{\sin(2\pi kb)}{\sin(\pi n/M)}\right| \; n = 1, 3, 5, \ldots . \quad (17b)$$

All satellites of even order are extinct. The main reflexions, if normalized to the amplitude of the idealized structure, vary with k like a simple cosine function. The diffraction pattern as described by equations (17) is illustrated in Fig. 3 for the case of $M = 8$. Some characteristic features should be pointed out:

(1) If the modulation is along **a**, the satellites are observed along **a***.

(2) For a transverse modulation with an amplitude parallel to **b**. the intensity depends only upon k. There are no satellites for $k = 0$.

These features are common to all transverse modulations, as was pointed out by Korekawa (1967).

(3) Looking along **b*** there is a zero for all satellites midway between two zeros of the main reflexions, and *vice versa*. The main reflexions arrive at a maximum ($|\tilde{A}| = 1$) when the satellites disappear. By finding the zeros of the satellites and/or the main reflexions on X-ray photographs the amplitude b can be determined.

In order for an X-ray photograph to be analysed, however, the intensities (or the amplitudes) have to be normalized to the intensities of the idealized structure. This can easily be done by the following relation:

$$\sum_{n=-M/2}^{M/2} |A\left(h + \frac{n}{M}, k, l\right)|^2 = N_1^2 N_2^2 N_3^2 \sum_{n=-M/2}^{M/2} F^2 \times |\tilde{A}\left(h + \frac{n}{M}, k, l\right)|^2 . \quad (18)$$

From the identity

$$\frac{4}{M^2}\sum_{p=0}^{M/2-1}\frac{1}{\sin^2\frac{\pi}{M}(2p+1)} = 1 \quad (19)$$

and with $F^2 = 1$ for the structure of Fig. 2 it follows readily from equation (17) that

$$\sum_{n=-M/2}^{M/2} |\tilde{A}\left(h + \frac{n}{M}, k, l\right)|^2 = 1 \,. \quad (20)$$

Equations (18) and (20) simply establish that the amplitude of the idealized structure may be obtained by adding all the satellite intensities from $n = -M/2$ to $n = M/2$ to the intensity of the corresponding main reflexion and by taking the square root. This also holds for transverse modulations other than the square-wave type. If a satellite is exactly midway between two main reflexions its intensity has to be shared by them.

Triangular modulation

A specific type of twinning may be described by a lattice modulated by a triangular wave. The twin

lamellae must be much smaller than the range of coherence. This kind of lattice modulation will be discussed as a second example for the approach given by equation (12). The structure is shown in Fig. 4.

For the case shown in Fig. 4 the modulation function can be written in the form

$$g(s)=\begin{cases} a_1(s-\frac{1}{2}) & 0\le s<(D_1+1)/2 \\ a_2(M/2+\frac{1}{2}-s) & (D_1+1)/2\le s<M-(D_1-1)/2\,. \end{cases} \quad (22)$$

D_1 and D_2 are the widths of the two domains. After substitution of equation (22) into equation (12) a solution for $|\tilde{A}|$ can be obtained for any integer D_1 and D_2 (or M respectively):

$$|\tilde{A}|=\left|\frac{\sin\pi(a_1+a_2)k\,\sin\pi D_1(n/M+a_1k)}{M\sin\pi(n/M+a_1k)\,\sin\pi(n/M-a_2k)}\right|. \quad (23)$$

The four parameters in equation (23) are not independent; the following relation must hold:

$$a_1D_1=a_2(M-D_1)=a_2D_2=b/2\;; \quad (24)$$

b = amplitude of the modulation.

The diffraction pattern for the case $D_1=3$, $D_2=5$ and $b=0{\cdot}12$ is shown in Fig. 4. The characteristic features which are pointed out in the previous section and which are common to all transverse waves are also found here. The parameters of equation (23) can be determined by fitting the observed data to the exact solution given by equation (23). The zeros of the main reflexions can be used for this purpose. For example, the first and second zeros are given by the two relations:

$$k_0=1/(a_1D_1) \quad (25a)$$

and

$$k_0=1/(a_1+a_2)\,. \quad (25b)$$

Since M is known from the diffraction pattern, a_1, a_2, and D_1 can be determined too with equations (25) and (24). The satellites are not symmetrical about the main reflexions; this is different from sinusoidal and rectangular modulations. At k_0 given by equation (25b) the main reflexions and all but one satellite disappear. The order of the only satellite present is given by

$$n=M[1-a_1/(a_1+a_2)]\,. \quad (26)$$

This is a specific feature of triangular modulations: at a certain k value the structure factors of all but one satellite vanish; if this k_0 is an integer only one satellite is observed, its order being given by equation (26), (in Fig. 4, $k_0=7$). The normalized amplitude can be obtained as in the case of rectangular modulation. In this case an identity different from equation (19) has to be applied to prove that equation (20) is valid also for triangular modulation.

Comparison

The results given above for rectangular and triangular modulations will be compared with those given by Korekawa (1967) for a sinusoidal modulation. His result for the amplitude is:

$$|\tilde{A}(h\pm n/M,k,l)|=\left|\sum_{q=-\infty}^{\infty} J_{qM\mp n}(2\pi kb)\right|; \quad (27)$$

J_m = Bessel function of order m

b = amplitude of the sine wave.

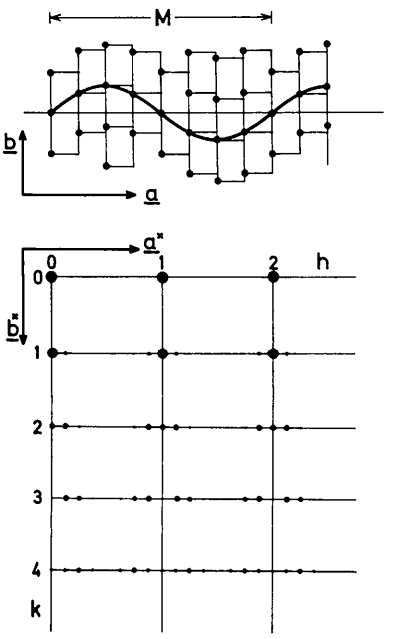

Fig. 5. Lattice modulated by a sinusoidal modulation function and the corresponding diffraction pattern. The amplitude is 0·125, which is exaggerated in the drawing.

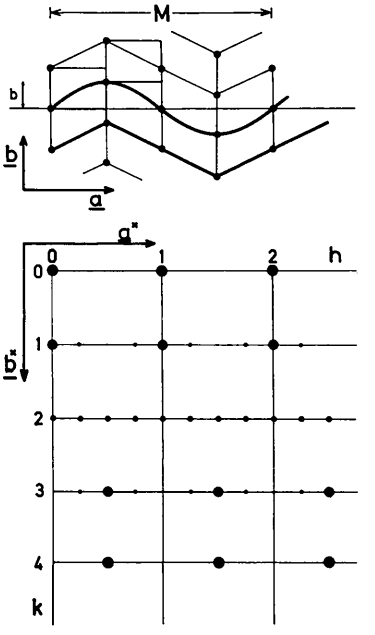

Fig. 6. Lattice with $M=4$, which can be described by both a triangular or sinusoidal modulation function, and the corresponding diffraction pattern.

The structure and the corresponding scattering pattern are shown in Fig. 5. For small arguments of the Bessel function the series of equation (27) can be approximated by just the term with $q=0$. Thus, the satellite of the nth order is represented by the Bessel function of order n. In this case equation (27) simplifies to

$$|\tilde{A}(h\pm n/M,k,l)|=|J_n(2\pi kb)|\,. \qquad (28)$$

Consequently, the main reflexions are described by $J_0(2\pi kb)$. The validity of this approximation will be checked by an example for $M=4$, which is shown in Fig. 5. Apparently this lattice can be exactly described by both a sinusoidal and a symmetric triangular type modulation; therefore the results must be identical for both kinds of modulation. By replacing M by 4 in equations (23) we obtain (for $a_1=a_2$, $D_1=2$)

$$|\tilde{A}|=\cos^2\pi kb \qquad n=0 \qquad (29a)$$

$$|\tilde{A}|=\sin^2\pi kb \qquad n=2 \qquad (29b)$$

$$|\tilde{A}|=\tfrac{1}{2}|\sin 2\pi kb| \qquad n=1\,; \qquad (29c)$$

b = amplitude of the triangle or the sine wave.
The diffraction pattern is shown in Fig. 6. Equation (27) with $M=4$ yields

$$|\tilde{A}|=\Big|\sum_{q=-\infty}^{\infty} J_{4q\mp n}(2\pi kb)\Big|\,. \qquad (30)$$

By application of the relations between Bessel functions and trigonometric functions the equivalence of equation (30) and equation (29) (for the proper n) can readily be established. Fig. 7 illustrates the variation of the main reflexion with k as given by equation (29a); it also shows the Bessel function $J_0(2\pi kb)$, which is an approximation for the k dependence of the main reflexion according to equation (28). It is apparent that this approximation only holds for $k\leq 2$ (for $b=0{\cdot}12$).

If for determination of b the root of equation (28) had been used instead of the one of equation (29a) the value of b would have been found to be $b=0{\cdot}092$. The correct value is $b=0{\cdot}12$. A second example will be given to compare the variation of the main reflexion and the first satellite for the three basic types of symmetric transverse modulations; sinusoidal, triangular, rectangular. The period M is eight and the amplitude is the same ($b=0{\cdot}12$) in all three cases. The dependence upon k is shown in Figs. 8 and 9 for the main reflexion and the first satellite. Apparently there is a considerable difference in this dependence. For the rectangular wave the maximum intensity ($|\tilde{A}|=1$) is attained periodically by the main reflexions [at $k=0$, $1/(2b), 2/(2b)\ldots$]. For these values of k all satellites vanish. For the sinusoidal wave there is only the absolute maximum at $k=0$; there is no value of k, other than $k=0$, where all satellites become zero. In the case of a triangular modulation the absolute maxima (at $k=0, 1/a, 2/a, \ldots$) are followed by relative maxima in between. All satellites disappear only at k values $k=0, 1/a, 2/a\ldots$, the main reflexions and all but one satellite disappear at $k=1/(2a)$.

If on an X-ray photograph the main reflexions arrive at the maximum intensity ($|\tilde{A}|=1$) periodically, a sinusoidal modulation can be excluded. The rectangular wave is characterized by the fact that all maxima of main reflexions are absolute maxima. This shows that the intensities differ considerably for the three cases and so do the roots of the functions describing the k dependence.

When an X-ray pattern is analysed, it is therefore imperative to plot the measured intensity and to

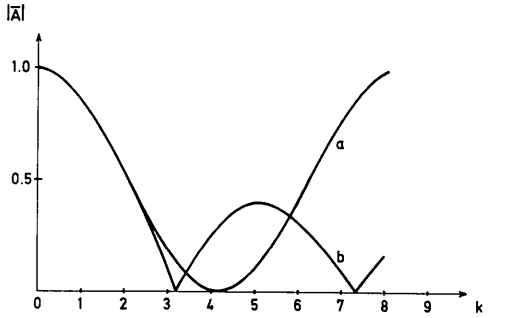

Fig. 7. (a) k dependence of the normalized amplitude of the main reflexion for the example of Fig. 6, and (b) the Bessel function $J_0(2\pi k\times 0{\cdot}125)$.

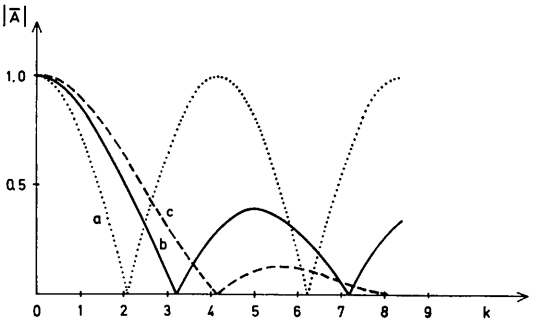

Fig. 8. k dependence of $|\tilde{A}|$ of the main reflexion for (a) a rectangular, (b) a sinusoidal and (c) a triangular modulation function for the symmetric case of $M=8$ and $b=0{\cdot}125$.

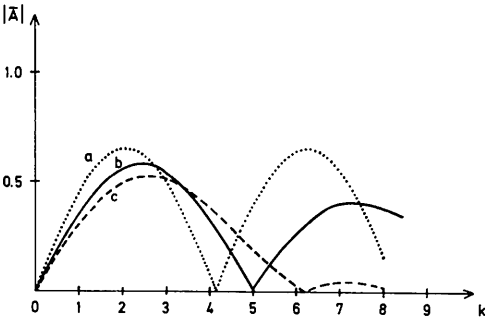

Fig. 9. k dependence of $|\tilde{A}|$ of the first satellite for (a) a rectangular, (b) a sinusoidal and (c) a triangular modulation function for the symmetric case of $M=8$ and $b=0{\cdot}125$.

decide which one, if any, of the three fundamental modulations is applicable, before any parameter can be determined from the zeros of the main reflexions and the satellites.

This paper only deals with positional fluctuations of the transverse type. The rules given here are therefore only applicable if the features characteristic for this type of modulation are observed. However, if the structure is affected by density fluctuations or positional fluctuations of the longitudinal type different criteria have to be applied.

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A Probable Crystallographic Path for the Thermal Phase Transitions in Single Crystals of KNO_3

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A probable crystallographic path for the thermal cycle of phase transformations, II–I–III–II, in KNO_3 single crystals is proposed. It is based on the symmetry of the phases and a least-motion hypothesis that the 'shuffles' of the transformations (so remarkably like martensitic transformations in metals) are the minimum possible readjustments subject to accepted van der Waal distances between chemically non-bonded atoms. Twinning is adequately explained by the alternative paths provided by the symmetry of the parent phase. The observed disorientation of 2°9′ in the *c*(II) axes of the end-phase twinned crystals is calculable by the well known Bowles–Mackenzie matrix method. The calculated value is now found to be 2·5°. Crystallographically an important possibility emerges: the structure of the higher-symmetry phase of a transformation may be predicted from only its unit-cell dimensions and space group if the crystal structure of the low-symmetry phase is known.

Introduction

Martensitic transformations in metals and alloys are characterized by well-defined orientation relationships between the parent and product phases. This characteristic is found in phase transformations of crystals of some non-metallic compounds also. For example, calcium carbonate transforms from room-temperature orthorhombic aragonite to rhombohedral calcite at 478 °C. The twofold *c* axis of aragonite becomes the unique axis of calcite (Shoji, 1933).

It has been shown that the reverse transformation, calcite to aragonite, is brought about by shear processes that occur only during crushing and grinding but not by uniform pressure (Leiserowitz, Schmidt & Shamgar, 1962). Shear is also a specific characteristic of martensitic transformations.

At room temperatures phase II KNO_3 crystals are isomorphous with aragonite, space group *Pmcn* (No. 162, *International Tables for X-ray Crystallography*, 1952). On heating they transform at 128 °C to the rhombohedral phase I, space group $R\bar{3}m$ (No. 166). This space group is very close to $R\bar{3}c$ (No. 167) of calcite. X-ray oscillation photographs show that in KNO_3 also the *c* axis of phase II transforms into the unique axis c_H of phase I.

On cooling, phase I KNO_3 returns to phase II not directly but through another rhombohedral phase III of the noncentrosymmetric space group $R3m$ (No. 160). The transformation sets in at 125 °C, and phase III persists till 110 °C.

The crystal structures of all three phases have been determined (Tahvonen, 1949; Edwards, 1931; Barth, 1939). Their crystallographic data are in Table 1; the three structures in their respective (001) projections are shown in Figs. 1 and 2.

Such closely related symmetry, the similar orientation relationships and the fact that in one of them