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X-ray diffraction study of NH_4HSeO_4 and ND_4DSeO_4

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Résumé. — Nous présentons des résultats de diffraction des rayons X obtenus dans les nombreuses phases des monocristaux de NH_4HSeO_4 et ND_4DSeO_4 . En liaison étroite avec les problèmes d'incommensurabilité, nous avons découvert : — une phase de surstructure 3c présente à la fois dans AHSe et ADSe, — une phase de surstructure 2c uniquement dans ADSe. Les processus hors d'équilibre ont, grâce à cette technique, pu être identifiés et ont clarifié la situation du diagramme de phase.

Abstract. — This paper reports results obtained from an X-ray diffraction study of NH_4HSeO_4 and ND_4DSeO_4 single crystals in their various phases. In connection with incommensurability : a) a 3c-superstructure phase has been found both in AHSe and in ADSe, b) a 2c-superstructure has been discovered in ADSe. The non-equilibrium processes have been identified clarifying the situation about the phase diagram.

1. Introduction.

Because of incommensurability, ferroelectricity and superionic conduction properties, compounds of the hydrogenated selenate family have attracted considerable interest during the last few years. In this family, NH_4HSeO_4 seems particularly interesting. Sandwiched between the high-temperature superionic phase of unknown structure (stability range : $T_{\text{melting}} = 427$ K, $T_{\text{si}} = 417$ K) [1] and the ferroelectric triclinic phase of P1 space group (stability range : $T_{c_1} = 251.3$ K, $T_{c_2} = 100$ K) [2], a large non-ferroelectric phase of monoclinic B2 symmetry has been reported [3]. Below 100 K, the spontaneous polarization disappears giving rise to a non-ferroelectric phase of unknown structure [4]. Abundant literature emphasizes additional complications between room temperature and T_{c_1} :

i) a reexamination of the dielectric properties by Gesi [5] reports a small break in the curve $\epsilon'(T)$ at about 286 K, and DTA measurements [5] confirm the existence of a phase transition at this temperature,

ii) a careful ^{77}Se high-resolution NMR study by Aleksandrova *et al.* [6] reveals spectra with an anomalous line-shape continuum limited by two-edge singularities in the temperature range [$T_1 =$

261 K, $T_{c_1} = 251.3$ K], typical of an incommensurate phase,

iii) non-equilibrium processes are revealed by ^{77}Se NMR (local technique) but also by dielectric measurements (macroscopic technique) [7-9]. They are described as an « instability » of the structure between $T_f \sim 271$ K and T_{c_1} with « life time » varying between a few hours and a few tens of hours, depending on the sample quality and external stresses,

iv) crystals with a high level of deuteration ($\% \text{D} > 50$) lose their ferroelectric properties [10] and simultaneously change their symmetry to $\text{P} 2_1 2_1 2_1$ [11]. On heating, a polymorphic phase transition from the « metastable » orthorhombic structure to the supposed monoclinic structure (up to now there is no direct crystallographic evidence) of the paraelectric phase was registered at $T_p \approx 330$ K (60 % D) [8, 12] (cf. Fig. 1) ; after this transition, the single crystals have the same phase transition sequence as the non-deuterated and low-deuterated crystals [9, 12]. A very strong broadening of the supposed incommensurate phase in crystals with a high deuterium content has also been described [9] (Fig. 1). In order to obtain structural evidence for incommensurability and metastability

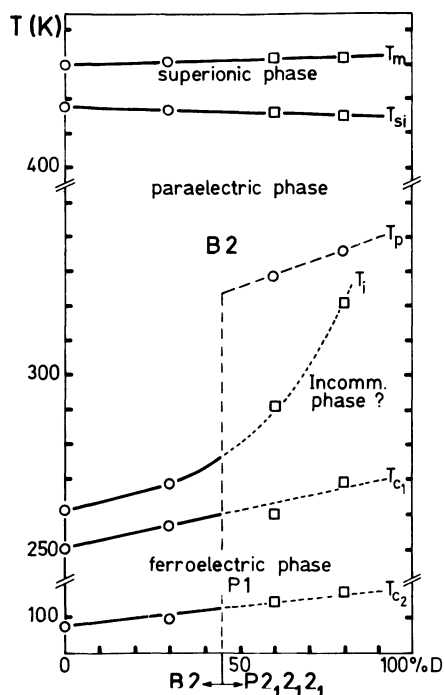


Fig. 1. — (Temperature, % D) phase diagram in $(\text{NH}_4)_{1-x}(\text{ND}_4)_x\text{H}_{1-x}\text{D}_x\text{SeO}_4$, from reference [9]. ($x = \% \text{D}$).

problems in this rather complicated and unusual phase diagram, X-ray diffraction experiments have been performed.

The present paper is organized as follows. After a description of the different known structures (Sect. 2), we discuss results obtained from a detailed monochromatic X-ray diffraction study on NH_4HSeO_4 labelled (AHSe), and ND_4DSeO_4 labelled (ADSe) monocrystals as a function of temperature in their various phases (Sect. 3). Concluding remarks close this paper in section 4.

2. The known structures of AHSe and ADSe.

2.1 AHSe.

2.1.1 Structure of the paraelectric phase. — The structure of AHSe has been determined at 293 K by X-ray diffraction [3]; its symmetry is monoclinic with space group B2 ($Z = 6$, $a_{\text{monocl.}} = 19.745 \text{ \AA}$, $b_{\text{monocl.}} = 4.611 \text{ \AA}$, $c_{\text{monocl.}} = 7.552 \text{ \AA}$, $\gamma = 102^\circ 35'$). Figure 2 shows a projection of the structure on the ab plane. The structure is often also described with a pseudo-orthorhombic cell ($Z = 6$, $a_{\text{p-orthorh.}} = 19.272 \text{ \AA}$, $b_{\text{p-orthorh.}} = 4.611 \text{ \AA}$, $c_{\text{p-orthorh.}} = 7.552 \text{ \AA}$, $\gamma_{\text{p-orthorh.}} = 89^\circ 54'$) with a « non standard space group I2 » [3]. This can be easily converted to the standard space group B2 by taking the $a_{\text{p-orth.}}$ axis parallel to $[110]_{\text{monocl.}}$. Later we shall see that the pseudo-orthorhombic setting seems more appropriate in the investigation of AHSe.

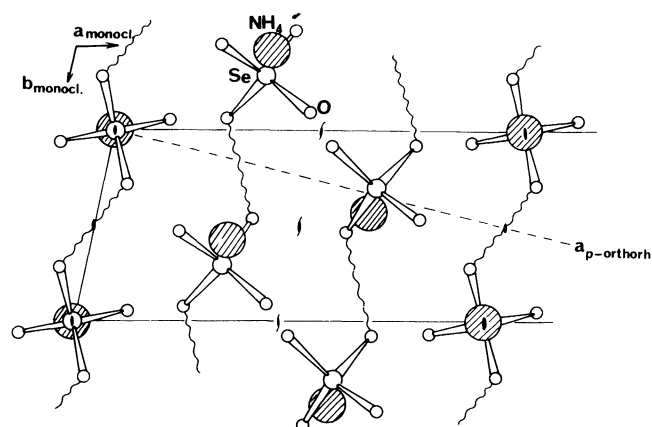


Fig. 2. — Projection of the paraelectric structure of NH_4HSeO_4 on the (a, b) plane from reference [3], showing a half-cell at 300 K.

2.1.2 Structure of the ferroelectric phase. — The ferroelectric phase [13] results from a small distortion of the monoclinic B2 cell giving rise to a pseudo-monoclinic « non standard space group B1 ». Figure 3 shows a projection of this pseudo-cell in the a, b plane. (At $T = 223 \text{ K}$: $Z = 6$, $a_{\text{p-monocl.}} = 19.593 \text{ \AA}$, $b_{\text{p-monocl.}} = 4.598 \text{ \AA}$, $c_{\text{p-monocl.}} = 7.507 \text{ \AA}$, $\alpha_{\text{p-monocl.}} = 90.02^\circ$, $\beta_{\text{p-monocl.}} = 89.03^\circ$, $\gamma_{\text{p-monocl.}} = 102.13^\circ$, the spontaneous polarization being parallel to the b axis). The true symmetry is described by a

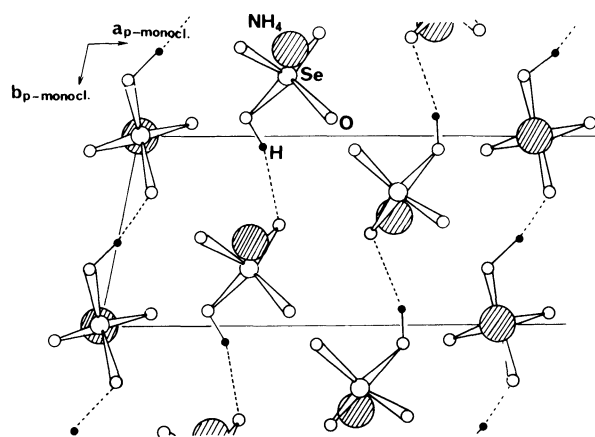


Fig. 3. — Projection of the ferroelectric structure of NH_4HSeO_4 on the $(a_{\text{p-monocl.}}, b_{\text{p-monocl.}})$ from reference [13], showing a half « B1 » cell at 223 K.

triclinic cell with space group P1 ($Z = 3$, $a_{\text{tricl.}} = 10.487 \text{ \AA}$, $b_{\text{tricl.}} = 4.598 \text{ \AA}$, $c_{\text{tricl.}} = 7.507 \text{ \AA}$, $\alpha_{\text{tricl.}} = 90.02^\circ$, $\beta_{\text{tricl.}} = 110.91^\circ$, $\gamma_{\text{tricl.}} = 101.67^\circ$); the relations between the two settings being

$$\begin{aligned} \mathbf{a}_{\text{p-monocl.}} &= 2 \mathbf{a}_{\text{tricl.}} + \mathbf{c}_{\text{tricl.}}, \\ \mathbf{b}_{\text{tricl.}} &= \mathbf{b}_{\text{p-monocl.}}, \\ \mathbf{c}_{\text{tricl.}} &= \mathbf{c}_{\text{p-monocl.}} \end{aligned}$$

2.2 ADSe. — As mentioned previously, ADSe crystallizes in orthorhombic symmetry with space group $P 2_1 2_1 2_1$ [14]; figure 4 shows the projection of the structure on the a, b plane ($Z = 4$, $a_{\text{orth.}} = 12.887 \text{ \AA}$, $b_{\text{orth.}} = 4.599 \text{ \AA}$, $c_{\text{orth.}} = 7.515 \text{ \AA}$). Comparing the structures of AHSe and ADSe, we note that

- i) $\mathbf{a}_{\text{orth.}}(\text{ADSe})$ is parallel to $\mathbf{a}_{\text{p-orth.}}(\text{AHSe})$,
- ii) $\mathbf{a}_{\text{orth.}}(\text{ADSe}) \simeq \frac{2}{3} \mathbf{a}_{\text{p-orth.}}(\text{AHSe})$.

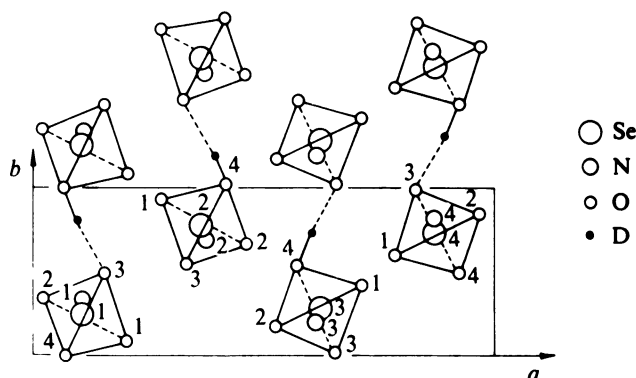


Fig. 4. — Projection of the orthorhombic $P 2_1 2_1 2_1$ cell of ND_4DSeO_4 on the (a, b) plane from reference [14].

3. X-Ray diffraction study.

3.1 EXPERIMENTAL METHOD. — AHSe and ADSe crystals were prepared by mixing an excess of H_2SeO_4 (or D_2SeO_4), 0.75 M, with $(\text{NH}_4)_2\text{SeO}_4$ (or $(\text{ND}_4)_2\text{SeO}_4$). Colorless and transparent single crystals were grown in aqueous solution by slow cooling from 327 K to 317 K; several months are necessary to obtain crystals of about 2 cm^3 . Since AHSe (ADSe) crystals are highly hygroscopic, manipulation of the specimen was done in an atmosphere of dry nitrogen gas. Three types of platelets respectively perpendicular to the three pseudo-orthorhombic (or orthorhombic) axes were cut and then polished; they have typical dimensions $3 \times 1.5 \times 0.3 \text{ mm}^3$ and they were mounted in Lindemann-glass capillaries. In this way, using the monochromatic (Molybdenum $K\alpha$ radiation: $\lambda = 0.711 \text{ \AA}$) precession technique, reciprocal planes with the $[100]$, $[010]$ and $[001]$ pseudo-orthorhombic (or orthorhombic) axes respectively parallel to the precession axis were investigated.

3.2 RESULTS AND DISCUSSIONS.

3.2.1 AHSe. — Typical photographs of the $(\mathbf{a}^*, \mathbf{c}^*)$ equatorial reciprocal plane are shown in figure 5, for several temperatures. The results obtained at 300 K in the monoclinic phase of space group B2 are shown in figure 5a; $(h0l)$ reflections obey extinction rules $h + l = 2n + 1$ in perfect agreement with the previous structural analysis [3].

Figure 5b shows the diffraction pattern in the ferroelectric state at $T = 223 \text{ K}$; in this experiment, the sample was *directly* cooled from room temperature to 223 K at a cooling rate of 0.4 K/min; in the pseudomonoclinic setting $(h0l)$ reflections for $h + l = 2n + 1$ are not observed. With long exposure time (about 15 hours) additional $(h0l \pm 1/3)$ superstructure reflections of *extremely weak intensity* are revealed for $h + l = 2n + 1$, giving for the first time, evidence for a new *unit cell tripled along the c axis*.

If we suppose the existence of an incommensurate phase between 261 and 251.3 K, as suggested by ^{77}Se NMR spectra [9], it is reasonable to assume the \mathbf{c} direction as the direction of the modulation wave vector \mathbf{q} , the ferroelectric phase transition at 261 K being considered as a lock-in phase transition not at the zone centre (as for example in thiourea, NaNO_2 , ...) but at $q = 1/3$ (as for example in K_2SeO_4 , etc.). Associated with this lock-in phase transition is the appearance of a macroscopic spontaneous polarization along the \mathbf{b} direction. This raises some questions. How is this polarization generated? Is it for example, induced by anharmonic couplings to the lattice modulation order parameter giving rise, for example, to an improper ferroelectric? Both these remain open questions.

Many attempts to detect X-ray satellite reflections in AHSe between 251.3 K and 261 K have remained *practically unsuccessful* for several reasons:

i) Aleksandrova *et al.* [9] have shown that the ^{77}Se NMR « incommensurate » spectrum has a « life time » varying between a few hours and few tens of hours (depending on sample quality, stresses, temperature cycling, ...)

ii) the satellite intensity is probably twice or three times smaller than the superstructure intensity measured at 223 K. In practice, we conclude that under our experimental conditions, the necessary exposure time is too long compared with the « life time » of the « incommensurate » state.

Figure 5c shows a photograph typical of those obtained not only between $T_{c_1} = 251.3 \text{ K}$ and 261 K, but also above T_i (here $T = 265 \text{ K}$). If we compare with the room-temperature diagram, figure 5a, modifications appear *essentially* along the \mathbf{a}^* direction. Such a diagram can be interpreted as resulting from a coexistence of the B2 phase plus another unknown X phase. All the reflections can be indexed with the help of two lattices:

i) a monoclinic crystal of B2 symmetry. The measured reciprocal parameters correspond to

$$a^* = \frac{2\pi}{a \sin \gamma} = 0.327 \text{ \AA}^{-1}$$

and
$$c^* = \frac{2\pi}{c} = 0.835 \text{ \AA}^{-1};$$

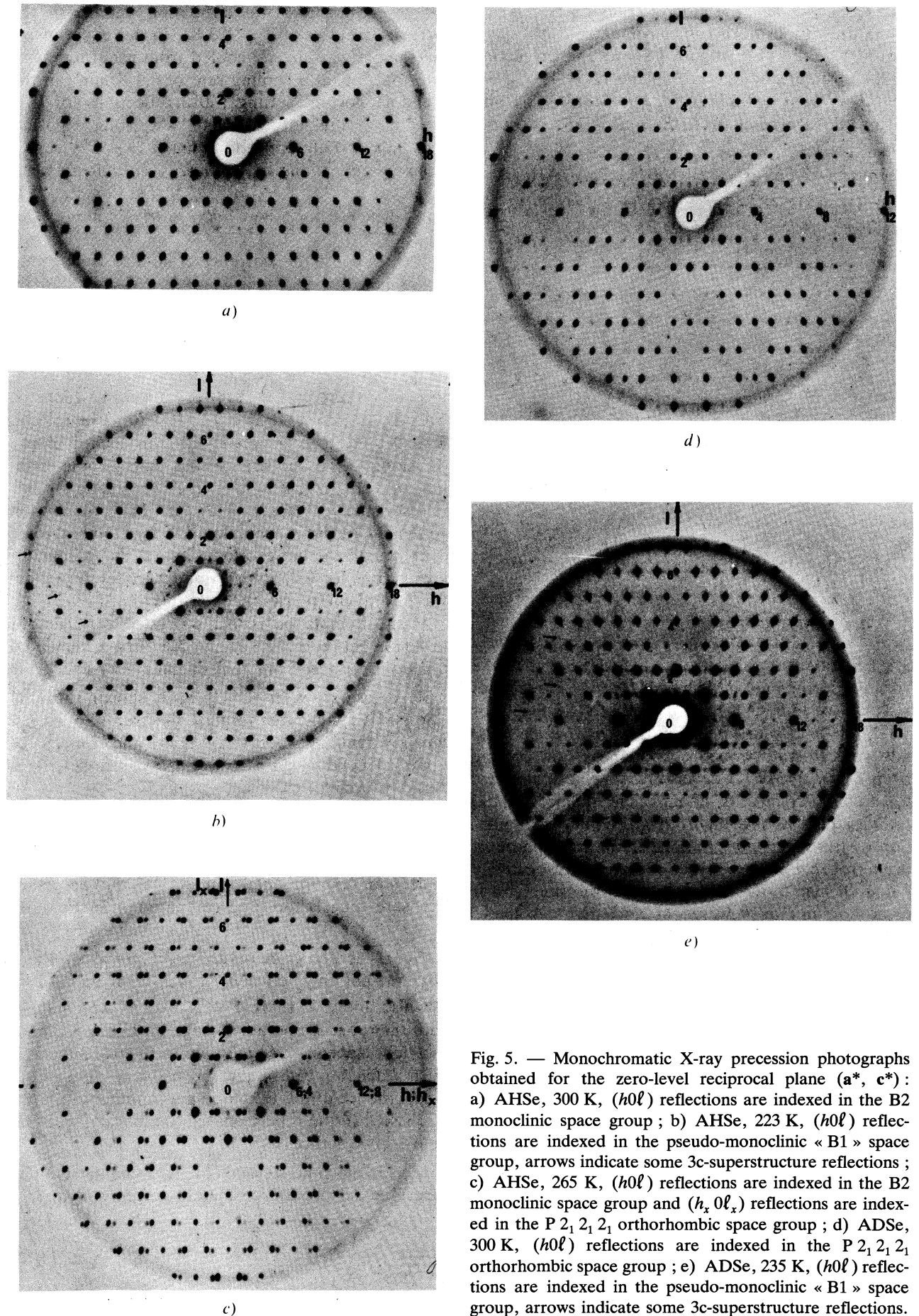


Fig. 5. — Monochromatic X-ray precession photographs obtained for the zero-level reciprocal plane (a^* , c^*): a) AHSe, 300 K, $(h0l)$ reflections are indexed in the B2 monoclinic space group; b) AHSe, 223 K, $(h0l)$ reflections are indexed in the pseudo-monoclinic « B1 » space group, arrows indicate some 3c-superstructure reflections; c) AHSe, 265 K, $(h0l)$ reflections are indexed in the B2 monoclinic space group and $(h_x 0l_x)$ reflections are indexed in the $P 2_1 2_1 2_1$ orthorhombic space group; d) ADSe, 300 K, $(h0l)$ reflections are indexed in the $P 2_1 2_1 2_1$ orthorhombic space group; e) ADSe, 235 K, $(h0l)$ reflections are indexed in the pseudo-monoclinic « B1 » space group, arrows indicate some 3c-superstructure reflections.

$(h0\ell)$ reflections obey extinction rules $h + \ell = 2n + 1$ (n integer);

ii) unknown X crystal.

The measured reciprocal parameters are $a_x^* = 0.489 \text{ \AA}^{-1}$, and $c_x^* = 0.839 \text{ \AA}^{-1}$, $(h_x 0 \ell_x)$ reflections obeying extinction rules $(h_x 00)$: $h_x = 2n + 1$ and $(\ell_x 00)$: $\ell_x = 2n + 1$. We deduce $a_x^*/a^* \approx 3/2$, $c_x^* \approx c^*$.

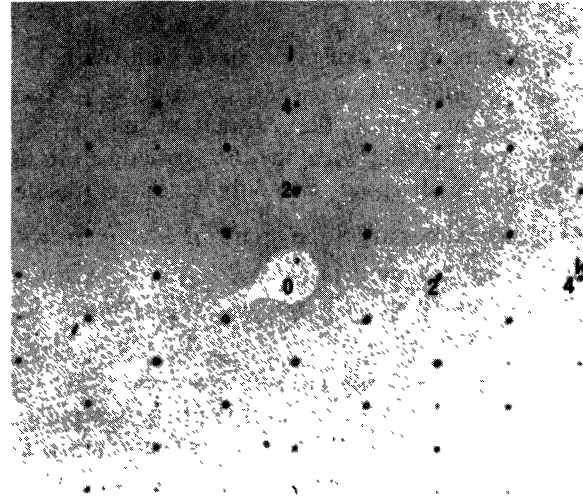
If we refer now to section 2, it is tempting to assume the unknown X structure, growing in the B2 phase, to be the $P 2_1 2_1 2_1$ orthorhombic modification. When this transformation takes place, we notice, as previously mentioned by Aleksandrova [9], the appearance of milky white areas localized within the crystal. Figure 5d shows the diffraction pattern obtained from a virgin ADSe sample in its $P 2_1 2_1 2_1$ original growing phase. Figure 5c can be viewed as resulting from the superposition of figure 5a (B2 phase) and figure 5d ($P 2_1 2_1 2_1$ phase). This gives a direct probe for our interpretation. Complementary experiments in different geometries lead to the same conclusions.

A question arises now as to what is the « growing » mechanism. We have seen a) that this mechanism of polymorphic transformation was found both in incommensurate and paraelectric phases; from the NMR results in reference [9], it seems to operate only in a temperature interval restricted to ($T_{c_1} = 250 \text{ K}$, $T_f \approx 271 \text{ K}$); b) that the reciprocal cell parameters $2a_x^*$, $3a^*$ and c_x^* , c^* , respectively, do not strictly coincide, leading us to the conclusion that the two phases coexist in a *non-coherent* way.

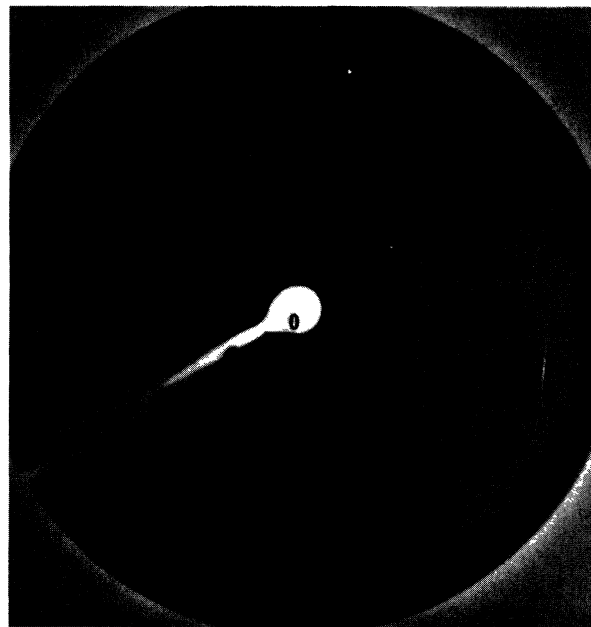
Returning to figure 1, showing the (temperature, x deuterium concentration) phase diagram of $\text{AH}_{1-x}\text{D}_x\text{Se}$, why was the T_p line not revealed for $x < 0.45$? Does it exist? A plausible explanation is that all the samples studied were always grown in the B2 phase above the unknown T_p curve. To solve this problem, it will be interesting to grow AHSe samples at a lower temperature in order to determine if it is possible to crystallize them in the $P 2_1 2_1 2_1$ phase.

3.2.2 ADSe. — Until now, no direct crystallographic measurements have been performed in the deuterated ammonium selenate when the phase sequence has been restored. To be complete, we show some photographs recorded for different phases of ADSe. To have a better understanding of the AHSe results, we show a diffraction photograph obtained with ADSe in the original growing phase (Fig. 5d) as in the previous section. After transforming the ADSe crystal in the paraelectric B2 phase, by heating the sample at 363 K for 4 hours, the temperature was gradually decreased at a cooling rate of 0.4 K/min down to a temperature $T = 235 \text{ K}$, below T_{c_1} . The photograph obtained at this temperature (reciprocal plane (\mathbf{a}^* , \mathbf{c}^*)) (pseudomonoclinic set-

ting) (cf. Fig. 5e), is quite similar to the diagram of figure 5b obtained for the ferroelectric phase of AHSe. Moreover, diffuse streaks located at the position of Bragg spots of the $P 2_1 2_1 2_1$ phase and elongated along the \mathbf{a}^* direction, are clearly seen in this photograph; they show the presence of very small nuclei (local order) of the $P 2_1 2_1 2_1$ phase.



a)



b)

Fig. 6. — Monochromatic X-ray precession photographs obtained for the zero-level reciprocal plane (\mathbf{b}^* , \mathbf{c}^*) (orthorhombic or pseudo-orthorhombic setting): a) ADSe, 300 K, $(0k\ell)$ reflections indexed in the $P 2_1 2_1 2_1$ orthorhombic space group; b) ADSe, 310 K, reflections $(\bar{h}h\ell)$ are indexed in the monoclinic B2 space group. Arrows indicate the existence of $2c$ -superstructure reflections.

A photograph of the equatorial (\mathbf{b}^* , \mathbf{c}^*) reciprocal plane is shown in figure 6a. At room temperature, in its original orthorhombic $P 2_1 2_1 2_1$ phase, $(0k\ell)$ reflections obey extinction rules $(0k0) : k = 2n + 1$, $(00\ell) : \ell = 2n + 1$. Figure 6b shows the same reciprocal plane in the « intermediate » phase at 310 K (after heating the sample at 363 K for 4 hours, the temperature was gradually decreased at 0.4 K/min down to $T = 310$ K where the temperature was stabilized while the photograph was recorded). The strong Bragg spots can be indexed with the help of the monoclinic setting. They correspond to $(\bar{h}h\ell)$ reflections and obey the extinction rule $h + \ell = 2n + 1$ compatible with the B2 structure. In addition, figure 6b shows two supplementary results :

i) Bragg superstructure spots of *extremely weak intensity* are revealed in $(\bar{h}h\ell \pm 1/2)$, giving, for the first time, evidence of a *new unit cell doubled along the c direction*,

ii) diffuse scattering is located around $(\bar{h}h\ell)$ with $h + \ell = 2n + 1$ (position of Bragg spots typical of the $P 2_1 2_1 2_1$ phase). They prove here again the presence of very small nuclei (local order) of the $P 2_1 2_1 2_1$ phase.

Finally, we would like to point out that, as in AHSe, we have observed in several samples growth of the $P 2_1 2_1 2_1$ phase not only in the intermediate phase, but also below T_c . The temperature interval in which this phenomenon manifests itself is restricted to about twenty degrees in AHSe, and broadens considerably in ADSe. Annealing time and annealing temperature (above T_p) are the parameters that play an important rôle in the subsequent temperature behaviour.

4. Concluding remarks.

The main experimental results can be summarized as follows :

1) A superstructure of period 3 along the \mathbf{c} direction has been observed below T_{c_1} in hydrogenated and deuterated samples. The structure of this phase should be reconsidered now.

2) In the ADSe intermediate phase, a doubling of the unit cell along the same \mathbf{c} direction has been revealed, raising a few questions. Does an incommensurate phase sandwiched between the B2 and the 2c-superstructure phase exist in deuterated samples ? What is the nature of the intermediate phase in AHSe ? Is it incommensurate ? Does a 2c-superstructure phase exist ? In order to answer these important questions, neutron diffraction experiments are now in progress and will be published soon.

3) Non-equilibrium processes, previously revealed by Aleksandrova *et al.* [9] have been studied and identified. These correspond to the growing of the orthorhombic $P 2_1 2_1 2_1$ phase not only in the paraelectric and incommensurate phases for AHSe, but also below T_c for ADSe, the two phases coexisting in a non-coherent way. Defects probably play an important rôle in the nucleation processes and this phenomenon demands now a complete and detailed study as a function of time, temperature and uniaxial stresses.

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