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SYMMETRY AND PHASE TRANSITIONS IN $(AsO_4)_2H_2(UO_2)_2 \cdot 8H_2O$

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Some reasonable guesses on the point group symmetry of the paraelectric, antiferroelectric and ferroelectric phases of synthetic hydrogen uranospinite have been made, taking as starting points the previously known facts and macroscopic symmetry considerations. The most probable point group for the paraelectric phase is $4/mmm$, for the antiferroelectric phase II most probable point groups are 1, $\bar{1}$, 2 and 222, for the ferroelectric phase III is 1 and for the forced ferroelectric phase IV, $4mmm$, Some mechanisms are proposed to explain the structural features observed.

INTRODUCTION

$(AsO_4)_2H_2(UO_2)_2 \cdot 8H_2O$ is a member of the family of uranium micas of general formula $A^z(UO_2XO_4)_z \cdot nH_2O$ and has been called synthetic hydrogen uranospinite by Mrose[1] and troegerite by Weisbach (Strunz).[2]

In a previous paper Benyacar and Abeledo[3] reported a phase transition that occurs at room temperature between a tetragonal, high temperature phase (phase I) and a low-symmetry phase (phase II). Benyacar and Dussel[4] observed another phase transition at $-20°C$ between this low-symmetry phase and a ferroelectric phase (phase III). Besides, they concluded that the high temperature tetragonal phase is paraelectric and phase II is antiferroelectric.

The crystal structure of tetragonal synthetic hydrogen uranospinite has not been solved and although the general features must be the same than those determined by Ross and Evans[5] and Ross, Evans and Appleman[6] for other members of the group, the system of hydrogen bonding will be known only through neutron diffraction studies. No X-ray single crystal diffraction study of phase II can be performed since such crystals are invariably twinned.

The crystals dehydrate in the electron microscope, so no electron diffraction studies have been tried.

We do not know the point group of any of the three phases. Notwithstanding, some inferences can be made on the probable mechanisms and symmetry of the phases involved in the phase transitions observed, and further experiments can be suggested to help answer some of the questions posed by this compound.

We will here summarize all the information already known:

1) The phase transition from phase I to phase II is reversible, non quenchable, from a tetragonal phase to a low-symmetry pseudo-tetragonal low-temperature form, which is invariably twinned.

2) The two sets of anisotropic domains, observed on the (001) tetragonal plates, are oriented at approximately 90° to each other and have domain walls parallel to {110}. Walls between the tetragonal matrix and the low symmetry domains are also also {110} planes.

3) Domain walls are visible as fine striae even in plain unpolarized light, with perpendicular incidence.

4) Parallel domains alternate their vibration directions and could be interpreted as twin-related lamellar individuals with composition planes parallel to {110} tetragonal.

5) Domain of both orientations have approximately equal volumes.

6) If a slight pressure is applied with a needle in any direction in the plane of the plates, domain walls move, and domains change their orientation.

7) Each domain is usually a composite of two or more subdomains. Subdomain walls, mostly parallel to {100} tetragonal usually cannot be observed with perpendicular incidence.

8) The subdomains in the same domain can be grouped into two sets, according to the orientation of their indicatrix elipsoids. A principal axis of the elipsoids makes an angle of approximately 7° with the plane of the plates, pointing alternatively downwards and upwards in neighbouring subdomains.

9) Subdomains sets are of approximately equal volumes.

10) Precession photographs of the twinned crystals failed to show any departure from tetragonal symmetry.

11) A first order phase transition at room temperature is suggested by the presence of a peak in the DTA curve and by thermal hysteresis observed in the dielectric susceptibility peak.

12) The observed ferroelectric hysteresis loop (phase III) is symmetric.

13) Once the crystal has become ferroelectric at about −20°C, it can be heated even above the temperature of the phase I–phase II transition, remaining in the ferroelectric state.

DISCUSSION

Bearing these starting points in mind, we will begin by assuming that, as the phase I–phase II transition is reversible with little or non appreciable thermal hysteresis (at least when observed in the optical microscope), only small free energy changes are involved. There should be no changes in the first coordination of the atoms and no breaking of atomic bonds. We can consider this phase transition to be of the displacive type and there should be only small distortions of the crystal lattice. This assumption is further supported by the pseudo-tetragonal symmetry of the low temperature form, as shown by the x-ray precession photographs. There is no clear evidence for the formation of a supercell.

We shall first consider the distortions observed in the (001) plane of the tetragonal lattice.

Domain walls are visible even with perpendicular incidence and unpolarized light because the index of refraction at both sides of the walls are appreciable different: we may conclude that the slight distortion of the crystal lattice is partly accomplished through contractions and expansions along the *a* and *b* tetragonal axes. As the two sets of domains are oriented at approximately 90° to each other, we will assume that in one domain the tetragonal cell contracts, let us say, along *a* and expands along *b*, while in the neighbouring domain the cell expands along *a* and contracts along *b*. The *a* and *b* axes being crystallographically equivalent in the tetragonal system, both distortions are equally probable and both kind of domains will have approximatively equal volumes: the tetragonal crystal becomes a polysynthetic twin when it transforms into phase II. Besides, in this way no large strains are developed, the crystal does not break when going through the transition, the asymmetric distortion is different in alternate small regions so as to produce a macroscopically undistorted crystal.

According to this model, {110} tetragonal planes remain almost undistorted, except for slight rotations around [001] which should not be discarded, and they can appear as domain walls. Domain walls reaction to even small pressures in the (001) tetragonal plane also supports this expansion-contraction model.

Subdomain walls are usually invisible with perpendicular incidence and unpolarized light; we can assume that no appreciable change in the index of refraction is encountered when going through the subdomain walls: no contraction or expansion of the crystal lattice should be associated with subdomain formation, which could be related to small tilts of structural units and with small shear deformations of the crystal lattice.

The indicatrix elipsoids of both sets of subdomains have a principal axis lying on the plane of the plates, parallel to the direction of maximum refractive index and approximately parallel to ⟨100⟩ tetragonal. This direction should be associated with the contraction direction of the tetragonal cell. In this proposed monoclinic model (M_1), this direction may be related to the *b* axis of the monoclinic lattice, and a shearing deformation of the tetragonal plane perpendicular to it can be assumed. Shearing is equally probable in the [101] and [101] tetragonal directions, as they are crystallographically equivalent in the tetragonal form: both subdomain orientations should have equal probabilities and equal volumes and the unsheared {100} tetragonal planes can now appear as subdomain walls.

The point group of none of the phases is known, but some information can be obtained from the twinned structure of phase II. We will analyze only the changes observed in the isotropic section of the tetragonal crystals, the mica-like habit of the crystals precluding observations in any other section.

We know that the paraelectric (tetragonal) crystal becomes a polysynthetic twin when it transforms into phase II. (Figures 1 and 2 Benyacar and Dussel.)[4] The symmetry planes of the tetragonal phase appear as twin planes of the low-symmetry phase: they are not symmetry elements of the low-symmetry phase and they were symmetry planes of the tetragonal crystal. In consequence, possible point groups for the tetragonal phase are *4mm* and *4/mmm*.

We shall consider each of the point groups *4mm* and *4/mmm* as possible point groups for the initial phase and we shall try to gain new insight into the probable symmetry of phases II and III.

Initial Phase Point Group 4mm

Phase II can belong to *point groups 1 and 2* as we have ruled out point group *4* on the basis of the optically biaxial character of the sample and *point groups m and mm2* on the basis of the observed twin planes. For

point group 2, the two-fold axis should be parallel to the initial tetragonal axis. This is not the case, as in the subdomains no principal axis of the indicatrix elipsoid remains perpendicular to the initial (001) tetragonal plane. Besides, it is not easy to justify the fact that both optical elipsoids observed in the same domain are rotated around a principal axis which coincides with a monoclinic crystallographic axis (*a* or *c*) when this is not necessitated by symmetry considerations. Were not the rotation direction coincident with a crystallographic axis, two more types of subdomains should be observed.

Initial Phase Point Group 4/mmm

Only optically biaxial point groups for phase II will be considered.

Point groups mmm, mm2 and 2/m (two-fold axis perpendicular to the initial tetragonal axis) are ruled out on the basis of the observed twin planes.

Point groups 2/m, 2 (both with two-fold axis parallel to the initial tetragonal axis), can be ruled out for the same reasons discussed for initial point group *4mm*.

Point group 222 involves no shearing of the tetragonal phase and it is not easy to justify the observed forward and backward rotations of the indicatrix elipsoids if the (001) tetragonal surface remains smooth. Nevertheless, this alternating orientation of neighbouring subdomains should result in a subdomain surface relief with a "saw-tooth" like profile. Were this the case, this "saw-tooth" like profile would be associated with the expansion direction of the initial tetragonal crystal and it should be reflected in a rippled texture of the surface of the crystal. Ripples should run in perpendicular directions and might be observable at an atomic level. They should be visible in micrographs of shadowed replicas of the surface of the plates taken while the crystals are in phase II. On the other hand, this surface structure would not be a conclusive proof of orthorhombic symmetry as it can be related, for example, to the previously discussed monoclinic model M_1, in which the contraction direction of the tetragonal cell was assumed to be parallel to the two-fold axis of the monoclinic phase. The expansion of the cell in a perpendicular direction could give rise to a similar rippled surface relief.

Point group m involves shearing in the (001) tetragonal plane, which has not been detected. Furthermore, the same objection discussed for point group 2, with the two-fold axis parallel to the initial four-fold axis are still valid, as a principal axis of the indicatrix elipsoid must be perpendicular to the mirror plane.

Point group 2 (with the two-fold axis perpendicular to the initial four-fold axis), has been discussed when analyzing the most probable distortions of the tetragonal cell.

Point group 4/mmm appears as the most probable group for the tetragonal phase of synthetic hydrogen uranospinite. This is also the point group of some members of this family of uranium micas, as determined by Ross and Evans[5] for $K(UO_2AsO_4).3H_2O$, $NH_4(UO_2AsO_4)\ 3H_2O$ and $K(H_3O)(UO_2\,AsO_4).6H_2O$.

The described monoclinic model M_1 is only compatible with an initial phase of symmetry *4/mmm*, as the two-fold monoclinic axis was assumed to be perpendicular to the initial four-fold axis.

Point-groups 1, $\bar{1}$, 2 and 222 are the only possible point groups for phase II.

Up to here, only macroscopic symmetry considerations governing structural phase transitions have been discussed and the influence of polarization has not been taken into account.

We have implicitly assumed that two interacting, though independent in origin, mechanisms are responsible for the structural and the ferroelectric properties observed.

Following Megaw[8] in her discussion of structure and transitions in perovskites we have considered that in synthetic hydrogen uranospinite "the ferroelectricity is, as it were, accidental". In this compound with a mica-like structure, arsenate tetrahedra and uranyl octahedra construct infinite waffle-like $(UO_2AsO_4)_n^{n-}$ sheets with the H^+ and hydrogen-bonded water molecules lying between successive layers. The concept of hard and soft structural features defined by Megaw will undoubtedly be most useful to understand, at an atomic level, the phase transitions observed in this layered material. Tilting of the structural units in each sheet could account for expansion and contraction of the initial tetragonal *a* and *b* axis; tilting of the structural units in a sheet should influence tilting in neighbouring sheets via the hydrogen bonded water molecules. Disorder along the initial four-fold axis should occur if this influence is not strong enough to achieve an homogeneous tilting orientation across the crystal layers.

The ferroelectric character can be linked to displacement of ions: ordering of H^+ ions and off-centering of the central ion in a hard structural unit. It is worth mentioning that Ross and Evans[5] in their study of the crystal structure of the NH_4^+, K^+ and $K^+(H_3O)^+$ members of the series state that the asymmetrical environment of the uranyl ion may cause polarization of the uranyl ion.

Benyacar and Dussel[4] have shown that the ferroelectric phase appears at $-20°C$, when an electric field is applied parallel to the axis of the linear $(O\text{-}U\text{-}O)^{2+}$ ion. We will not discuss these mechanisms further.

In trying to learn something about the symmetry of the ferroelectric phases, we will follow Shuvalov[9] conclusion that the paraelectric phase can be considered the initial phase for all the ferroelectric phases observed.

Not much can be guessed about the symmetry of ferroelectric phase III as its domain structure is not known, but the symmetric electric hysteresis loop observed when the crystal is cooled down to −20°C justifies the assumption that in phase III the material is a classical, reversible ferroelectric with Ps oriented parallel or nearly parallel to the initial tetragonal axis. No mirror plane and no two-fold axis can be present perpendicular to the initial four-fold axis. If the gross main features of the domain structure are the same that those of phase II, space groups *mm*2 and *m* are ruled out; a possible point group for phase III is then 1.

Once the crystal has been switched to the ferroelectric state at −20°C it can be kept up to 25°C in the ferroelectric state sometimes for as long as a week. In the heating process, the major domain-structure features of phase II and the isotropic character of the plates at high temperature, are still observed. We shall call this high symmetry forced ferroelectric phase, with an isotropic section parallel to the plane of the plates, phase IV and its point group symmetry must be 4*mm*. We do not know whether any intermediate forced ferroelectric phase exist between phase III and phase IV. The existence of phase IV further supports our assumption that two interacting mechanisms are responsible for the structural and ferroelectric properties observed.

CONCLUSIONS

Starting from the known domain structure of phase II and symmetry considerations an attempt was made to elucidate the point group symmetry of the different phases observed in $(AsO_4)_2H_2(UO_2)_2 \cdot 8H_2O$ at different temperatures. The following are considered to be the most probable point groups for the different phases:

Phase I		Phase II		Phase III
paraelectric	$\simeq 20°C$ →	antiferroelectric	$-20°C$ →	ferroelectric
P.G. 4/*mmm*		P.G. 1, $\bar{1}$, 2, 222		P.G. 1

Phase IV
forced ferroelectric ← ? ←
P.G. 4*mm*

The proposed mechanisms involve expansions, contractions and shearing of the initial tetragonal cell to account for the structural changes observed. These modifications may be accompanied by the tilting of structural units. The ferroelectric character, on the other hand, must be related to displacement of ions; most probably H and O ions; this is an independent process as can be deduced from the presence of the forced ferroelectric phase IV.

REFERENCES

1. M. E. Mrose, *Am. Mineral.* 38, 1159 (1953).
2. H. Strunz. Mineralogische Tabellen 5 Auflage, (Akademische) Verlagsgesellschaft Geest und Portig. K. G. Leipzig, 1970).
3. M. A. R. de Benyacar and M. E. J. de Abeledo, *Am. Mineral.* 59, 763 (1974).
4. M. A. R. de Benyacar and H. L. de Dussel, *Ferroelectrics*, 9, 241 (1975).
5. M. Ross and H. T. Evans Jr. *Am. Mineral.* 49, 1578 (1964).
6. M. Ross, H. T. Evans Jr. and D. E. Appleman, *Am. Mineral.* 49, 1603 (1964).
7. M. J. Buerger, *J. Chem. Phys.* 15, 1 (1947).
8. H. D. Megaw, *J. de Physique, Suppl.* 33, C2, 1 (1972).
9. L. A. Shuvalov, *J. Phys. Soc. Japan* 28, Suppl. 38 (1970).