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## ORDER-DISORDER PHENOMENA IN COMPLEX CRYSTAL-STRUCTURES

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**Résumé.** — Il est démontré que, sous certaines conditions, la phase et l'amplitude de la diffraction diffuse sont déterminables. Il y a des relations très compliquées entre la diffusion inélastique et la diffraction élastique dans les plagioclases de composition chimique  $An_{80}-An_{100}$ .

**Abstract.** — It is shown that the phases and amplitudes of diffuse scattering may be determined experimentally under certain conditions. There are complicated correlations between the elastic and the inelastic part in the case of plagioclases with the chemical composition  $An_{80}-An_{100}$ .

**1. Introduction.** — There is a great number of papers reporting on diffuse scattering of order-disorder phenomena in crystals, but only very few of them offer the complete interpretation in terms of a unique structural model as a function of the temperature and the diffraction angles, which are the most relevant parameters of a crystal with a given chemical composition. The reasons for this are obvious : Any defect has an internal structure and a surrounding strain field, where the atoms are displaced in a more or less complicated way. In the case of complex structures the atomic displacements may not even be described approximately by a homogeneous deformation, which can be calculated with the aid of the elastic tensor of the crystal. Hence, a complete structure determination of the defect is necessary which has to take into account the symmetries of the host crystal and the defect. It will be shown that refinement methods are possible at least in principle, but may become extremely difficult.

Since atomic reactors with a thermal neutron flux of sufficient intensity are available now, additional information can be received for the solution of the complex diffraction problem. The most important contribution of neutron diffraction to disorder phenomena resulted from its inelastic part. The anomalous behaviour of thermal diffuse scattering shed some new light on the kinetics in the temperature range of phase transitions, where sometimes soft modes produce characteristic diffuse scattering which is completely or at least partly inelastic in its nature.

For the reasons mentioned above it seems to be hopeless to start the investigation of disorder phenomena of crystals with a complicated structure, but sometimes there are apparently conditions facilitating the problem essentially. This happens generally when the strain field surrounding any defect is small, and the host lattice remains undistorted, such, that the geometry of the unit cell is not completely des-

troyed. It is the aim of this paper to clarify the limiting conditions for solving any diffuse diffraction problem in a complicated crystal structure.

**2. Theory.** — As has been pointed out above, the strain field surrounding any type of defect is one of the most difficult problems in complex structures. Therefore, it seems to be reasonable to restrict all investigations to problems of vanishing strain fields. There are two simple approaches to the theory of diffraction which are normally used :

- The method of random distribution of defects.
- The method of strongly cooperative defects.

Both methods include all cases of disorder in principle, which one is the more useful can best be judged by analyzing the diffuse diffraction picture qualitatively. Figure 1 shows a distribution of defects

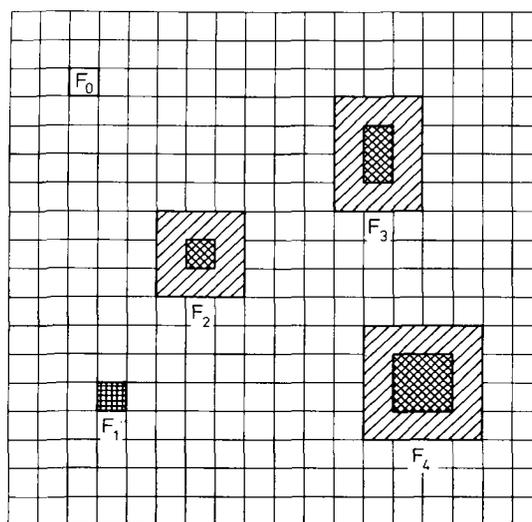


FIG. 1. — Model of a random distribution of defects with structural kernels and boundaries.

in a geometrically perfect lattice. Each of these defects is distributed over a certain number of unit cells of the crystal. The central core of the defect contains the relevant structural deviations, and its surrounding contains the changes of the neighboring cells. Each of the various *particles* described by  $F_i$  in figure 1 may have its own structural kernel, but there may also be similarities between them. The X-ray diffraction pattern is generally described in the following way : There are sharp reflections with intensities

$$I_s(\mathbf{h}) = R \sum_{i,k} p_i p_k \bar{F}_i \bar{F}_k^* \quad (1)$$

where  $R$  is the usual Laue-factor.  $p_i$  is the *a priori* probability to find a particle with the incoherent scattering amplitude  $\bar{F}_i$  which is given by

$$\bar{F}_i = \sum_v F_{iv}, \quad \bar{F}_0 = F_0 \quad (2)$$

$F_{iv}$  represents the scattering amplitude of the  $v$ -th cell in the  $i$ -th defect, and  $F_0$  is the scattering of one undistorted cell. The diffuse intensity  $I_d(\mathbf{h})$  is then given approximately by

$$I_d(\mathbf{h}) \approx \sum_i p_i |F_i|^2 - \sum_{i,k} p_i p_k \bar{F}_i \bar{F}_k^* \quad (3)$$

where

$$F_i = \sum_v F_{iv} e^{2\pi i \mathbf{h} \cdot \mathbf{r}_{iv}},$$

$\mathbf{r}_{iv}$  = position vector of the  $v$ -th cell in the  $i$ -th defect.

Eq. (1) means that an averaged structure analysis is possible, projecting the whole information of the distorted structure into one unit cell. It is only the diffuse intensity given in eq. (3) which enables a complete determination of the disorder problem under investigation. One important property of the scattering of the diffuse background may be interpreted much easier if eq. (3) is restricted to two  $F$ 's,  $F_0$ , the scattering amplitude of the host lattice, and  $F_1$ .

For the sake of simplicity we may assume furthermore that  $F_1$  refers to one unit cell only (this does not involve any restriction for the following discussion). Eq. (3) becomes then

$$I_d(\mathbf{h}) = p_0(1 - p_0) |F_0 - F_1|^2. \quad (4)$$

Eq. (4) gives a very general and important result : The concentration of defects within a given lattice regulates the intensity of the diffuse background, but its general structure is not changed ; there is no weighted contribution of  $F_0$  and  $F_1$  to the diffuse scattering as indicated for the intensity of sharp reflections. Another important property of the diffuse scattering is indicated by eq. (4) : Let us assume that the structure amplitude of the undistorted lattice is well known, eq. (4) then gives some information on amplitudes and phases of  $F_1$ . This information

is unique if  $F_0$  and  $F_1$  are real (lattice and defect are centrosymmetric). In this particular case the structure of the defect may be solved directly without any restriction. It may also be shown, that the structure of an acentric defect may be solved with the aid of anomalous scattering. It is obvious that this method of structure determination of the defect is possible if one  $F_1$  is unknown. But there is another considerable difficulty. The reciprocal vector  $\mathbf{h} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c}$  is not restricted to integral values ( $hkl$ ). Therefore, a given structure of any defect may have its origin anywhere in the unit cell of the host lattice. Eq. (4) indicates that the relative phases of  $F_0$  and  $F_1$  enter the diffraction problem and change the intensity distribution considerably. This statement is specifically important in the case of non-centrosymmetric structures of the defects. This means : The diffuse scattering of any defect in a complicated lattice is heavily influenced by the position of the interface between the defect and the host lattice. It can easily be shown that eq. (3) may be applied to any problem but in the case of cooperating defects distribution functions  $P_{ik}(\mathbf{j})$  of defects have to be introduced, giving the probability that a cell (scattering amplitude  $F_k$ ) at a distance  $\mathbf{j}$  from any given reference cell has the scattering amplitude  $F_i$ . This procedure has been described in the literature [1] and shall not be presented in this paper. But it should be pointed out that equations similar to (3) may be given if the  $P_{ik}(\mathbf{j})$  may be derived from the diffraction picture.

**3. Plagioclases.** — The anomalies of the feldspar-structures represent the most complex system of order-disorder phenomena that have been investigated for many years. Consequently, it is impossible to give a real comprehensive review on all disorder phenomena observed, and more so, to state all opinions and interpretations of the complex behaviour of this complicated system. Therefore, we shall restrict ourselves to one part of this multi-component system, the plagioclases, in the composition range  $An_{50}$  to  $An_{100}$ . They may be described by the chemical formula



for the sake of simplicity the compound with  $x = 1$  is called  $An_{100}$  (100 % anorthite =  $CaAl_2Si_2O_8$ ),  $x = 0$  corresponds to  $An_0$  (100 % albite =  $NaAlSi_3O_8$ ), etc. The structure may be described in terms of a (Si, Al) $O_2$ -framework structure, where the Si, Al distribution may be ordered as it holds for  $An_{100}$  which has a framework structure with alternating Si-Al distribution. But the degree of order in  $An_{50}$  is not yet known. For details of the crystal structure the reader may be referred to the text book on feldspars by Smith [2], and the papers cited therein. The cations Ca and Na occupy relatively large holes in the framework with a complicated coordination of the oxygens. Figure 2 shows one plane of the arrangement of cations

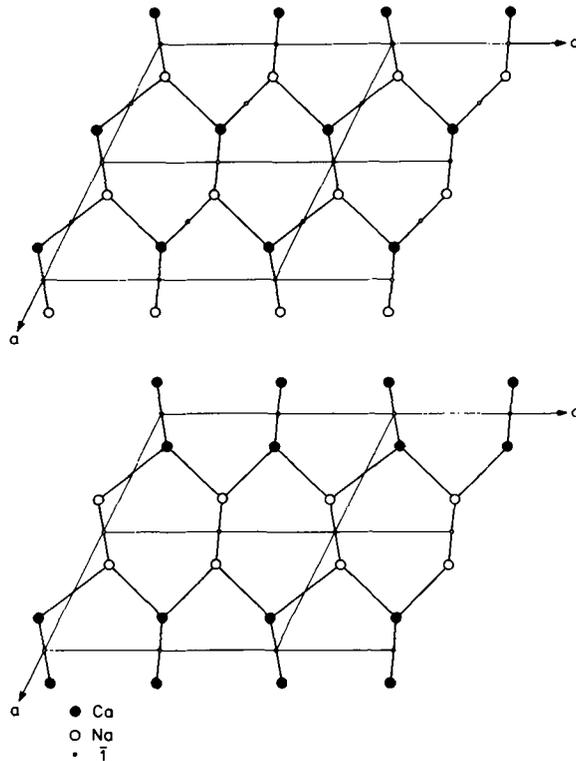


FIG. 2. — Two possible super-structures of Ca, Na in  $An_{50}$ : a) acentric distribution, the small open circles indicate the positions of the centres of symmetry in the  $An_{100}$ -structure; b) centrosymmetric distribution generating a doubling of the  $a$ -lattice constant (not observed for  $An_{50}$ ).

which has been found by a complete structure determination for anorthite. In order to give an idea of the order-disorder phenomena observed, we shall start with the pure anorthite, which is known to have a phase transition from the primitive to a body-centered structure [3]. Neutron experiments showed that this transition is dynamic in its character for  $An_{100}$  [4]. The sharp Bragg peaks with

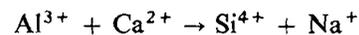
$$h + k + l = 2n + 1$$

become diffuse in the X-ray diffraction pattern (Laves and Goldsmith [5]), but they remain to be visible beyond the critical point (Czank [6]). But none of the X-ray experiments were suited to fix a precise critical temperature  $T_c$  of this transformation. For this reason another sample (location: Monte Somma,  $An_{98}$ ) was chosen for a renewed neutron experiment which showed that the elastic and integrated intensities of the diffuse reflections  $h + k + l = 2n + 1$  now have an elastic component, which increases near the critical temperature (where the sharp Bragg peak decreases in intensity) and decreases again above  $T_c$ . The energy-integrated intensity measurements of the diffuse part of the reflection,

$$h + k + l = 2n + 1$$

were appreciably larger than the elastic part. The quantitative evaluation of these measurements is going to be published soon [7].

It is clear that the diffuseness of the reflections  $h + k + l = 2n + 1$  indicates anti-phase domains of a primitive domain structure with a displacement vector  $1/2(\mathbf{a} + \mathbf{b} + \mathbf{c})$ . This observation has been checked by dark field electron microscopy by various authors (see Czank, van Landuyt, Laves, and Schulz [8]). They report that the domain walls observed at room temperature became weaker with increasing temperature, show some fluctuation near the critical temperature, and vanish above the critical temperature. On cooling below the critical temperature the anti-phase domain walls reappear in their original position, thus indicating a memory effect of positions of the domain walls. This behaviour has been explained by Jagodzinski and Korekawa [9] by assuming that the replacement reaction



takes place in a strictly correlated manner. Assuming further that the (Si, Al)-framework does not contribute essentially to the intensity of the reflection  $h + k + l = 2n + 1$ , the picture of the domain wall may vanish, since the contrast is only given by the primitive arrangement of the Ca-positions. Na is probably concentrated at the domain walls, but this cannot be resolved with the resolution power available in dark field methods. This assumption explains the memory, but in diffraction there should be an elastic peak decreasing in intensity with increasing temperature.

The measurements of the nuclear magnetic resonance (NMR) of  $Al_{27}$  have been done by Staehli and Brinkmann [10] with a specimen  $An_{95}$  (which should have smaller domains than  $An_{98}$ ). They report on a clear splitting of the  $Al_{27}$  resonances between 230 °C which collapse to one resonance above 240 °C, but there is an intermediate temperature range between 230-240 °C, where clear resonances may not be detected. This result is again in agreement with the domain model given above.

A renewed study of the reflections  $h + k + l = 2n + 1$  as a function of temperature with a high resolution single crystal method (described by the author [11]) yielded the surprising result that their diffuseness is already visible at 120 °C, the broadening also begins at this temperature and increases continuously up to 250 °C (above  $T_c$ , see figure 3). This is in contradiction to the neutron measurements and has caused much confusion. Therefore  $T_c$  cannot be given for the Monte Somma sample, and it will be checked soon whether this statement also holds for the  $An_{100}$ . On the other hand it may be concluded from symmetry considerations that any phase transformation from a primitive to a body-centered lattice should have a critical temperature. Thus, the only conclusion

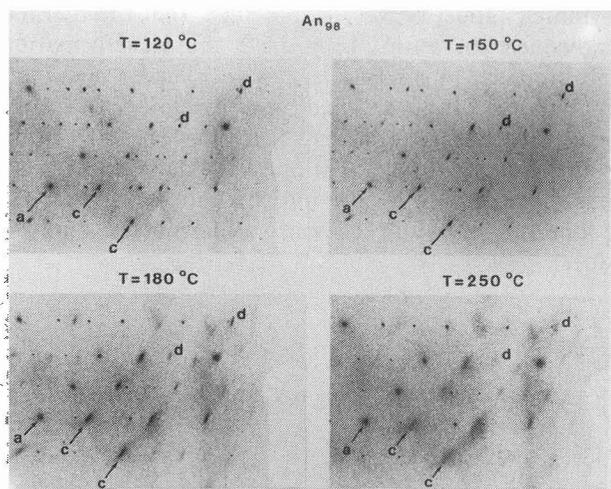


FIG. 3. — The diffuseness of reflections  $h+k+l=2n+1$  as a function of temperature for a sample  $An_{98}$  (Monte somma).  
 $b$  :  $h+k=2n+1$ ,  $l=2n+1$ ;  $c$  :  $h+k=2n$ ,  $l=2n+1$ ;  
 $d$  :  $h+k=2n+1$ ,  $l=2n$ .

to be drawn may be : The phase-transition is not a simple change from a P- to an I-lattice. There should be another structural element in the transition, at least in the samples containing some albite. One possibility is the absence of the center of symmetry, which is assumed to exist in the An-structure.

This suggestion is supported by another observation. The reflections

$$h+k=2n+1, \quad l=2n+1,$$

which are called  $b$ -reflections in the literature, show a typical diffuse behaviour as shown in figure 4, for a specimen of  $An_{80}$ ; this diffuseness begins to condense into a pair of satellite-reflections. Applying the so-called Noromosaic-technique, which is similar to the monochromatic oscillation-technique, replacing the angle of oscillation by a series of photographs with a standing crystal at different settings (figure 4), it may be shown that the diffuse reflections

$$h+k+l=2n+1$$

and the diffuse  $b$ -reflection (anisotropic halo vanishing at the  $b$ -reflection itself) are clearly correlated. Consequently, there must be a structural relationship between both kinds of defects. It seems to be reasonable to assume that the satellites are due to a very complicated superstructure of Na, Ca and Si, Al [12].

Figure 2 shows two possible orderings of cations; one of them is centrosymmetric but seems to be unfavorable from an electrostatic point of view, because of the higher electrostatic repulsion energy of Ca-Ca, Na-Na when compared with two Ca-Na pairs. A similar result may be obtained from the Al, Si-distribution of  $An_{50}$ . This means, that at least in small areas an acentric structure should be realized. If this behaviour continues up to  $An_{98}$  (Monte Somma), the asymmetric element should also be expected with this composition.

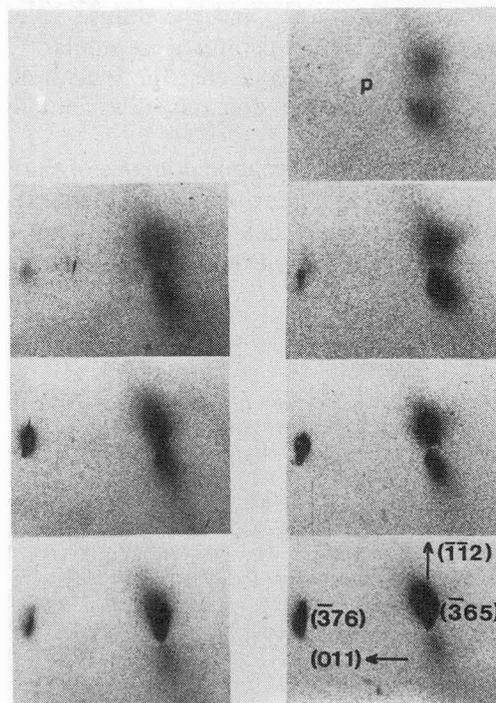


FIG. 4. — Diffuse reflections  $h+k=2n+1$ ,  $l=2n+1$  (Noromosaic-technique, see text),  $CuK_{\alpha_1}$ ; the diffuse streaks given by the various angular settings are connected with the diffuse reflections  $h+k+l=2n+1$ , not shown in this picture.

As may be seen in figure 5 with two arbitrary plagioclases, the diffuse reflections of any composition

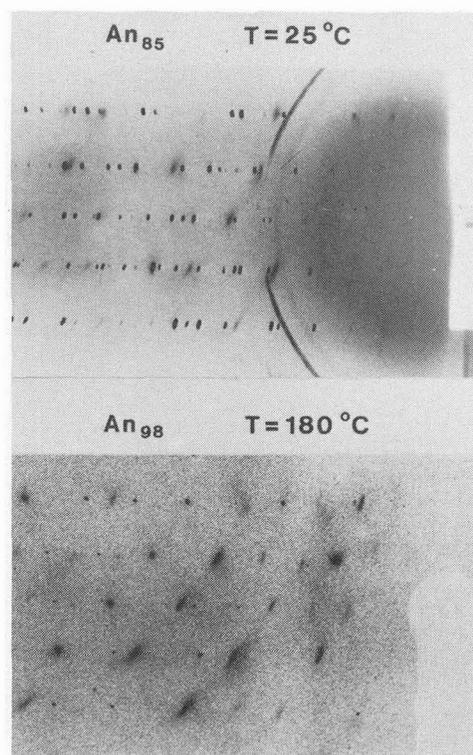


FIG. 5. — Comparison of the (predominantly elastic ?) diffuse scattering of a sample  $An_{85}$  at room temperature with a sample  $An_{98}$  at 180 °C. Note the same anisotropy of the diffuse scattering.

between  $An_{50}$  and  $An_{98}$  and the diffuse reflections observed at elevated temperatures are similar. Consequently, it is most probable that the structural basis of static and dynamic domains is essentially the same.

Furthermore, if the dynamic domains of the  $An_{100}$  specimen are not different from the others, we have to face the situation that the structure of  $An_{100}$  itself may be acentric. But the deviation from centro-

symmetry must be very small, such, that the thermal movement of atoms may drive the transformation of domains. It is obvious that this very preliminary model has to be checked very carefully. But even if it turns out to be incorrect, it is at least interesting to learn how an investigation of the diffuse scattering may give more precise informations on structural properties than a conventional structure analysis does.

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