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Structure solution problems for crystals containing planar defects at a high density

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Features of the diffraction patterns due to the presence of twin boundaries in tetragonal crystals and stacking faults in the form of extra or missing layers in perovskite structures are discussed. It is shown that at a high density of defects, a shift of the diffraction peaks from the basic structure causes a significant discrepancy between the observed diffraction pattern and the results expected from a naive application of Bragg's law. For some cases, approaches are proposed that allow to prevent the determination errors of the lattice constants and other parameters of the disordered structures.

Анализируются особенности дифракционных картин, обусловленные наличием двойниковых границ в тетрагональных кристаллах и дефектов упаковки в виде дополнительных или отсутствующих слоев в перовскитных структурах. Показано, что при высокой плотности таких дефектов смещение пиков от базисной структуры вызывает существенные несоответствия между наблюдаемой дифракционной картиной и результатами, ожидаемыми исходя из простого применения закона Брэгга. Для некоторых случаев предлагаются подходы, позволяющие избежать трудностей при определении параметров решетки и других характеристик таких разупорядоченных структур.

1. Introduction

Crystal lattices of many functional materials are distorted, among other factors, by the presence of planar defects (PD). Twin boundaries and stacking faults are the PD observed often in crystalline materials. Twinning is known to be a common feature for a number of the materials undergoing diffusionless (martensitic) transformations resulting in a reduced symmetry of parent phase structure. The interest in the study of twinned structures is intensified in the last decade in connection with the relationship of the shape-memory phenomenon to the formation of the so-called modulated structures [1–6]. According to the high resolution TEM results [3, 4] the modulated structures are to be considered as a stacking sequence of twin-related lamellae of several interplanar distances thick; the stacking sequence is not well-ordered, but a predominant twin thickness is only observed.

The recent studies of complex perovskite-like oxides (ferroelectric, piezoelectric, magnetoresistive, and high-T_c superconducting materials) have found the structure disorder in the crystals due to missing or extra layers resulting in faulting of a basic structure along **c** axis, with no disorder along **a** and **b** axes being observed [7–15]. Such defects in the perovskite-related structures are often interpreted as a special kind of stacking faults. Considering that the defects affect considerably the material properties, the methods are required that would provide the characterization of such disordered structures. The direct observation of the stacking sequence in layered materials by HRTEM is, of course, a very useful method. However, HRTEM provides data from a very limited area and the data may not represent the entire sample. So, the use of HRTEM only may be insufficient if the specific characteristics of the disordering

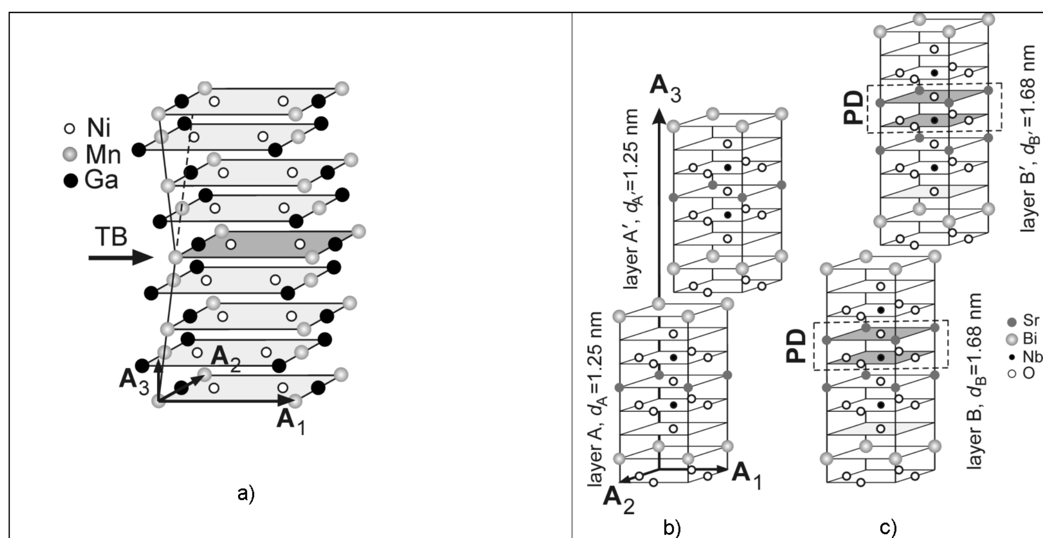

Fig. 1. Representation of crystals as layered structures: (a) stacking sequence of the (101) atomic layers in tetragonal crystal containing TB (Ni_2MnGa structure as an example); (b) structural layers in perfect $SrBi_2Nb_2O_9$ structure; the layer A(A') is a half of the unit-cell; (c) the presence of PD as two extra $SrO–NbO_2$ planes in layer A results in the formation of a new layer B which is considered as a half of the unit cell of perfect $Sr_2Bi_2Nb_3O_{12}$ structure.

have to be found. In this case, diffraction methods seem to be very useful to find the structural properties of the disordered stacking sequence in a bulk sample. This is confirmed by the fact that the regularity disruption in the stacking order or, in other words, the PD appearance, affects considerably the electron, neutron, and X-ray diffraction patterns.

The peak broadening, streaking, shift of peak positions, and intensity modulation are the diffraction features well-known from the experimental data and theoretical works aimed at the study of crystal structures disordered by PD. In many cases, these features are pronounced and, therefore, they should be used to examine stacking disorder, provided that a correlation between parameters of the diffraction pattern and stacking pattern is known. On the other hand, the same diffraction features may cause difficulties in structural characterization of the basic structure where the PD are occurred. This is especially true in regard to the positions of the basic structure diffraction peaks which the PD, if present, may shift considerably from those related to the values for the basic structure lattice constants. So, a significant discrepancy between the observed diffraction pattern and the results expected from a naive application of Bragg's law could arise.

Thus, the problem is that on the one hand, the basic structure structural properties are to be determined properly to characterize the stacking sequence. On the other hand, if the PD effect is disregarded, the shift of the peak positions due to the presence of PD presents difficulties in an attempt to determine these structural properties basing on the peak positions. This work discusses problems in the crystal structure solution caused by the effect of various PD on the basic structure peak positions and the approaches intended to correlate the PD density and distribution with the peak positions.

2. Models of crystals and calculation technique

To calculate the intensity diffracted by a layered structure, it is convenient to choose the coordinate system where two axes lie in one of the layers where the stacking is considered and third axis is normal to the layer. The structures and the coordinate systems ($\mathbf{A}_1$, $\mathbf{A}_2$, $\mathbf{A}_3$) taken in the calculations are shown in Fig. 1. So, the new coordinate system $\mathbf{A}_1 = \mathbf{c} - \mathbf{a}$; $\mathbf{A}_2 = \mathbf{b}$; $\mathbf{A}_3 = \mathbf{a}\cdot\eta^2/2(\eta^2 + 1) + \mathbf{b}/2(\eta^2 + 1)$ derived from the axis ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$) is suitable for representing tetragonal crystal containing TB of the system (101), <10−1> ($\eta = c/a$); for perovskite-like structures, $\mathbf{A}_1 = \mathbf{a}$; $\mathbf{A}_2 = \mathbf{b}$; $\mathbf{A}_3 = \mathbf{c}$ where ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$) is the conventional coordinate system of a tetragonal crystal.

The Monte Carlo simulation technique based on the matrix method by Kakinoki and Komura [16] and the difference equation method by Wilson [17] have been used to calculate the scattering intensity, $I(H, K, \zeta)$, in the reciprocal space. Here, H, K, ζ are coordinates along the directions parallel to the $\mathbf{A}_1$* $\mathbf{A}_2$*, and $\mathbf{A}_3$*. The calculation procedures are detailed e.g. in [18–25], we only emphasize some important things. The assumption of structural order in the planes of layers and a disorder in the stacking sequence of the layers results in that the scattering intensity should be calculated along the reciprocal lattice rods prespecified by integers H and K considering ζ as a continuous variable along $\mathbf{A}_3$*. The Monte Carlo approach allows the intensity calculation for any PD type, provided that stacking model of the layers is given. The stacking model describes in a probabilistic way the position and type of the next layer depending on the preceding layers. The probabilistic laws will be discussed where appropriate in the following sections.

3. Crystals containing coherent twin boundaries of the (101), 10–1 system

The diffraction patterns have been shown to be very complex for crystals containing coherent twin boundaries at a high density [18–23]. It was found that no simple correspondence is observed between any characteristic of the diffraction pattern and a parameter of the twinned structure. In particular, both average thickness of the twins and dispersion of the twin thickness distribution affect the peak profile widths and even positions of the tetragonal doublet components.

Crystal of a low cell tetragonality: single mode distribution of twins. The results discussed in this section relate to tetragonal crystal with the ratio $c/a = 1.01$. An example of such crystal is the ferroelectric $BaTiO_3$ where a variety of twinned structures was found depending mainly on the material grain size. The twins are assumed to be distributed in the crystal according to a log normal function $P(n) = f(\mu, \sigma)$, where n is number of the (101) planes in a twin, μ is the distribution midline, and σ is the distribution dispersion. The thickness distributions were the same for both twin-related domains, so that the twin distribution over the whole crystal is a single-mode function.

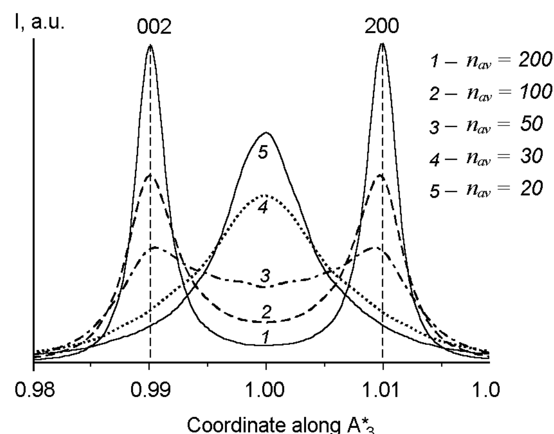

Fig. 2. Intensity distributions calculated in a range of the reciprocal lattice sites 002/200 for a crystal containing twins of various average thickness, n_{av}. To provide different values n_{av}, μ value of the log normal distribution was varied in the calculation, the distribution dispersion, $\sigma = 2.0$, being constant. The vertical dashed lines show the positions related to the given ratio $c/a = 1.01$.

A change in the diffraction pattern due to a decrease of the average twin thickness, other structural parameters being constant, is illustrated in Fig. 2. It is seen that the components of the tetragonal doublet tend to be broadened with decreasing twin thickness, n_{av}. The broadening has a pronounced asymmetry; as a result, a "plateau" is formed between the peaks that increases in its intensity as the average twin thickness decreases. A further increase of the "plateau" intensity with decreasing average twin thickness down to a critical value, n_{cr}, results in the formation of one very broad peak instead of the tetragonal doublet. It is to note that the peak width decreases as the average twin thickness decreases still further, and the peak position is consistent with a 'cubic' structure with the lattice constant value $(a + c)/2$.

Value of the twin thickness distribution dispersion may be considered as an indication of order (or disorder) in the twin boundary distribution in the crystal. For low values of the twin distribution dispersion meaning that twins tend to order to form a superstructure, the number of peaks and their positions are closely related to the average twin thickness. Fig. 3 demonstrates what the diffraction changes occur due to a decrease of the dispersion, σ, in the case of relatively thick twins. At first, profiles of the tetragonal peaks tend to be broadened

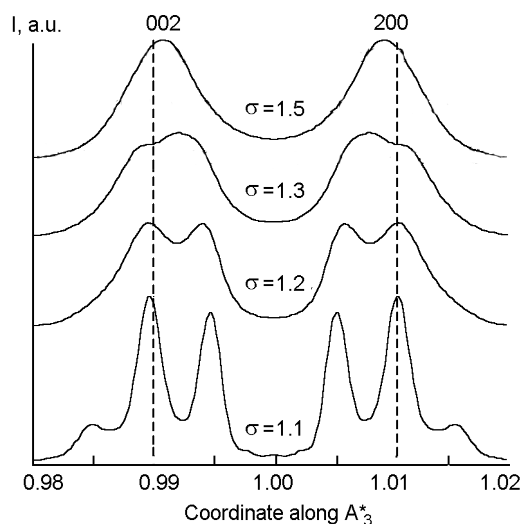

Fig. 3. Intensity distributions calculated in a range of the reciprocal lattice sites 002/200 for a crystal containing twins distributed in the crystal according to a log normal function at different distribution dispersion values, σ, the average thickness $n_{av} = 100$ layers being constant.

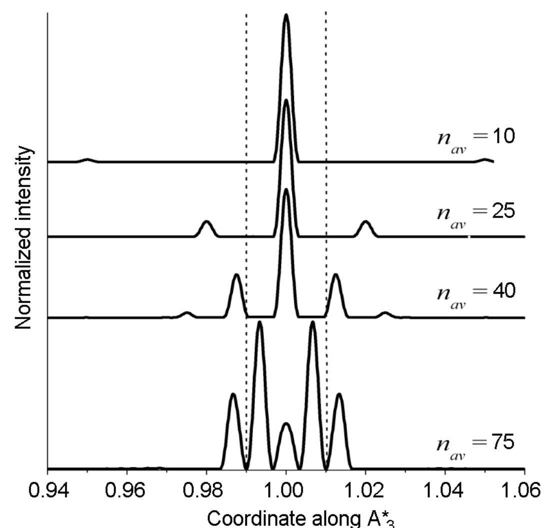

Fig. 4. Intensity distributions calculated in a range of the reciprocal lattice sites 002/200 for a crystal containing twins of various average twin thickness, n_{av}, the distribution dispersion $\sigma = 1.1$ being constant.

as the σ decreases and then the peak profiles take an irregular form and split into components. The number and positions of the peaks depend on the average twin thickness. No peaks at the positions of the "cubic" structure are observed if the average twin thickness is relatively large as it is seen, for example, in the curves calculated for n_{av} value of 100 layers (Fig. 3). However, an intense peak at this position is already seen in the curve calculated for $n_{av} = 75$ layers (Fig. 4). The peak intensity increases still further with decreasing average twin thickness, and other peaks become less intense.

An important point is that if the crystal constitutes a sequence of thin twins at any twin thickness distribution dispersion, no peaks in the diffraction pattern are observed at the positions directly related to a specified c/a ratio. The same is also true when crystal is composed of thick twins at a low dispersion value of the twin thickness distribution. So, a decrease of the twin thickness distribution dispersion and average twin thickness may result in such positions of the diffraction peaks that wrong values of the lattice constants and even wrong symmetry of the lattice could be concluded if the effect of the twins on the diffraction will be disregarded.

Crystal of a high cell tetragonality: bimodal distribution of twins. The diffraction features due to coherent twin boundaries in tetragonal crystal of a high cell tetragonality are demonstrated in what follows taking the so-called modulated structures as an example. It is just the ordering in the twin boundary distribution that is supposed to cause the formation of the modulated structures, and examples are found in such materials as magnetic shape memory alloys. The twins in those structures are very thin and consist of several atomic layers, and the most structures show the twin-related domains of different thickness. So, two various functions are required to describe the thickness distributions for the ordered domains of two orientations. A short range order in the twin boundary distribution described by two probabilistic functions, $P_1(n_1, \alpha)$ and $P_2(n_2, \alpha)$, was taken as a model of the twinned crystal. This model assumes that a next twin boundary cannot be formed closer to the previous one than at a certain minimum distance of n_1 (101) layers and n_2 (101) layers; at other distances, n, it is formed with a constant probability α.

To be specific, let us consider the cases when the most probable twin thickness values are $n_1 = 3$ and $n_2 = 2$, and the distribution dispersion and the related average twin thicknesses, n_{av1} and n_{av2}, decrease at increasing α from a near-zero value to that approximating unity. Fig. 5 demonstrates the changes in the diffraction pattern from a tetragonal crystal if the crystal is twinned

so that the twins are arranged in the above way. It is seen that after the correlation in the twin distribution has progressed to the point where extra peaks formed (the curves *4–7* in Fig. 5), no diffraction peaks are observed in the positions that should be for the non-twinned crystal with the specified lattice constants. This raises the question of whether any peak in such diffraction pattern can be considered as relating to the basic tetragonal structure. It is an important question, because the most intense peaks in the diffraction patterns of this kind are usually associated with a basic crystal with corresponding, that is modified, lattice constants.

In addition, positions of the peaks near to the most intense ones depend on the order parameter so that the distance between the peaks increases as the structure becomes more and more ordered. The point may be a problem in finding true modulation period of such structure if the twin ordering is insufficient to provide all peaks of a detectable intensity related to the structure.

4. Crystals containing extra or missing layers as random stacking faults

To show what problems are encountered in the solution of such disordered structures using the diffraction techniques, let consider the analysis results of the diffraction patterns for two *c*-oriented SBN films [24]; one of the films has the stoichiometric composition $SrBi_2Nb_2O_9$ (Film #1) and other is bismuth deficient (Film #2). Similar problems with structure solution may occur for other disordered perovskite-like crystals, for example for high-temperature superconductors of the Bi–Sr–Ca–Cu–O system [25].

The HRTEM study [10] of a non-stoichiometric composition sample has shown the presence in of structural fragments with a periodicity along *c*-axis other than that of the structural fragments in the stoichiometric sample. The additional structural fragments did not always form a whole unit cell, but were often only a half of the unit cell and, therefore, they should be considered to be occurred due to stacking faults. The film #1 has shown the diffraction pattern where peaks related to the $SrBi_2Nb_2O_9$ compound structure with *c* lattice constant of 2.505 nm are only presented. Basing on complex profiles of the diffraction peaks in the pattern from the film #2, it was suggested that the film

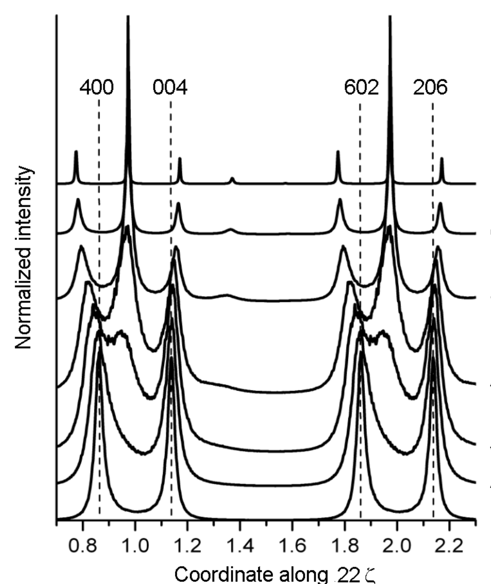

Fig. 5. Intensity distributions calculated in a range between the reciprocal lattice sites 400/004 and 602/206 for a tetragonal crystal with the ratio $c/a = 0.87$ containing twin-related domains of different average thicknesses n_{av1} and n_{av2}: (*1*) — $\alpha = 0.1$, $n_{av1} = 12$, $n_{av2} = 11$; (*2*) — $\alpha = 0.2$, $n_{av1} = 7$, $n_{av2} = 6$; (*3*) — $\alpha = 0.3$, $n_{av1} = 5.3$, $n_{av2} = 4.3$; (*4*) — $\alpha = 0.3$, $n_{av1} = 4.5$, $n_{av2} = 3.5$; (*5*) — $\alpha = 0.6$, $n_{av1} = 3.7$, $n_{av2} = 2.7$; (*6*) — $\alpha = 0.8$, $n_{av1} = 3.25$, $n_{av2} = 2.25$; (*7*) — $\alpha = 0.95$, $n_{av1} = 3.05$, $n_{av2} = 2.05$. The vertical dashed lines show the positions related to the given ratio c/a.

structural state should be characterized as a mixture of at least two phases rather than a single one. The phase $SrBi_2Nb_2O_9$ (the so-called phase "$m = 2$" or SBN) should assumed to be one of the phases. Considering the HRTEM results, the compound $Sr_2Bi_2Nb_3O_{12}$ (phase "$m = 3$") should be the second phase. The attempts to measure the *c* lattice constants of the structures "$m = 2$" and "$m = 3$" from the peak positions have shown that no regularity in the measured scattered c lattice constants is observed (Fig. 6). Note that the zigzag dependences (like that shown in Fig. 6) of the lattice constant on the peak index are typical of one-dimensionally disordered structures. Thus, we may conclude that both structural parts, "$m = 2$" and "$m = 3$", are imperfect and contain stacking faults.

The question arises as to what of these calculated values is true value of the *c* lattice constant. (The term "lattice constant" in a disordered structure has obviously a local meaning in the areas where there are more than two adjacent structure layers). The answer is of interest not only as such, but it

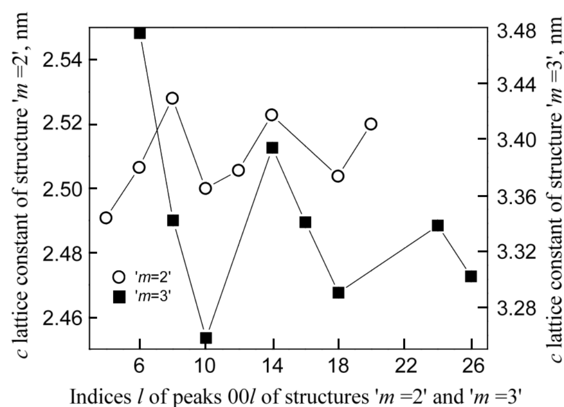

Fig. 6. The c lattice constant values for structures "$m = 2$" (left vertical axis) and "$m = 3$" (right vertical axis) derived from positions of the peaks attributed to the structures in experimental X-ray diffraction scan from a film of the xx composition [24].

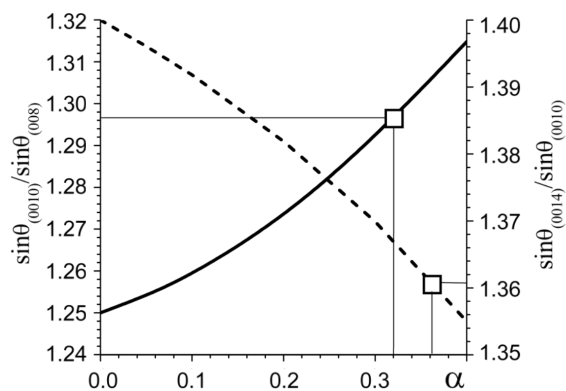

Fig. 7. The ratio $\sin\theta_{00l_i}/\sin\theta_{00l_j}$ calculated for the diffraction angles related to the (0010) and (008) peaks of the "$m = 2$" structure containing random layers "B" of density α (left vertical axis and solid curve) and to the (0014) and (0010) peaks of the "$m = 3$" structure containing random layers "A" of density α (right vertical axis and dashed curve). The squares in the plot show the values of $\sin\theta_{00l_i}/\sin\theta_{00l_j}$ derived from the related peak positions in the experimental XRD pattern.

is necessary to find features of the structure disorder, first of all, the density of stacking faults. A problem is that the position of each peak is dependent on the density of stacking faults and, in addition, on the ratio between the sizes, d_A and d_B, along c axis of the layer "A" related to the matrix structure and the layer "B" formed due to the stacking fault (as to the "A" and "B" layers, see Fig. 2b, c). Unfortunately, there is no way to find the lattice constant directly from the peak positions. However, assuming that the film structure is a random stacking of the two structural layer kinds, estimation of the stacking fault density, α, is possible at unknown values of the lattice constants, using the relative positions of certain pairs of the peaks. So, first step in the structure solution should be characterization of the stacking fault density rather than of the lattice constants values.

The relative position of peaks $00l_i$ and $00l_j$ is expressed in terms of the ratio $k(\alpha) = \sin\theta_{00l_i}/\sin\theta_{00l_j}$ between sines of the diffraction angles corresponding to the peaks. The relative positions were shown to depend on the density of random stacking faults, but independent of the ratio between d_A and d_B. Some of the dependences are shown in Fig. 7 where the values k_{exp} are shown as well derived from positions of the peaks in the experimental XRD pattern. From these results, the stacking fault density in the "$m = 2$" phase (the stacking fault is a half of the "$m = 3$" unit cell) is about $\alpha_1 = 0.32$ and in the "$m = 3$" phase (the stacking fault is a half of the "$m = 2$" unit cell) is about $\alpha_2 = 0.36$.

The next step in the structure solution would be determination of the lattice constant c by a fitting procedure with the given stacking fault density. The c value variation range is limited by the fact that some peaks in the experimental pattern are slightly distorted single lines in contrast to other peaks having profiles as complex curves indicating that the peaks are composed of two lines. The positions of the single-line peaks are nearly consistent with the peaks 006, 0012, 0018 of the structure "$m = 2$" and with the peaks 008, 0016, 0024 of the structure "$m = 3$". The values $c_{"m=2"}$ and $c_{"m=3"}$ of the lattice constants derived from the positions of these special peaks are in the 2.495–2.505 nm and 3.330–3.342 nm range, respectively. As Fig. 6 shows, these values are closer to one another than those derived from the positions of other peaks. In addition, these peaks appeared to be considerably less broadened than other observed peaks. So, the c value in the fitting may be varied in the range resulted from the positions of the special peaks $00l$. When comparing the intensity distributions calculated under these assumptions with the experimental pattern, it was found that the two curves are in a

good agreement for $c_{"m=2"} = 2.505$ nm and $c_{"m=3"} = 3.334$ nm.

The presence of such special peaks is due to a minimal shift of the peaks from the regular positions if stacking faults occur in the crystal. The indices l of the peaks follow a rule which is determined by the ratio between the sizes (measured along c axis) of the structural layer related to the matrix structure and that formed due to the stacking fault. Only in the case that the ratio $d_{"A"}/|d_{"A"} - d_{"B"}|$ equals exactly to an integer, peaks are possible having the positions and profiles absolutely unaffected by the presence of stacking faults. It seems to be clear that this integer is just the periodicity in the indices l of the peaks $00l$ which should show their positions related to the same value of the c lattice constant.

5. Conclusion

The presented results show that interpretation of the crystal containing planar defects at a high density as a system "basic structure and deviations from the basic structure" may result in misinterpretation of the diffraction pattern from the crystal. This is due to that the diffraction pattern from such a crystal differs considerably from that should be for the defect-free crystal. The difference consists in a change of both number and positions of the diffraction peaks. The latter fact presents a problem when applying standard structural analysis methods to solve such disordered structures disregarding the presence of the defects. Because the diffraction pattern depends in a complicated way on many parameters of the basic structure and planar defects, no methods are yet proposed that would provide a means to identify the disordered structures within a general approach.

The structural properties of the crystals containing stacking faults in the form of extra or missing layers appear to be solvable basing mainly on the positions of diffraction peaks. A necessary condition for such a structure to be solved in this way is the prior knowledge of the dependence between density of the intergrowths and relative positions of the peaks like that discussed above in Section 4. In contrast, for crystals containing twins that tend to order, estimation of structural parameters from the peak positions seems to be impossible even as a first step of the structure solution. Our preliminary study has shown that the cell tetragonality of a twinned crystal affects strongly the relative intensities of the diffraction peaks, other crystal parameters being constant. A fitting procedure using relative intensities of peaks in addition to the peak positions is expected to provide a way to identify the structures properly. There is no doubt that a relation between structure properties of a disordered crystal and parameters of the diffraction pattern from the crystal is too complex to solute the crystal structure by using the diffraction methods only. So, a complex of experimental techniques should be used to study such structures. In this regard, the electron microscopy data on the type of the planar defects may be of particular usefulness if not critical.

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Проблеми визначення структури кристалів з високою концентрацією планарних дефектів

Л.Оліховська

Аналізуються особливості дифракційних картин, що обумовлені наявністю двійникових меж у тетрагональних кристалах і дефектів пакування у вигляді додаткових або відсутніх шарів у перовскітних структурах. Показано, що при високій густині таких дефектів зміщення піків від базової структури спричиняє істотні невідповідності між дифракційною картиною, що спостерігається та результатами, очікуваними виходячи з простого застосування закону Брегга. Для деяких випадків пропонуються підходи, що дозволяють запобігти труднощам при визначенні параметрів гратки та інших характеристик таких розупорядкованих структур.