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A New Diffraction Approach To Crystal Structure Determination of Nano-twined Martensites

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Abstract. The intensity diffracted by crystals containing twin boundaries of the system $\{110\}$, $\langle 1\,\bar{1}\,0\rangle$ were calculated in the reciprocal space assuming a short-range order in the twin-boundary distribution. The calculated intensity distributions have been analyzed to find the effect on the diffraction pattern of such parameters as (i) ratio b/a (c/a) between the crystal lattice constants, (ii) density of the twin boundaries, (iii) ratio between thicknesses of the twin-related lamellae, and (iv) crystallographic direction along which the intensity distribution is simulated. It is found that each of these parameters affects the diffraction-peak profiles and positions including the diffraction peaks of the basic structure. Therefore, the problem of the diffraction pattern identification for a twin-modulated crystal should be approached only by a combined consideration of the diffraction features.

1. Introduction

The diffraction patterns of martensite crystals often show the presence of extra peaks which is associated with the formation of the so-called modulated structures. In the strict sense, a modulated structure is that formed by structural variations of a simpler basic structure, and the structural variations are described by a modulation function which necessarily is a wave function [1]. This is a 'wave modulated structure'. In a board sense, polytypes and twin modulated structures may be placed into category of modulated structures as the structures resulted from more or less periodic shifts along a planar interface of a basic structure [2]. These are 'stacking modulated structures'. It is important that both these definitions use the concept of a basic structure, and the identification of the basic structure is a central problem for the modulated structure solution. With a known basic structure, the modulations would be obtained by structure refinement against main and extra peaks taken an appropriate model of the structural variations.

It is known that twinning is a common feature of the structures resulted from martensitic transformations; the thicknesses of the twin-related lamellae vary in a wide range from micrometers up to nanometers. The results of HREM study are reported [3, 4] suggesting that a selection of modulated structures that were observed in martensites could be considered as 'stacking modulated structures' resulted from twinning of orthorhombic and tetragonal crystals by the system $\{110\}$, $\langle 1\,\bar{1}\,0\rangle$. The stacking sequences of the twin-related lamellae in the structures are not perfect, and two (or rarely one) the most probable twin-thicknesses are observed in more or less broadened twin-thickness frequency diagrams. Such structures should be considered as a kind of the so-called aperiodic structures.

Like a stacking fault, twin boundary is a kind of layer defects. Stacking faults are widely known to have considerable effect on the diffraction patterns. Contrary to the diffraction pattern from a 'wave modulated structure' where each main (strongest) diffraction peak is in the same position as the corresponded Bragg reflection of the basic structure [1], the occurrence of the stacking faults affects diffraction-peak positions of the basic structure [5-9]. It is true for an ordered 'stacking modulated structure' as well. If so, difficulties emerge when standard methods of structural analysis are applied to solve the 'stacking modulated structure'.

Therefore, attempts have been made to find the diffractions features for aperiodic twin modulated structures. The calculated diffraction data have been analyzed for the purpose of finding the dependence, mainly, of the diffraction-peak positions on the crystal properties. An approach being as yet rather a caution than a procedure is proposed to be a starting point for the structural analysis of the stacking modulated crystals based on the diffraction data. A model of an orthorhombic nano-twinned crystal Ni-Mn-Ga is used to demonstrate the results.

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2. Crystal model and calculation technique

Orthorhombic crystal is represented as a stacking sequence of the (110) atomic layers by change of the coordinate system $(\mathbf{a},\mathbf{b},\mathbf{c})$ derived from the axis $L2_1$ austenite structure to a new coordinate system $(\mathbf{A}_1,\mathbf{A}_2,\mathbf{A}_3)$:

$$\mathbf{A}_1 = \mathbf{c};\quad \mathbf{A}_2 = (\mathbf{b}-\mathbf{a})/2;\quad \mathbf{A}_3 = \eta^2\cdot\mathbf{a}/2\left(\eta^2+1\right)+\mathbf{b}/2\left(\eta^2+1\right) \tag{1}$$

where $\eta = b/a$.

The basic equation for calculation of the intensity diffracted by such a layered crystal of the form

$$I(HK\zeta) = C^2\sum_{m=-N}^{m=N}(N-|m|)exp\left[\pi i(\mathrm{H}+\zeta)m\right]\left\langle exp\left(2\pi iK\Delta_m\right)\right\rangle \tag{2}$$

is based on the approach proposed by Wilson [10] and it is detailed elsewhere [11]. Here, H, K, ζ are coordinates along the directions parallel to the $\mathbf{A}_1^*$, $\mathbf{A}_2^*$ and $\mathbf{A}_3^*$; C is the structural factor for unit layer and it is given by the sort and relative positions of the atoms in the layer; N is total number of the layers in the crystal; $(N-|m|)$ is the number of all possible pairs of the (110) layers being at "distance" m layers; Δ_m is the relative displacement of two layers being at "distance" m layers with respect to one another, <...> signifies averaging over all possible pairs of the layers.

The value $\left\langle exp\left(2\pi iK\Delta_m\right)\right\rangle$ in Eq. (2) has been expressed in terms of a pair correlation function $T(m, k_m)$ that gives the probabilities of finding two layers that are m layers distant from each other; of these m layers k_m layers are in the twin-related orientation. Then,

$$\left\langle exp\left(2\pi iK\Delta_m\right)\right\rangle = \sum_{k_m=0}^{k_m=m} T\ (m,k_m)exp\left(2\pi iK\Delta_{k_m}\right). \tag{3}$$

The twin boundary (TB) distribution law must be known or given to calculate the correlation function. A simple step-like model of the TB distribution has been taken to generate the layer stacking sequence in the crystal. This model assumes that the next TB must not be formed closer to the previous one than at a given minimal distance, l_i; it occurs at other distances, l, with a constant probability α. Two various probabilistic functions, $P_1(l_1,\alpha)$ and $P_2(l_2,\alpha)$, have been given to take into account the experimental observations for the presence of two the most probable thicknesses of the twins. The crystal as a statistical ensemble characterized by values l_1, l_2 and α has been generated using Monte Carlo procedure. The grown in such a way crystal was comprised of 10000 layers, and the correlation function $T(m, k_m)$ was calculated over 300 layers. For this crystal intensity $I(HK\xi)$ has been calculated by Eq. (2) along the reciprocal lattice rods with integer indices H and K ($K \neq 0$). The Eq. (1) implies no effect of the twinning along the reciprocal lattice rods with $K = 0$.

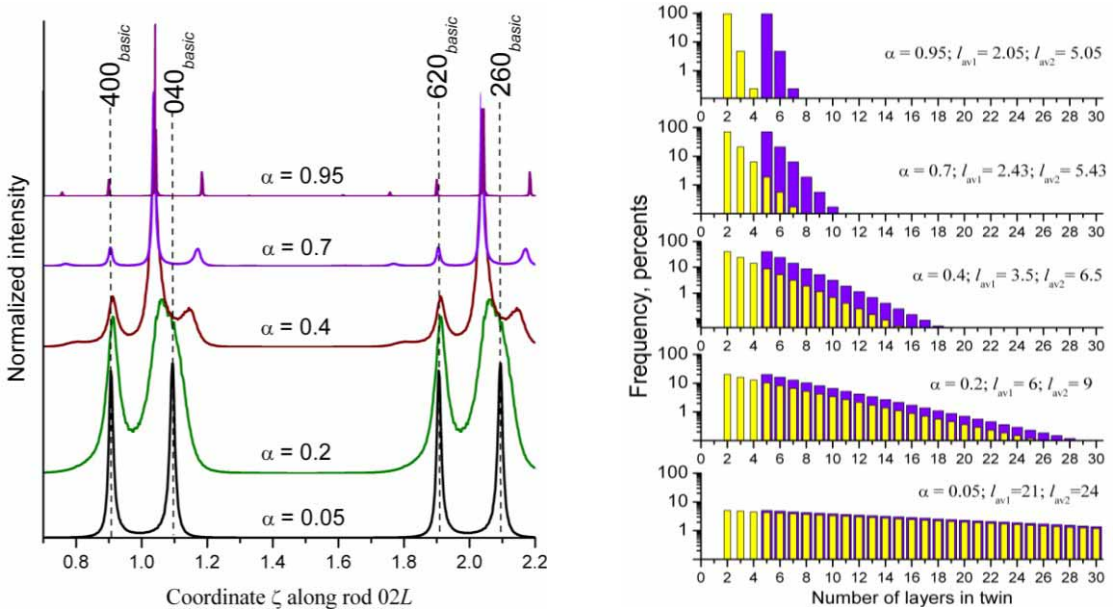
3. Results and discussion

3.1. Effect of twin thickness distribution

The change of the intensity distribution due to an increase of the probability α is shown in Fig. 1a using a seven-layer structure as an example. Such a structure is often derived from the diffraction data for martensite crystals. Scientific papers report a five-layer structure which is often observed in martensites as well as. The diffraction by the five-layer structure resulted from nano-twinning of an orthorhombic crystal is studied in the work [11]. The seven-layer structure has been modeled as the occurrence of TBs with various probabilities α at minimal distances $l_1 = 5$ and $l_2 = 2$ layers in the orthorhombic crystal with a given ratio b/a. Fig.1b shows the twin thickness frequency diagrams corresponded to the intensity distributions in Fig. 1a.

The diffraction peaks related to the basic orthorhombic structure tend firstly to change their profiles and positions with increase of α, that is with decrease of the average thicknesses of the twins. As α increases further, intensity distribution appears as a triplet composed of a strong central diffraction line and two lines of much lower intensity looking as satellites and located to both the left and the right of the central line. It is important that the positions of these strongest lines differ considerably from those related to the lattice constants of the orthorhombic crystal. The strongest lines are much closer to the values of the coordinate ξ that would be if the basic structure was tetragonal or cubic. These special values of ξ are $0\pm n$ and $0.5\pm n$ (n is an integer) for reciprocal lattice rods with, respectively, even and odd values of the index K.

Another diffraction feature is a change of the positions of the strongest lines with increasing α and a non-equidistant arrangement of the satellites with respect to the strongest central lines up to the value α = 1.0. In addition, distances between the satellites and the strongest lines depend on the value of α in such a manner that a decrease of the structure period would be derived if the period is derived from the distances. For example, two different values of the structure period such as P_1 = 8.11 and P_2 = 9.22, P_1 = 7.69 and P_2 = 7.36, P_1 = 7.04 and P_2 =6.99 are derived from the distences between the left and right satellites in the intensity distributions calculated, respectively, for α = 0.4, α = 0.7 and α = 0.95. These values correspond to average periods of 8.66, 7.52 and 7.02 layers.



a) b)

Fig. 1. Intensity distributions along a reciprocal lattice rod 02*L* calculated for various value of the probability α at the ratio *b*/*a* = 0.9 (a) and the frequency diagrams for these values α (b). The frequency in the part (b) is in the logarithmic scale, and the l_{av1} and l_{av2} are average numbers of the atomic layers in the lamellae of the two twin-related orientations, calculated for a given value of the probability α.

From here on, the dashed lines in the figures show the positions related to the peaks of the basic orthorhombic structure with a given ratio *b*/*a* ; the subscripts 'basic' and '7*l*' at the indices of a peak means that the peak is indexed according to the orthorhombic coordinate system derived from $L2_1$ austenite structure and according to the ordered seven-layer $(5\bar{2})_2$ structure, respectively.

3.2. Effect of ratio between the crystal lattice constants

Value of the relative shift of the atomic layers depends on the difference between the crystal lattice constants and, consequently, the ratio *b*/*a* should affect the intensity distribution. The curves in Fig. 2 when compared to each other point out at least two features.

So, strongest peaks of the seven-layer structure are between the positions of the peaks related to the basic orthorhombic structures with the lattice constants resulted in the ratio *b*/*a*=0.94. Main or fundamental peaks are conventional terms to denote such peaks, and the peaks of much lower intensity that located between these are commonly referred to as satellites. However, relative intensities of satellites increases as the difference between the values of *a* and *b* increases (the curves for *b*/*a* = 0.9, 0.87, 0.85) and this progressive increasing can reach a point where some satellites are of a higher intensity than the main peaks (the curve for *b*/*a* = 0.82). Therefore, a high intensity of peak is not necessarily denotative that the peak is one of the main peaks.

As Fig. 3 shows, a similar intensity redistribution between the main and satellite peaks is observed if the intensity distributions along the rods with more and more high *K* are studied. Note also, that both a decrease of the ratio *b*/*a* and an increase of the value K lead to a considerable decrease of the peak intensity of the diffraction reflections.

Second feature of the basic lattice orthorhombicity is that the difference, δ, between positions of the main peaks of multilayer structure and positions of the peaks related to the basic structure increases

progressively as value of the ratio b/a decreases. As to the curves given in Fig. 2, value of the δ increases from 0.039 for $b/a = 0.94$ to 0.115 for $b/a = 0.82$.

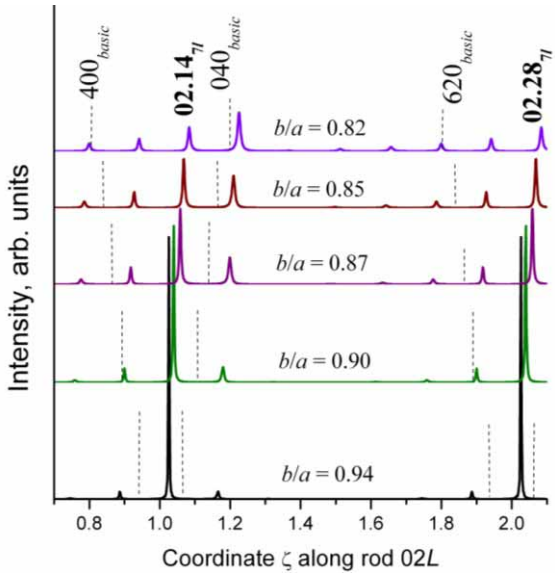


Fig. 2. Intensity distributions along reciprocal lattice rod 02L calculated for various values of b/a at a constant value $\alpha = 0.9$.

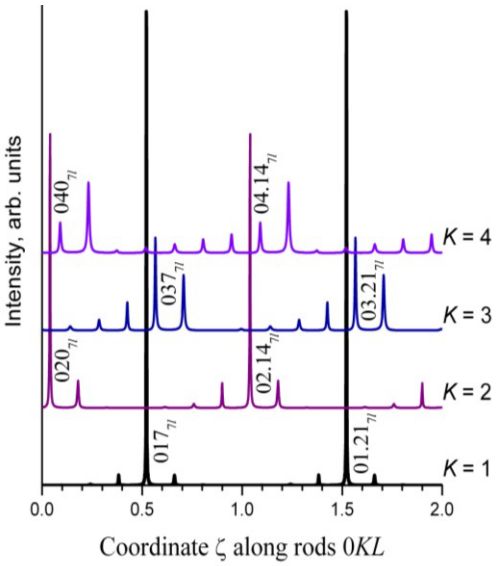


Fig. 3. Intensity distributions along reciprocal lattice rods 0KL calculated at $\alpha = 0.9$ and $b/a = 0.9$.

3.3. Effect of ratio between thicknesses of twin-related lamellae

It seems to be clear that structures resulted from alternation of the twin-related lamellae composed of l_1 and l_2 layers should differ from one another, even though the structure periods, $P = l_1 + l_2$, are the same. For example, seven-layer structure can be obtained by stacking of the twins composed of 4 and 3 layers and of 6 and 1 layers, in addition to the above discussed structure where $l_1 = 5$ and $l_2 = 2$ were given. So, different diffraction pattern for these seven-layer structures must be expected.

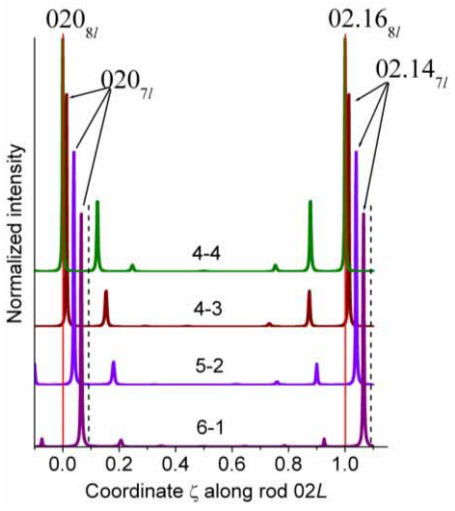


Fig. 4. Intensity distributions along reciprocal lattice rod 02L calculated for various values l_1 and l_2 (6 and 1; 5 and 2; 4 and 3; 4 an 4) at of $b/a = 0.9$ and $\alpha = 0.9$.

Fig. 4 shows the intensity distributions along one of the reciprocal rods calculated for various values l_1 and l_2 with α and b/a hold constant. Because of that $\alpha \neq 1$, the modeled structures are aperiodic with an average period of 7.2 layers instead of 7.0 layers that should be in the case of the ordered seven-layer structures. One of the curves given in Fig. 4 is not related to a seven-layer structure, but it is added to the figure to show a diffraction feature of multilayer structures for which $l_1 = l_2$.

Again, the difference between l_1 and l_2 affect both the peak intensities and the peak positions. A change of the ratio between l_1 and l_2, the period $P = l_1 + l_2$ being kept constant, results in a change of the diffraction peak positions, even though the lattice constants are unchanged. The change appears as a shift of the intensity distribution as a whole toward values of $\xi = 0 \pm n$ or $\xi = 0.5 \pm n$ depending on that even or odd is the value K.

In general, the closer is the ratio l_1/l_2 to unit, the closer are main peaks to these special values of ξ (See, the curves 6-1, 5-2 and 4-3). In the case that $l_1 = l_2$, main peaks are exactly at these special

positions (the curve 4-4). It is not an unexpected result. From the crystallographic point of view, the stacking-modulated structures where structural variations occur at the same distances should be considered as those having a hexagonal symmetry.

4. Conclusion

It is shown that the diffraction pattern of a twin-modulated structure differ considerably from that associated with the basic structure modified by the twin boundaries. The difference is not only in the appearance of satellites but in different positions of main diffraction peaks of the twin-modulated structure and Bragg diffraction peaks of the basic structure. Whatever the period modulation is, the main diffraction peaks are between the positions relating to the basic structure with given values of the lattice constants, a and b. This could be interpreted as apparent increase of the lattice constant b and an apparent decrease of the lattice constant a if these are directly would be derived.

In the case that a modulated structure is not totally ordered, the diffraction peaks are shifted with respect to the positions characteristic of the ordered modulated structure. For given values of the lattice constants of a basic structure and the period of a modulated structure, the value of the shift depends on the twin-thickness distribution (in other words, on a degree of the disorder).

The intensity distributions of the twin modulated structures where the twin boundaries locate at two various the most probable distances, l_1 and l_2, are asymmetric about the point $\xi = 0$. The shift of the intensity distribution with respect to the point $\xi = 0$ increases with increasing the difference between the values l_1 and l_2. So, the main peak, for example, 020 related to the seven-layer structure ($l_1 = 5$; $l_2 = 2$) should be father away from the $\xi = 0$ than the peak 020 of the five-layer structure ($l_1 = 3$; $l_2 = 2$).

It seems to be clear that such an asymmetry inevitably leads to the powder diffraction pattern with splitted both main peaks and satellites. In the type are the structures composed of the nano-twins 3 and 2 layers thick (five-layer martensite) or 5 and 2 layers thick (seven-layer martensite). The only twin modulated structures with the twin-related lamellae of the same thickness should give the powder diffraction patterns where neither main peaks nor satellites are splitted. If the powder diffraction pattern shows, for example, splitted main peaks, and each of the satellites appear as a single peak, other structural features, in addition to the structure modulation, should be supposed.

It is obvious, that all of the diffraction features above discussed can be extended to the modulated structures resulted from a tetragonal crystal where the twins are on the {101} atomic planes. As a final remark, we can conclude that the structure solution of the twin-modulated crystals is a complicated problem, even though the modulated structure is ordered. The structure disorder makes the interpretation of the diffraction patterns more difficult.

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