

Modulated structures at phase transitions

HORST BÖHM

*Institut für Mineralogie der Universität D-44 Münster
Federal Republic of Germany*

Abstract

The characteristic features of modulated structures which appear as intermediate phases between a high-symmetry high temperature phase and a low temperature phase of lower symmetry are described. Two examples (NaNO_2 and LiAlSiO_4) are discussed. For NaNO_2 previously published results are reviewed. For LiAlSiO_4 , the modulation of the structure is interpreted as being caused by the formation of domains which fluctuate in their width. This domain hypothesis is supported by model calculations. The course of structure determination is outlined.

Introduction

In the last two decades an increasing number of examples has been described in which X-ray scattering patterns exhibit features other than the regular arrangement of main Bragg reflections. Among these features are groups of reflections which are usually weak and arranged adjacent to some of the main reflections and which are called satellites. These satellite reflections, which subdivide the unit cell in reciprocal space, can be explained by a periodic distortion of the basic structure. The basic structure which gives rise to the main reflections is thus modified by a modulating function which has a period of several unit cells of the basic structure. The period of such modulated structures may be commensurate or incommensurate with the lattice of the basic structure. It is mainly the incommensurate phases on which scientific interest is focused at present. For these structures the period of the modulation function is an irrational number. The structure cannot be described by a simple superstructure; it has lost its translational symmetry in at least one direction.

The periodic distortion of the basic structure by a modulating function can roughly be classified into two categories: (1) a displacive-type modulation and (2) a modulation of density. In the first case the modulation function affects the atomic positions of the structure, causing periodic shifts in a transverse or longitudinal mode. In the schematic diagram of Figure 1 the case of a transverse modulation is depicted. In the second case the scattering density of otherwise equivalent atomic positions is varied periodically. A real modulation may comprise both

types. Modulated structures have been observed in a large variety of compounds, in minerals as well as in synthetic materials. Some exhibit only one simple pair of satellite reflections, while others show a complex diffraction pattern.

Many compounds (especially minerals) are studied at room temperature as metastable phases which are not in thermodynamic equilibrium. As an example, the intermediate plagioclase feldspars may be mentioned, where pairs of satellites (the so-called "e-reflections") can be observed around the positions of the "b-reflections" (Jagodzinski and Korekawa, 1976). This paper reviews the results for one of the most extensively studied modulated structures, NaNO_2 , as well as presenting new results for LiAlSiO_4 (eucryptite). In NaNO_2 satellite reflections were observed for the first time by Tanisaki (1962) and a first interpretation was given by Tanisaki (1961, 1963) and Yamada *et al.* (1963).

Two examples

Experiments which yield deeper insight into the mechanism of structural modulations have been carried out on phases which are in an equilibrium state. Such phases occur as intermediates between a low temperature phase of low symmetry and a high temperature phase of higher symmetry. It is the knowledge of the structures of both neighboring phases and the study of the phase transition which yields the necessary information for a complete understanding of the modulated structure.

The most prominent feature of an incommensurate modulated structure is the shift of the satellite positions with temperature. The distance between

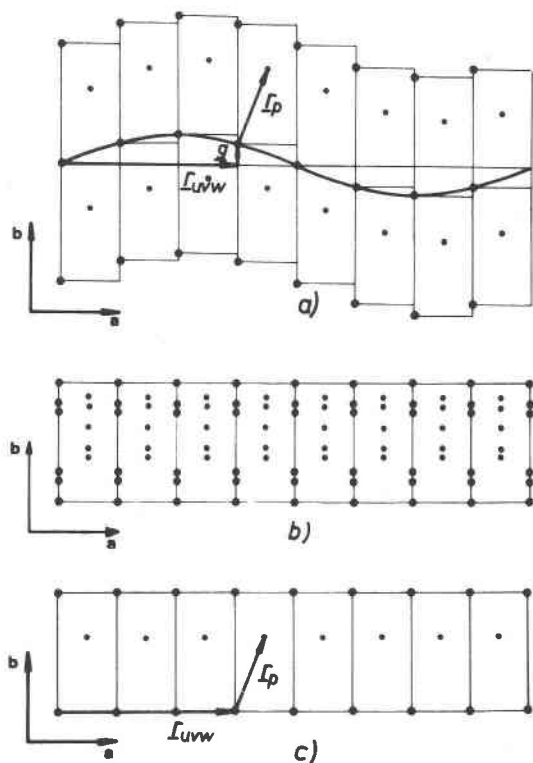


Fig. 1. Modulation of a structure due to a transverse wave (a), the average structure (b), and the basic structure without modulation (c).

satellites and the main reflections seems to vary continuously, which means that the period of the modulation adopts not only rational but also irrational values. This is actually the final proof that a structure has an incommensurate modulation. Figure 2 exhibits such a variation of the modulation period M with temperature in NaNO_2 (Böhm, 1978). The author's results quoted here were obtained from single crystals grown from aqueous solution. Figures 3a and b reveal the characteristic features of a phase transition from a low temperature phase into a modulated phase (Böhm, 1978). In Figure 3a the variation of the 042 reflection of NaNO_2 is exhibited. The photographs were taken on a modified Weissenberg camera (graphite monochromator, $\text{Cu}\alpha$ -radiation, rotating crystal technique). All but the reflections shown were screened by a specially designed screen. By rotating the cassette by a small angle after each exposure the whole sequence of reflections was recorded on the same film as a function of temperature. The 042 reflection is in the center of each row; the direction of the satellite pair is parallel to a^* . This indicates that the structure is modulated along a with a period

of 8 to 10 subcells. In order to obtain reproducible results in such a narrow temperature range, the heating device on the camera needed a long term stability of 0.01°C . In Figure 3b the intensity as a function of temperature is shown for the main and the satellite reflections. It depicts the photometer results from the film of Figure 3a. At the transition temperature there is a sudden appearance of the satellite reflections. In this case just one pair is observed in a very narrow temperature range around 164°C and this particular main reflection 042 disappears at the transition into the modulated phase. When the phase transition into the high temperature phase occurs, the satellites disappear. The lower part of Figure 3a exhibits the phase transition on cooling. It is obvious that there is a small temperature range where both the low temperature phase and the modulated phase coexist. This fact as well as the thermal hysteresis indicate that the transition from the low temperature phase into the modulated phase is of first order. The transition from the modulated phase into the high temperature phase apparently is of second order, since the criteria of the Landau Theory (Landau and Lifshitz, 1958, p. 366) for second order phase transitions are fulfilled. To satisfy the necessary criteria for a second order phase transition (1) the low-symmetry phase must be a subgroup of the space group of the high-symmetry phase, (2) the transformation must correspond to a single irreducible representation of the space group of the high-symmetry phase, and (3) there must not exist third-order invariants constructible from the functions of the irreducible representation to which the distortion of the structure corresponds. Group theoretical treatment based on the Landau Theory was applied to NaNO_2 by Heine and McConnell (1981).

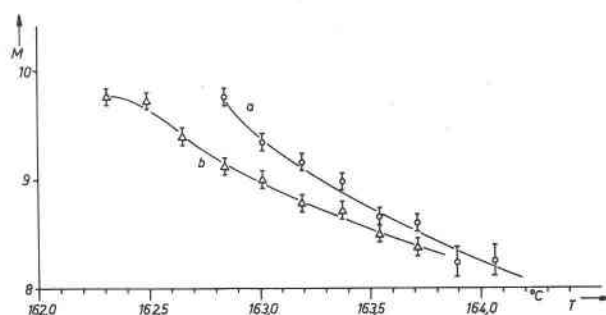


Fig. 2. The variation of the modulation period (M) of NaNO_2 with temperature. The two curves were measured on heating (a) and on cooling (b) (Böhm, 1978).

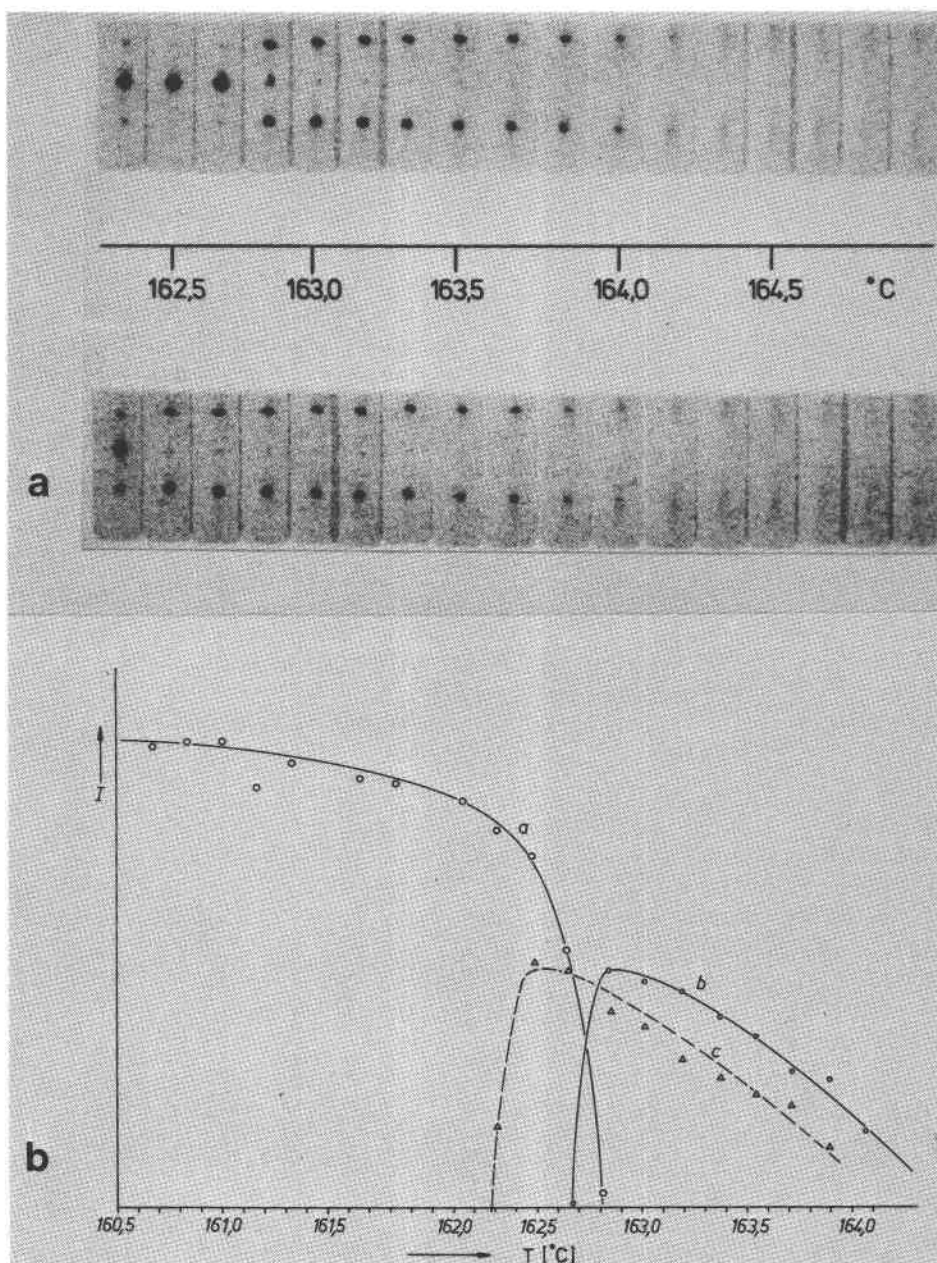


Fig. 3. (a) The intensity variation of the 042 reflection and its adjacent pair of satellites of NaNO_2 with temperature on heating (upper row) and cooling (lower row); (b) the photometer curve of (a) for the main reflection (curve a) and one satellite (curve b) on heating and for the same satellite on cooling (curve c). (Böhm, 1978)

NaNO_2 is an example of a structure that transforms reversibly into a modulated structure. Here a pair of satellites appears around the position of a main reflection in a first order phase transition on heating. In other structures (*e.g.*, K_2SeO_4) the modulated phase is characterized by satellites which are shifted until they lock in at a rational number to become superstructure reflections when

the temperature is lowered (Iizumi *et al.*, 1977). The lower temperature phase of K_2SeO_4 is thus characterized by a superstructure $3a_0$ (a_0 = lattice constant of the high temperature phase).

Another example of a modulated structure is β -eucryptite, which shows that the intermediate modulated state is not peculiar to the ferroelectric salt NaNO_2 . In β -eucryptite, LiAlSiO_4 , the same char-

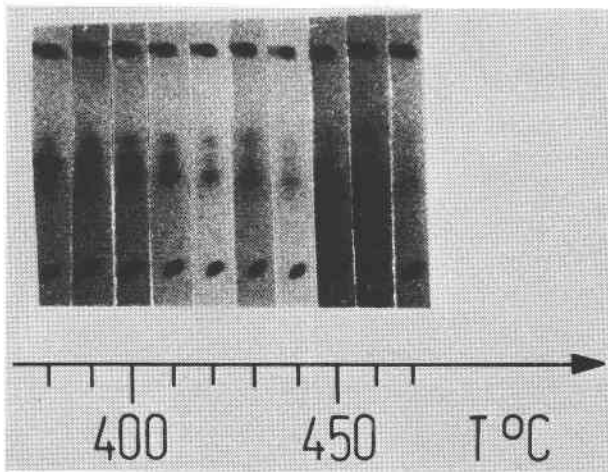


Fig. 4. The variation of the $\bar{4}33$ reflection and its adjacent pair of satellites of β -eucryptite with temperature.

acteristic features are found at the “high-low” transformation of the quartz-like structure. According to Schulz and Tscherry (1972), the structure can be regarded as being “twinned” in an ordered way according to the Dauphiné law. The two configurations of the Dauphiné twins in quartz are adopted alternately by the tetrahedra in the β -eucryptite structure. In β -eucryptite the modulated phase was first observed by neutron scattering (Press *et al.*, 1980). Figure 4 shows the author’s most recent results of X-ray scattering, the variation of the $\bar{4}33$ main reflection and its adjacent satellites with temperature. It consists of a sequence of portions taken from precession photographs (graphite monochromator, $\text{MoK}\alpha$ -radiation). The pair of satellites appears around the so-called “ a -reflections” (here $\bar{4}33$). When compared with quartz, these a -reflections are additional reflections, which double the quartz cell in each of the three hexagonally equivalent directions of a . The direction in which satellite reflections are observed is parallel to a ; thus, the planes of constant phase of the modulating function run parallel to the three directions of a . The period M of the modulation varies between 5 and 7.5 a in the temperature range between 380°C and 450°C. Again there is a temperature range of coexistence for the $\bar{4}33$ main reflection and the adjacent pair of satellites, which reveals a first order phase transition from the low temperature phase into the modulated state. Although the structures, the chemical bonds, and the symmetries are very different in NaNO_2 and LiAlSiO_4 there is apparently the same basic mechanism for the modulation. In both substances the transitions are of the order-disorder

type. There are two energetically equivalent configurations in each compound. At low temperatures only one configuration is occupied by atoms; at high temperatures both are occupied equally. The structure determination of the modulated state of NaNO_2 has proven that the occupancy of both configurations is modulated in space (Böhm, 1978). In the ferroelectric NaNO_2 these are the two configurations for the positive and negative polarization (Fig. 5a). In β -eucryptite the configurations are characterized by two equilibrium values of the tilt angle between neighboring tetrahedra (Fig. 5a) of the low quartz structure. By tilting all tetrahedra into the alternate position the other configuration is obtained.

Interpretation

One may ask how a modulation of the occupancy of two configurations is realized by a structure. To answer this question we may be guided by the

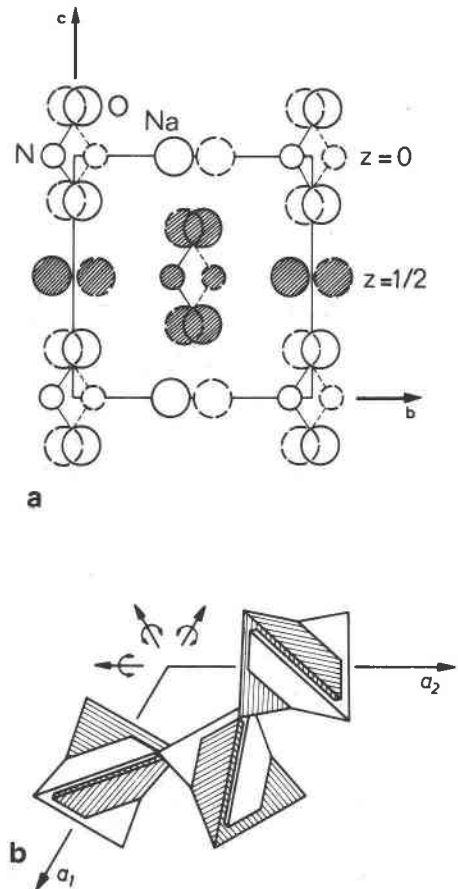


Fig. 5. The two equilibrium configuration, for NaNO_2 (a) and β -eucryptite (b).

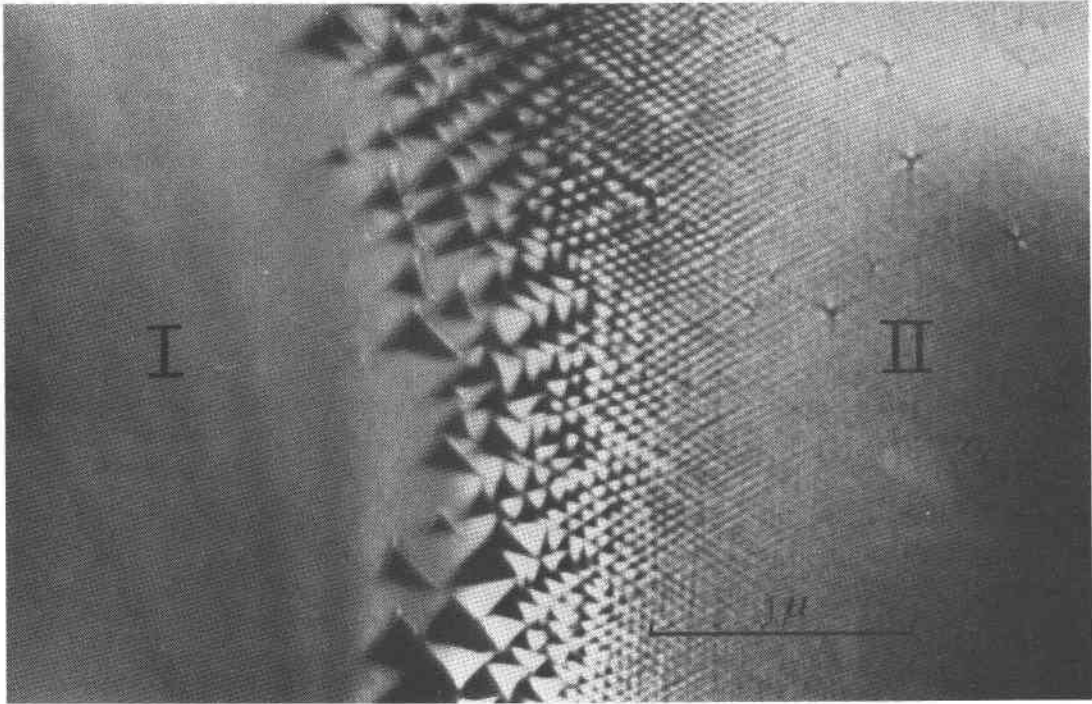


Fig. 6. Dauphiné domains in quartz at the phase transition; the temperature in (I) is below and in (II) is above the transition temperature. (Picture taken with the electron microscope by v. Tendeloo *et al.* 1976.)

results which van Tendeloo *et al.* (1976) obtained with the electron microscope on quartz at the α - β transformation. When the transition temperature is approached from below, a grid of α_1 , α_2 microdomains of the Dauphiné type is observed, which seem to be regularly arranged on a lattice (Fig. 6). With increasing temperature the grid is reduced to a smaller and smaller size, until the domains disappear at the transition temperature. In quartz the grid is too coarse to give rise to an X-ray scattering pattern. However, we may conjecture that in β -eucryptite or in NaNO_2 a fine grid of domains is also formed in the intermediate, modulated state, so that both configurations are present in the crystal simultaneously. Tanisaki (1961) proposed an 8-fold superstructure of 180° -domains equally spaced in the crystal for NaNO_2 . However, the regular arrangement of 180° -domains does not account for the two incommensurate lattices of main and satellite reflections. But Fujiwara (1957) has shown that a uniform and regular arrangement of antiphase domains which are fluctuating in size will yield an average period which is incommensurate. We carried out calculations on a one-dimensional model. Using a random number generator a sequence of domains was formed which fluctuate in width. In

Figure 7b a sequence of such domains is depicted which are characterized by an order parameter of $+1$ or -1 , respectively. The distribution curve $n(D)$ of the width D has a maximum at $\bar{D} = 7.8$ with a standard deviation $\sigma = 1.4$. In the Fourier expansion the first harmonic $H(x)$ (Fig. 7c) has a period of $M = 2\bar{D} = 15.6$; all higher orders are negligibly small. The corresponding Patterson function $P(u)$ exhibits a superposition of a decay function (short range order effect) and a cosine function. The Fourier transform of $P(u)$ (*i.e.*, the intensity $I(h)$) will therefore show one maximum; its width depends on the decay function and, consequently, on the distribution function $n(D)$. If Figure 7b describes the occupancy of an atomic configuration ($+1$ = occupied, -1 = not occupied), the structure appears to have a sinusoidal modulation of the occupancy in an X-ray diffraction experiment. Though the domain size fluctuates in one direction, the X-ray beam averages it in this direction. It only "sees" the average period, *i.e.*, the first harmonic. As the theory of satellite reflections proves, a sinusoidal density variation is the only type of modulation which will yield only one pair of satellite reflections without higher orders (Korekawa, 1967; Böhm, 1976). It is the degree of randomness

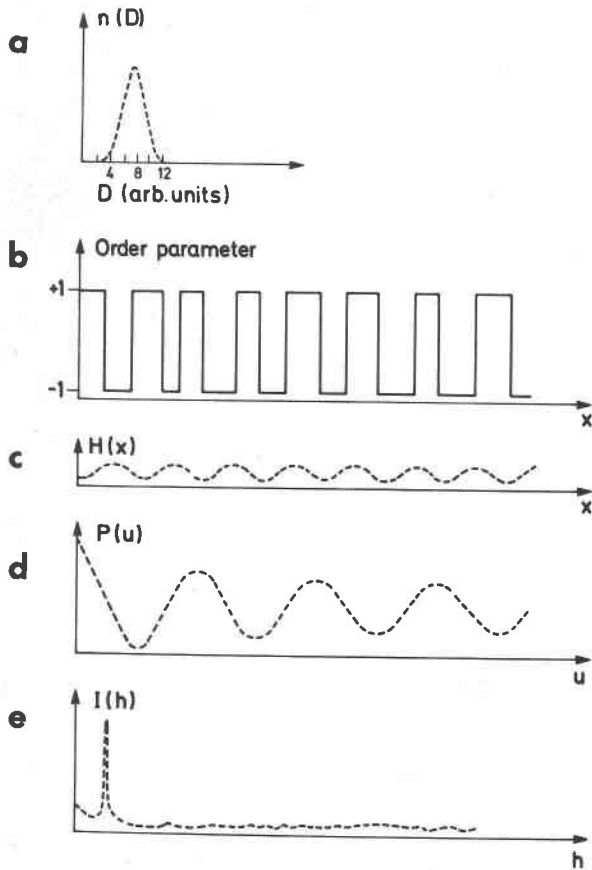


Fig. 7. The effect of structural fluctuations on diffraction: (a) the distribution function $n(D)$ of domain widths D , (b) domains fluctuating in widths according to $n(D)$; (c) the first harmonic of the structure (b); (d) the corresponding Patterson function $P(u)$; and (e) the intensity $I(h)$ of scattered X-rays from the structure (b).

in the structure which makes higher order satellites disappear; it is the averaging of the X-ray beam which yields some value for the period of the modulation function which is incommensurate with the basic structure. When the temperature is varied, the distribution function may change, which gives rise to a change of the average period. This model infers that the period of the modulation cannot adopt irrational numbers, since the average of integers is always rational. The period M hops between rational numbers. Apparently the formation of domains is inherently involved in the modulation of the basic crystal structure. It is the dynamics at the phase transition which promotes the formation of microdomains in order to minimize the Gibbs free energy. But it should be emphasized that microdomain patterns might be static at temperatures far below the transition temperature or they may

change with phonon frequencies very close to the transition point. The high time resolution of X-rays ($\sim 10^{-18}$ s) prevents a distinction between these cases.

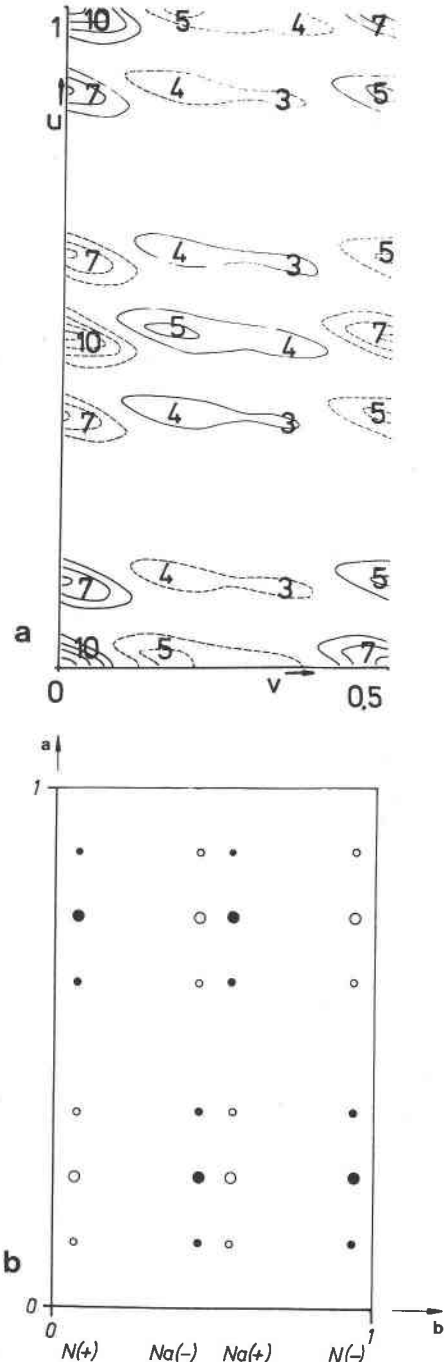


Fig. 8. (u,v) section of the Patterson function of the complementary structure of NaNO_2 (a) and the atomic positions (b); solid lines refer to positive, broken lines to negative values in (a), and the numbers indicate the peak height; solid circles refer to positive and open circles to negative scattering density of variable size in (b) (Böhm, 1978)

Structure determination

Structure determination of a modulated structure may be carried out by standard methods like least-squares refinements, Fourier, and Patterson methods; the satellite theory may be utilized to predict the type of the modulation (Korekawa, 1967; Böhm, 1976). The main reflections have the period of the basic structure; however, their intensities are related to the *average structure* which is the projection of the modulated structure into one sub-cell of the basic structure (Fig. 1). Therefore, the first step is to determine the average structure.

A structure determination which is based on the satellite reflections alone will yield a structure which is the difference between the average structure and the modulated structure; it is usually called the *complement structure*. A complement structure consists of positive and negative scattering density, because the deviation from the average structure may be positive or negative. A Patterson map can be calculated from the satellite reflections alone. For NaNO_2 the use of Patterson maps for the structure determination is outlined in detail in the author's paper of 1978. In the present paper, as an example, only one map of the complement structure will be reproduced; it exhibits positive maxima and negative minima (Fig. 8a). The peak heights follow exactly a sine function along the u -axis. For the calculation, the period of the modulation was taken to be integral (superstructure, $M = 8$); otherwise, one cannot index the satellites. A one-dimensional sinusoidal variation of the Patterson function corresponds to a one-dimensional sinusoidal variation of the density. The structure which can be derived from this map is depicted in Figure 8b; it is a section through the structure in the (a, b) plane. The atomic positions of both equilibrium configurations are found in the diagram; the scattering density varies like a sine function. Since it is a complement structure, positive and negative densities appear.

Structure refinements based on these evaluations of the Patterson map accounted only for the modulation of the occupancy. Additional calculations by Kucharczyk *et al.* (1978) have shown that the atomic positions are also shifted according to a transverse wave. Heine and McConnell (1981) have proven by symmetry considerations that in addition to the modulation of the occupancy, such a monoclinic distortion (*i.e.*, a shear) is required by the Landau theory. They have shown that at the Γ -point (*i.e.*, at $\vec{k} = (0, 0, 0)$) in reciprocal space, distortion of the high temperature phase due to

modulation of the occupancy and distortion due to a shear correspond to different irreducible representations. However, off the Γ -point at a point $\vec{k} = (q, 0, 0)$, both distortions correspond to a single irreducible representation. Therefore, according to Landau and Lifshitz (1958), a second order phase transition will take place at the $\vec{k} = (q, 0, 0)$, which is incommensurate with the lattice of main reflections. In the distorted modulated phase both kinds of distortions will occur simultaneously.

References

- Böhm, H. (1976). Interpretation of X-ray patterns due to modulation of positional parameters and of scattering density, *Zeitschrift für Kristallographie*, 143, 56–66
- Böhm, H. (1978). X-ray structure determination of the modulated phase of NaNO_2 . *Zeitschrift für Kristallographie*, 148, 207–220.
- Fujiwara, K. (1957). On the period of out-of-step of ordered alloys with anti-phase domain structure. *Journal of the Physical Society of Japan*, 12, 7–17
- Heine, V. and McConnell J. D. C. (1981). Origin of modulated incommensurate phases in insulators. *Physical Review Letters*, 46, 1092–1095.
- Iizumi, M., Axe, J. D., Shirane, G., Shimaoka, K. (1977). Structural phase transformation in K_2SeO_4 . *Physical Reviews B*, 15, 4392–4411.
- Jagodzinski, N. and Korekawa, M. (1976). Zur Kristallstruktur und Fehlordnung der Plagioklase $\text{Ca}_x\text{Na}_{1-x}[\text{Al}_{1-x}\text{Si}_{3-x}\text{O}_8]$. *Zeitschrift für Kristallographie*, 143, 239–277.
- Korekawa, M. (1967). Theorie der Satellitenreflexe. Habilitationsschrift der Ludwigs-Maximilians, Universität München.
- Kucharczyk, D., Pietraszko, A., Lukaszewicz, K. (1978). Modulation of the intermediate antiferroelectric phase of NaNO_2 . *Ferroelectrics*, 21, 445–447.
- Landau, L. D. and Lifshitz, E. M. (1958). *Statistical Physics*. Addison Wesley Reading, Massachusetts.
- Press, W., Renker, B., Schulz, H., and Böhm, H. (1980). Neutron scattering study of the one-dimensional ionic conductor β -eucryptite. *Physical Reviews B*, 21, 1250–1257.
- Schulz, H. and Tscherry, V. (1972). Structural relations between the low- and high-temperature forms of β -eucryptite (LiAlSiO_4) and low and high quartz. *Acta Crystallographica B*, 28, 2168–2173.
- Tanisaki, S. (1961). Microdomain structure in the paraelectric phase of NaNO_2 . *Journal of the Physical Society of Japan*, 16, 579.
- Tanisaki, S. (1963). X-ray study on the ferroelectric phase transition of NaNO_2 . *Journal of the Physical Society of Japan*, 18, 1181–91.
- van Tendeloo, G., van Landuyt, J., and Amelinckx, S. (1976). The $\alpha \rightarrow \beta$ phase transition in quartz and AlPO_4 as studied by electron microscopy and diffraction. *Physica Status Solidi (a)*, 33, 723–735.
- Yamada, Y., Shibuya, I., Hoshino, S. (1963). Phase transition in NaNO_2 . *Journal of the Physical Society of Japan*, 18, 1594–1603.