Diffraction effects due to modulation of orthorhombic crystals by aperiodically arranged twin boundaries

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Abstract. A number of the orthorhombic crystals formed due to diffusionless transformations, of which Ni\textsubscript{2}MnGa crystal is an example, show diffraction patterns suggesting a modulation along the $\langle 110 \rangle$ directions. Nanotwined substructures with aperiodically arranged twin boundaries (TBs) on the (110) planes are found in such crystals. In the work, peculiarities of the diffraction intensity distributions for orthorhombic crystals with the aperiodic TBs arrangement are analyzed. It is shown that the intensity distributions for the twin-modulated structures formed in given orthorhombic crystals differ from those resulted from a wave-modulation of the crystals.

1. Introduction

The crystal structure of Ni-Mn-Ca alloys has been the subject of numerous studies with special attention on the structure of the so-called modulated martensites. For martensitic structures, the neutron, X-ray and electron diffraction measurements have revealed the presence of extra-reflections that suggested ordering in the stacking sequence of the atomic planes along $\langle 110 \rangle$ directions.

Nature of such periodic displacement is still a question to be clarified. Two models are today discussed on equal terms to interpret the layered structures in Ni-Mn-Ga system: as a result of a periodic displacement of the atomic planes [1-4] or a periodic stacking of these planes [3] similar to what was defined for Ni-Al alloys [5,6].

Recent HRTEM studies have shown that nanotwinned substructures are characteristic of Ni-Mn-Ga modulated martensites [7]; the TBs on the (110) plane are not arranged periodically throughout an extended area so that the number of atomic layers in the twin-related lamella only predominantly equals 4 and 2; 5 and 2; 5 and 5; 7 and 5-layers for martensites are characterized by modulation periods of $6d_{110}$, $7d_{110}$, $10d_{110}$, and $12d_{110}$, respectively. Comparison between the SAED patterns and the HRTEM images gave evidence that the number of extra-spots correlates to the sum of the most probable thicknesses of twin-related lamella.

The number of layers in these lamellas (distances between nearest (TBs)) is not strictly fixed values of $l_1$ and $l_2$; these values are just the predominant thicknesses and there are domains of other thicknesses. Deviation from these values allows an assumption to be made that arrangement of the TBs in the crystals is rather of a short-range order than of a long-range order.

Effect of the wave-modulations on the diffraction patterns is well studied [8]. The manner in which aperiodic arrangement of the TBs affects the diffraction pattern of an orthorhombic crystal should be found to provide a means of distinguishing between the wave-modulated and twin-modulated structures. So, the diffraction intensity distributions from orthorhombic crystals containing
aperiodically arranged TBs on (110) plane have been calculated and a comparison has been made between the diffraction features caused by these two types of modulations.

2. XRD pattern simulation

Assuming that twinning only changes the stacking sequence of the atomic layers without changing the composition and structure of these layers, the crystal structure as a whole can be given as a stacking of the layers parallel to plane (110).

It is convenient to choose a new coordinate system \((A_1, A_2, A_3)\) instead the coordinate system \((a, b, c)\) derived from the axes of orthorhombic phase (Figure 1). The relation between \(A_1, A_2, A_3\) and \(a, b, c\) is seen to be the following:

\[
A_1 = c; A_2 = \frac{1}{2} \mathbf{a} - \mathbf{a}; A_3 = \frac{n^2 \cdot \mathbf{a}}{(n^2 + 1)} + \frac{\mathbf{b}}{(n^2 + 1)}
\]  

(1)

where \(n = b/a\). So in the new coordinate system, the close-packed planes are planes (001), and the plane shear direction is [010]. Further on the indexation of the crystallographic planes and the associated planes diffraction peaks will correspond to the new coordinate system.

The position of the \(n\)th layer (001) relatively origin in a twinned crystal can be given as

\[
r_n = \frac{1}{2} A_3 n + \frac{1}{2} A_2 n + \frac{1}{2} A_1 n + \delta_0 n - 2 k_n \delta_0
\]

(2)

where \(\delta_0 = \frac{n^2 - 1}{2(n^2 + 1)}\); \(k_n\) is the number of the layers being in the twinned orientations, as compared with the origin layer, between the origin and the \(n\)th layers. According to the kinematic diffraction theory [9], distribution of the diffraction intensity from a twinned crystal composed of \(N\) identical layers along [001] can be written as in the following form

\[
I_{HK} \approx C^2 \sum_{m=-N}^{m=N} \exp \left[ 2i \left( \mathbf{H} \mathbf{r} + \zeta \right) \right] \exp \left[ \pi \mathbf{K} A_m \right],
\]

(3)

where \(m\) is a distance between two atomic layers; \(A_m = \left[ \frac{n^2 m}{n^2 + 1} - \frac{(n^2 - 1) k_m}{n^2 + 1} \right]\); \(k_m\) is the number of the layers being in the twin orientation between two atomic layers are spaced at interval \(m\) atomic layers; \(\zeta\) is the variable along [001]. It is seen from Eq. (3) that the term \(\left\langle \exp \left[ \pi \mathbf{K} A_m \right] \right\rangle\) is a constant if \(K = 0\). So in this case the stacking of the layers does not affect the intensity distribution.

It follows from (3) that for the intensity to be calculated value of the factor \(\left\langle \exp \left[ \pi \mathbf{K} A_m \right] \right\rangle\) must be determined; the value is dependent on the TBs arrangement in the crystal. In the framework of the models, crystals containing the TBs of which arrangement has been given by different statistical lows were generated using the Monte Carlo procedure. The «grown» in such a way crystals were comprised of 10000 layers, and the \(\left\langle \exp \left[ \pi \mathbf{K} A_m \right] \right\rangle\) term was calculated over 300 layers. For this crystal intensity \(I_{HK} \approx \) was calculated by Eq. (3) along the reciprocal lattice rods with integer indices \(H\) and \(K\) (\(K \neq 0\)). The intensity distributions were calculated for a constant ratio between the lattice constants \(a\) and \(b\), \(b/a = 0.94\).
3. Results of XRD pattern simulation

Let us describe TB arrangement the crystal using a statistical approach based on assigning a priori probability $P(l)$ of a given TB location at $l$ interplanar distance from the TB nearest to it. Such a model of TB arrangement in the crystal follows from the assumption of establishment of an interaction between the nearest TB which depends on the distance between them only and does not depend on the arrangement of other TBs (short-range order in TBs arrangement).

In the simplest case if a “repulsion” between nearest TBs takes place at the distances smaller than $l_i$ layers, each 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 certain constant probability $\alpha$:

$$P(l) = \begin{cases} 0, & \text{if } l < l_i \\ \alpha, & \text{if } l \geq l_i \end{cases}.$$  

(4)

With such a arrangement of the nearest TB, the probability of detection of two TBs at distance of $L$ layers from each other can be expressed as $w(L) = \alpha(1-\alpha)^{L-1}$. Allowing for (4) at $L < l_i$, $w(L) = 0$, and at $L \geq l_i$, $w(L) = \alpha(1-\alpha)^{L-1}$. Therefore, the most probable distance, at which two nearest TBs can occur, will be at $L = l_i$. It is seen that if parameter $\alpha \to 1$, then $w(l_i) \to 1$, i.e. a long-range order in TB arrangement is established.

Considering that the nearest TBs, essentially, are boundaries of a twin domain, at crossing which the crystal orientation changes to a twin orientation, it may be assumed that the TB interaction will depend on orientation of the domain separating these TBs. Two models of the TBs distribution in the crystal, namely a single-mode and a bimodal, are possible in a general case. The single-mode distribution results from independence of the probability $P(l)$ on the twin lamellae orientation. If such dependence takes place, the parameters characterizing the TBs arrangement at various points of the crystal should be different so that a bimodal TBs distribution will be observed. In general case, the domain orientation could affect not only the most probable distance between two neighboring TBs, but also the probability of the TB occurrence. In the case that the probability distributions (4) are taken for both modes, the difference between the modes is given by different values $l_1 \neq l_2; \alpha_1 \neq \alpha_2$.

3.1. Single-mode arrangement TBs.

Let us the probability of the occurrence for each next TB is independent on the orientation of the twin-lamellae located just ahead the TB. This means that $l_1 = l_2 = l; \alpha_1 = \alpha_2 = \alpha$. A change of the diffraction pattern depending on the probability $\alpha$ is illustrated below by the example of a structure characterized by value $l_i = 5$. Figure 2 gives the intensity distributions calculated for the structures formed at various $\alpha$.

As at small values $\alpha$ (for instance at $\alpha = 0.1$), the crystal consists of alternation of relatively thick twin domains (average lamel thickness in this case will be equal to $\bar{L} = l / \alpha$ layers) the reciprocal lattice identity period will show two diffraction peaks near the positions related to $b/a = 0.94$. With increasing $\alpha$ to 0.3 the main diffraction peaks become progressively broader, and the intensity distribution as a whole is inhomogeneous. Notice that extra peaks appear at the positions related to a tetragonal structure ($a = b$). Intensities of these extra peaks increases as $\alpha$ increases and, for a range of the $\alpha$ values, intensity distribution along a reciprocal lattice rod appears as a set of triplets composed of central diffraction line and two strong lines. New extra peaks form as $\alpha$ increases still further (curves for $\alpha = 0.5-0.7$ in Figure 2). It is evident from comparison of the curves that all the peaks change their positions as $\alpha$ changes. The peaks are shifted towards both smaller and higher values of coordinate $\zeta$. In any case, as $\alpha$ increases every peak approaches the position of the closest peak inherent in the ordered structure.
Therefore, higher values $\alpha$ give the intensity distributions showing a series of almost regularly spaced peaks as it is shown in Figure 2 for $\alpha = 0.7$. The positions of the strongest peaks are worthy of special attention in that the peaks are at the positions corresponded to a crystal with $a = b$. So, a single-mode distribution of the TBs in an orthorhombic crystal causes the diffraction pattern along <110> rods that resembles the diffraction pattern from a modulated crystal of a tetragonal symmetry with period of $10d_{110}$. In the case that a tetragonal crystal is modulated by commensurate wave of the period $10d_{110}$ the related diffraction pattern should show the same series of regularly spaced peaks [8]. So, for $\alpha > 0.7$ the diffraction intensity from the aperiodic twin-modulated structure is very similar to that from the wave-modulated structure of the same modulation period. Such a similarity leads to problems in an effort to find symmetry (orthorhombic or tetragonal) of the crystal and nature of the crystal modulation (aperiodic twin-modulated or wave-modulated. On the other hand, it is should noted that unlike the diffraction patterns of a crystal with wave modulation, the diffraction pattern of a crystal aperiodically modulated by twin boundaries, has its special features. This is manifested, primarily, in that the most intensive peaks in the identity period (base peaks), the position and shape of which are determined by the parameters and symmetry of the crystal lattice and degree of its perfection, do not change their characteristics at wave modulation of the crystal, irrespective of the type of its wave modulation [8, 10]. The given example shows that the shape of the most intensive peaks, which can be identified as the base ones, i.e. inherent to the crystal proper, depends on the parameters of TB aperiodic arrangement. Therefore, comparison of the profiles of base diffraction peaks, located on reciprocal lattice rods with $K = 0$ and $K \neq 0$ allows establishing the type of crystal modulation without using HRTEM methods.

3.2. Bimodal arrangement TBs.

We will consider as an example the case when a bimodal arrangement of the TBs in an orthorhombic crystal takes place assuming that (4) holds for both modes with $l_1 = 2$ and $l_2 = 3$. We have restricted ourselves to the case when $\alpha_1 = \alpha_2 = \alpha$, although the difference between $\alpha_1$ and $\alpha_2$ should affect the diffraction pattern as well.

Figure 3 gives the intensity distributions calculated for structures at various $\alpha$. At small values ($\alpha = 0.1$) the diffraction pattern is similar to the one shown in Fig. 3 in the case of single-mode modulation of the crystal. However, as $\alpha$ increases to 0.3, the diffraction peaks tend to change both their profiles and positions in a different way. A redistribution of the intensity also occurs so that one of the peaks becomes much stronger than the other. As $\alpha$ increases to 0.3, a weak diffuse extra peak tends to form between the $a$- and $b$-diffraction components. The extra peak is only close to the position related a structure with $a = b$, as opposed to the case of $l_1 = l_2$ where such a peak is exactly in this position. New extra-peaks form as $\alpha$ increases still further (curves for $\alpha = 0.5-0.7$ in Figure 3). It is evident from comparison of the curves that all the peaks change their positions as $\alpha$ changes. In any case, as $\alpha$ increases every peak approaches the position of the closest peak inherent

![Figure 2. The intensity distribution simulated at various values of $\alpha$ for the crystal with single-mode arrangement of TB at $l = 5$.](image)
in the ordered structure \( \mathcal{B} \). Therefore, higher values \( \alpha \) give the intensity distributions showing a series of almost regularly spaced peaks as it is shown in Figure 3 for \( \alpha = 0.95 \).

Assuming that the intensity distributions given in Figure 3 are experimental diffraction patterns, let us analyze these in an effort to find structural characteristics of the crystal. A conclusion of a modulated structure follows from the presence of extra peaks. Number of the inter-peak intervals between two strongest peaks gives a modulation period of \( 5 \mathcal{d}_{110} \), and this agrees with the sum of the most probable distances between TBs, \( l_1 = 3 \), \( l_2 = 2 \).

As it is seen from Figure 4, the intensity distributions for structures of the same period \( (M = l_1 + l_2) \) but constructed using various values \( l_1 \) and \( l_2 \) show the same number of the peaks. Bimodal nature of the crystal twin modulation is manifested in the absence of symmetry in the distribution of intensity relative to the middle point in the reciprocal lattice identity period. The greater is the difference between \( l_1 \) and \( l_2 \), the more considerable asymmetry is observed. The asymmetry manifests itself as an inhomogeneous broadening and shift of the ‘orthorhombic’ components, if value \( \alpha \) is relatively low, similar to what is shown in Figure 3. When \( \alpha \) value is high enough for formation of extra peaks, the peak positions and intensities are asymmetrical with respect to the midpoint in between the strongest peaks.

Positions of strongest peaks with respect to integer-valued \( \zeta \) give an evidence of an orthorhombic symmetry of the crystal. However, the strongest peaks are markedly shifted from the positions related to the given cell orthorhombicity \( b/a = 0.94 \). The shift is 0.035 (in the units of coordinate \( \zeta \)), whereas the distance from the peak position to the nearest integer value of coordinate \( \zeta \) is only 0.025. Thus, at bimodal \( (l_1 \neq l_2) \) modulation of orthorhombic crystal the position of base peaks is similar to the crystal with orthorhombic symmetry, however, their position in the identity period, as in the case of single-mode modulation, will not correspond to the true crystalline lattice parameters. In this case, these parameters should be included into the range of varied parameters and should be determined from the
experimental data along side the parameters determining the statistics of TB arrangement in the crystal.

5. Conclusions

The results of the calculations demonstrate that aperiodic TBs on the {110} planes in orthorhombic crystals cause the presence of extra peaks in the diffraction patterns along <110> directions of the crystals. The peaks tend to be regularly spaced as the order in the TBs arrangement increases, and their take an δ-shape. The position of the most intensive (base) peaks in the identity period and their shape depend not only on the inherent values of lattice parameters, its symmetry and degree of perfection, but also on its type (single- or bimodal) and degree of TB ordering. Thus, the qualitative similarity of diffraction effects which are due to wave modulation, and aperiodic arrangement of TB in the crystal, makes analysis of experimental data more complicated, both in terms of determination of the symmetry and parameters of the lattice, and the nature of its modulation. In such cases it is necessary to perform quantitative analysis of satellite arrangement in the identity period and shape of base diffraction peaks. In the case of TB aperiodic arrangement, the arrangement of satellites in the identify period will not be equidistant, and the width of basic diffraction peaks located on rods with $K \neq 0$ will be greater that that for peaks with $K = 0$. It should be noted that these differences will be the greater the less ordered are the TB.

Despite the diffraction features resulted from aperiodic TBs arrangement are found to orthorhombic and tetragonal crystals, these would be used to analyze crystals where the formation of TBs occurs due to low twinning shear.

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References
[1] Chernenko V A, Seguí C, Cesari E, Pons J. and Kokorin V V 1998 Phys. Rev. B57 2659
[2] MartynovV V and Kokorin V V 1992 J. Phys. III (France) 2 739
[3] Pons J, Chernenko V A, Santamarta R and Cesari E 2000 Acta Mater. 48 3027
[4] Ullakko K, Huang J K, Kantner C, Kokorin V V and O’Handley R C 1996 Appl. Phys. Lett. 69 1996
[5] Martynov VY, Enami K, Khandros LG, Nenno S and Tkachenko A V 1983 Phys. Met. Metallogr. (USSR) 55 136
[6] Noda Y, Shapiro S M, Shirane G, Yamada Y and Tanner L E 1990 Phys. Rev. B42 10397
[7] Pons J, Santamarta R, Chernenko V A and Cesari E 2006 Mater. Sci. Eng. A 438-440 931
[8] S Van Smaalen 2007 Incommensurate Crystallography (Oxford: University Press)
[9] Wilson A J C 1942 Proc. R. Soc. A 180 277
[10] Ustinov A I, Olishkovskaya L A and Shmyt'ko I M 2004 Crystall. Reports 45 365 and 374