Z. Kristallogr. Suppl. **26** (2007) 99-104

Powder diffraction characterization of stacking disorder

E. Estevez-Rams[1*], A. Penton Madrigal[1], P. Scardi[2], M. Leoni[2]

[1]Instituto de Materiales y Reactivos. Universidad de la Habana. San Lazaro y L. CP 10400. Habana. Cuba
[2]University of Trento, Dpt. of Materials Engineering and Industrial Technologies, via Mesiano 77, 38050 Trento, Italy.

[*]E. Estevez Rams; e-mail: estevez@imre.oc.uh.cu

Keywords: stacking faults, diffraction, planar disorder, layer structures

Abstract. Different approaches used to analyze stacking disorder by powder diffraction will be reviewed. Some early treatments although general in its mathematical formulation were forced to make strong simplifying assumptions to make their applicability feasible without computer resources. In the most used, approaches, a model of layer interaction is assumed and approximate analytical expressions are. Other developments include the use of Monte Carlo procedures where crystals are "grown" in the computer and diffraction patterns simulated. Other recent approaches return to the general equations of diffraction for a layer structure as a starting point for computer simulations. Finally, other authors have explored the possibility of extracting the stacking information directly from the diffraction data taking into account that the diffraction pattern can be described by a Fourier.

Historical introduction

Many crystals can be considered to be built by the periodic stacking in one direction of atomic layers perfectly periodic in the two other directions. The kind of layer structures can range from the most simple type, where only one type of layer is found, to more complex structures with several type of layers. In any case, the disruption of the periodicity in the stacking order leads to measurable effects in the diffraction pattern of the crystal. In general information about planar disorder can be extracted from line profile analysis of the diffraction patterns. The information of the stacking arrangement contained in the diffraction pattern in most cases is not directly available, and can be further "hidden" by other effects such as other structural imperfections (eg. grain size, dislocation, stress) or instrumental response, both giving additional contribution to the broadening of the diffraction profiles.
The first mention of line broadening in diffraction patterns due to planar disorder was made on the context of stacking faults in hexagonal cobalt in 1930 [1], early analysis were also done by Landau and Lifschitz [2]. Already in 1942 Hendricks and Teller [3] developed the

main arguments to relate the diffracted intensity with the stacking variables. Their treatment considered not only the disorder due to the layer arrangement but also, the occurrence of different layers within the stacking. Their work introduced the idea of considering stacking as an n-layer process where the position and type of the next layer depends in a probabilistic way on the preceding n layers. In their original work, Hendricks and Teller applied their findings assuming a two layer interaction. Jagodzinski [4] on the other hand, worked out the case of a three layer influence, while Gevers [5] studied the four layer interaction considering both deformation and twin faulting which had been previously discerned by Patterson [6]. The general n-layer problem was solved in an elegant way by Kakinoki and Komura [7] that used a matrix formalism to write down the equations for the n-layer Markov process. Alegra [8] further modified the Kakinoki and Komura treatment. More recently, Treacy et. al. [9] showed an elegant recursive solution to the diffraction equations in the general case implemented in the now popular software Diffax. Tybulya et al. [10] has also used the Kakinoki and Komura formalism to study planar disorder in nanocrystals together with other structural defects.

Following the first investigations, Wilson [11] studied the simple model of random deformation faults in hexagonal close packed structures. Wagner [12] also analyzed the case of deformation and twin fault in fcc structures also under the assumption of random faulting. Warren [13] further developed the theory of random faulting in fcc, hcp and bcc metals. In spite of the simple approach of random fauling, the treatment of Warren has been the most used formalism to treat stacking faults in metals. An important correction to Warren approach was given by Velterop et al [14] who showed that in the case of fcc structures, the overlapping of reflections belonging to the same {h k l} family resulted in a more complicated behavior of experimental peaks than those predicted by Warren.

Computer simulations for the analysis of disordered layer structures were performed as soon as the availability of computer resources became widespread. Ising models for the simulation of the dynamics in layer sequencing for close packed structures have been in use for years [15]. The fact that the stacking in close packed structure can be translated to a binary sequence made the use of Ising models very attractive, This models do not only pretend to describe the stacking arrangement but also to give an inside in the actual mechanism of disordering. The works of Pandey and Krishna [16] must be mentioned, they studied several phase transition between different polytypes using the Ising models with a good agreement between the simulated patterns and the experimental ones. Recently, in a mostly overlooked paper [17], the use of Ising models have been strongly questioned on physical grounds which indicates that more theoretical work has to be done in this area. Varn et al. [18] has given a new light to stacking disorder by the use of a deterministic finite state machine as a computation model to stacking order. Their approach, which has received less attention than it deserves, goes beyond the particular interaction scheme adopted and the computational model put forward in their work should prove powerful enough to describe a wide variety of planar disorder problems and polytypes phase transitions. Monte Carlo simulation done initially by Berliner and Werner [19] adopt a “pragmatic” point of view, instead of assuming an interaction model, the computer simulates, on the bases of very simple physical assumptions, a family of stacking ordering which are discriminated against the experimental diffraction pattern until a favorable match is found. This approach has been used by a number of authors, notably Ustinov et al. [20] , Weiss and Capkova [21] and Gosk [22]. The Monte Carlo approach allows a flexible framework where any type of planar defects can be introduced and its effect on the diffraction pattern explored. Its mayor

drawback is the dependence on the researcher ingenuity to "guess" and appropriate stacking model.

Finally another approach recently used is to return to the basic equations of diffraction in a stacking sequence and try to extract physical meaningful information directly from the diffraction data without assuming any stacking or interaction model. Zachariasen [23] was the first to notice that the diffraction pattern of a stack of identical layers can be expressed as a Fourier series, where the coefficients have a direct physical interpretation. Estevez et al. [24] has further developed this idea and showed how to use the Fourier decomposition both as a theoretical and practical tool [25] to approach stacking disorder elucidation from diffraction experiments. This approached has showed that there is still space for analytical developments in the treatment of planar disorder and basic open questions remains to be answered.

The diffraction of disordered layer structures

Under kinematical conditions, the diffraction pattern of a layered crystal, periodic or not, can be described by use of the interference or modulation function Q proportional to the intensity of the diffraction pattern.

The interference function is given by the normalized Fourier transform of lattice equation [24] and can be written as

$$Q(\vec{r}^*) = \frac{1}{N_c}\sum_{w=0}^{Nc-1}\left|F_w(\vec{r}^*)\right|^2 + \frac{2}{N_c}\sum_{\Delta=1}^{N_c-1}\sum_{w=0}^{N_c-\Delta-1}\left|F_w(\vec{r}^*)\right|\left|F_{w+\Delta}(\vec{r}^*)\right|Cos\left[\varphi_w - \varphi_{w+\Delta} + 2\pi\vec{r}^*\cdot(\vec{R}_w - \vec{R}_{w+\Delta})\right] \quad (1)$$

$\vec{r}^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$ is the reciprocal vector and $F_w(\vec{r}^*) = \left|F_w(\vec{r}^*)\right|Exp(i\varphi_w)$ the structure factor. $\vec{R}_w$ is the position of the *w* layer with respect to a common origin for all layers.

All treatments of diffraction by layer structures start from equation (1) or an equivalent expression. The sole use of equation (1) for treating planar disorder implies that faulting affects planes as a whole and therefore, they cross completely the crystal from one side to the other. No account is given for the occurrence of dislocations at the end of faulting planes.

Hendricks and Teller [3], Kakinoki and Komura [7] and Treacy et al. [9] rewrites equation (1) in terms of Markov chain of order n. The layers are considered to be in a finite number of possible states accounting for different structure factors or displacements. Then, the probability of a new layer state is written as a function of the preceding n-layers states. The frequency of layers states is introduced and a transition probability is defined that accounts for the probability that given n-length subsequence, the next layer will be in a particular state. Hendricks and Teller, and the generalization of Kakinoki and Komura used a matricial for-

malism which leads to a secular equation. Treacy and co-workers stated the solution as a recursive procedure. These studies are essentially sequential, as a particular direction in the crystal is assumed as the "growing" direction. This sequential character seems not to be by itself a limiting factor, but the final result of the model is a set of transition probabilities which in general are good to reproduce the diffraction pattern and the crystal sequence, but whose physical meaning is far from clear if it responds to the true sequence dynamics. Furthermore, the seminal work of Blandin et. al. [26] have shown that for many metals and metallic alloys, an effective infinite long range interaction has to be taken into account to explain the occurrence of disorder and polytypes.

Warren [13] considered the case of fcc, hcp and bcc structures where all layers have the same structure factor. The treatment only random considers deformation and twin defects while in the fcc structure faulting only occurs along one of the <1 1 1> directions.

The formalism relates the peak shift and broadening with the deformation (α) and twin (β) faulting probability. Velterop et al. [14] showed that the simplifying assumptions of Warren treatment for the case of fcc structures makes its use unreliable. Especially the fact that a given reflection can be formed by the superposition of the contribution from different planes (h k l) belonging to the same {h k l} family. Each contribution, equivalent in the perfect sequence, can behave differently upon faulting and the broadening and shift of the resulting peak has then a much more complex behaviour than predicted by Warren expressions. Estevez and co-workers [27] have also looked into Warren formalism extending the formalism to higher density of faulting. As a result they have shown that the peak profile describing each component of a given reflection can be given by an analytical close expression which makes it suitable for its incorporation into fitting procedures.

Monte Carlo procedures are flexible enough to accommodate probably any stacking configurations and successful applications of these procedures have been reported by a number of authors [19-22] which gives a useful insight into the effect of different planar defects in the diffraction patterns. The main drawback of the Monte Carlo approach is its limited predictive character. While is very effective in reproducing the diffraction pattern and building the "typical" crystal for such pattern, its use is more limited if we pretend to go from the description of the disorder to the implications for the physical properties. Yet in pathological disordered, not that uncommon, cases Monte Carlo methods are probably the only approach possible to find a description of the layer sequence.

Equation (2) can be written as a Fourier series if we only assume that interlayer distance is kept constant along the stacking arrangement. We will only show here the case when we consider that the only shifts possible perpendicular to the stacking direction, are integer numbers of a fixed vector, then, when each layer has the same structure factor, the interference function can be written as

$$Q(h,k,l) = 1 + 2\sum_{\Delta=1}^{N_c-1} A_\Delta(h,k)Cos[2\pi\Delta l] + B_\Delta(h,k)Sin[2\pi\Delta l] \qquad (2)$$

where the A_Δ and B_Δ coefficients can be related to the probability $P_s(\Delta)$ of finding two layers, Δ-layers apart, and shifted *s* time the minimum shift vector. In the case of powder patterns

the second term in (2) can be dropped. Estevez et al. [24, 25] have used expression (2) to derive some important conclusion on the behaviour of the diffraction reflections as a result of faulting. They have shown that in general that the $P_s(\Delta)$ correlation function can be described as periodic oscillation function multiplied by a decaying term. The decaying factor allows to define a correlation length on the stack of layers as the characteristic scale over which the system losses its memory. The correlation length is a factor that allows comparing the amount of disorder without regard of the actual type of disorder. The oscillating term is a description of the departure of the stacking sequence from its original periodicity.
An important result of equation (2) is that the asymmetric component of a reflection can be related to its symmetric component in an unambiguous manner [27]. This allows reducing the arbitrariness of the peak function describing faulted affected reflections. The case of random faulting in fcc structures has been solved [27] and analytical expression for the peak profile functions have been derived. The asymmetric component for common used peak profiles have been reported [28] which can then be incorporated into fitting procedures.

Open questions

Although the analysis of planar faulting in crystals by X-ray diffraction goes a long way back almost to the beginning of diffraction analysis, there are still many developments to be made. The basic treatment of this type of disorder seems to be well understood but we are still lacking of easily available tools to make this kind of analysis more systematic. The incorporation of existing treatments into more general frameworks where other types of defects are considered is still in its infancy. Much work has to be done, theoretically and from the practical point of view. The question of whether, in the general case, we can split the effect of planar faulting and other defects, such as dislocations, in the diffraction profiles still needs to be answered. There have been recent advances in the understanding of the implications of planar disorder in peak profiles but here too there are still work to be done, especially in assessing the suitability of existing or new analytical peak profiles. How to go from experiment to physical understandable parameters describing disorder and from there to calculating materials properties waits for a complete proper treatment.

References

1. Hendricks, S. B., Jefferson, M. E., & Schultz, J. F., 1930, *Z. Kristallogr*., **73**, 376.
2. Landau, L., 1937, Phys. Z. SowjUn., **12**, 579; Lifschitz, M., 1937, *Phys. Z. Sowj. Un.*, **12**, 623.
3. Hendricks, S. & Teller, E., 1942, *J. Chem. Phys.*, **10**, 147.
4. Jagodzinski, H., 1949, Acta Cryst., **2**, 201; *Acta Cryst.*, **2**, 208.
5. Gevers, R., 1954, *Acta Cryst.*, **7**, 337; *Acta Cryst.*, **2**, 492.
6. Paterson, M. S., 1952, *J. Appl. Phys.*, **23**, 805.
7. Kakinoki, J. & Komura, Y., 1952, *J. Phys. Soc. Japan*, **7**, 30; Kakinoki, J. & Komura, Y., 1954, *J. Phys. Soc. Japan*, **9**, 169.
8. Allegra, G., 1961, *Acta Cryst.*, **14**, 535; 1964, *Acta Cryst.*, **17**, 579.

9. Treacy, M. M. J., Newsam, J. M. & Deam, M. W., 1991, *Proc. Roy. Soc. London A*, **433**, 499.
10. Tsybulya, S. V., Cherepanova, S. V. & Kryukova, G. N., 2004, in *Diffraction Analysis of the Microstructure of Materials*, edited by E.J. Mittemeijer & P. Scardi (Berlin: Springer), p. 93.
11. Wilson, A. J. C., 1942, *Proc. Roy. Soc. A*, **180**, 277.
12. Wagner, C. N. J., 1957, *Acta Metall.*, **5**, 427; *Acta Metall.*, **5**, 477.
13. Warren, B. E., 1969, *X-Ray Diffraction* (Addison-Wesley).
14. Velterop, L., Delhez, R., Keijser, Th. H., Mittemeijer, E. J., & Reefman, D., 2000, *J. Appl. Phys.*, **33**, 296.
15. Uppal, M. K., Ramasesha, S., Rao, C. N. R., 1980, *Acta Cryst. A*, **36**, 356.
16. Schestha, S. P. & Pandey, D., 1996, Europhys. Lett., **34**, 269; Schestha, S. P. & Pandey, D., 1997, *Proc. Roy. Soc. London A*, **453**, 1311.
17. Ahmad, S. & Khan, M. A, 2000, *Phys. Stat. Sol.*, **218**, 425.
18. Varn, D. P., Canright, G. S., & Crutchfield, J. P., 2002, *Phys. Rev. B*, **66**, 174110; Varn, D. P., & Crutchfield, J. P., 2004, *Phys. Letters A.*, **324**, 299.
19. Berliner, R. & Wener, S. A., 1986, *Phys. Rev. B*, **34**, 3586; Berliner, R., Fajen, O., Smith, H. G., & Hitterman, R. L., 1989, *Phys. Rev. B*, **40**, 12086.
20. Ustinov, A. I., Olikhovska, L. O., Budarina, N. M., Bernard, F., 2004, in *Diffraction Analysis of the Microstructure of Materials*, edited by E.J. Mittemeijer & P. Scardi (Berlin: Springer), p. 333
21. Weiss, Z. & Capkova, P., 1994, in *Defect and Microstructure Analysis by Diffraction*, edited by R. L. Snyder, J. Fiala, and H. J. Bunge (Oxford Science Publications), ch. 16.
22. Gosk, J. B., , 2001, *Cryst. Res. Techn.*, **36**, 197; 2003, *Cryst. Res. Techn.*, 38, 160.
23. Zachariasen, W. H., 1947, *Phys. Rev*., **71**, 715.
24. Estevez-Rams, E., Martinez, J., Penton-Madrigal, A., & Lora-Serrano, R., 2001, *Phys. Rev. B*, **63**, 054109; Estevez-Rams, E., Aragon-Fernandez, B., Fuess, H. & Penton-Madrigal, A., 2003, *Phys. Rev. B*, **68**, 064111.
25. Estevez-Rams, E., Penton-Madrigal, A., Lora-Serrano, R., & Martinez-Garcia, J., 2001, *J. Appl. Cryst.*, **34**, 730.
26. Blandin, A. I., Friedel, J. I., Saada, G. I., 1966, *J. Phys.*, **27**, 128.
27. Estevez-Rams, E., Leoni, M., Aragon-Fernandez, B., Scardi. P., & Fuess, H., 2003, *Phil. Mag.*, **83**, 4045.
28. Estevez-Rams, E., Penton, A., Martinez-Garcia, J., & Fuess, H., 2005, *Cryst. Res. Technol.*, **40**, 166.

Acknowledgements. One of the authors (EER) would like to acknowledge the support from the Alexander von Humboldt Foundation.