Acta Cryst. (1958). **11**, 307

Non-isomorphism of ferroelectric phases of ammonium sulfate and ammonium fluoberyllate.*

By Y. Okaya, K. Vedam and R. Pepinsky, *X-Ray and Crystal Analysis Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pa., U.S.A.*

(*Received* 4 *November* 1957)

Matthias & Remeika (1956) discovered that ammonium sulfate becomes ferroelectric below −49·5° C. It was subsequently found in this laboratory that ammonium fluoberyllate also becomes ferroelectric, below −97° C. (Pepinsky & Jona, 1957). The fact that $(NH_4)_2BeF_4$ at room temperature was reportedly isomorphous with $(NH_4)_2SO_4$ (Mukherjee, 1944; Wyckoff, 1951), and that we were interested in finding a ferroelectric containing no oxygen, led us to look for the fluoberyllate transition.

It is rather surprising to discover, therefore, in a re-examination of these two compounds, that there are sometimes differences in the room-temperature symmetries, and that the polar axes in the ferroelectric phases are not in the same directions—i.e., the low-temperature phases are surely not isomorphous.

Some confusion arises in the literature of these K_2SO_4-type crystals owing to variations in axial notation. The room-temperature structures are orthorhombic, and the axial designation should follow the convention $c < a < b$ (Donnay & Nowacki, 1954). Groth (1908) uses $a < c < b$, and Wyckoff (1951) uses $c < b < a$. We shall here use the proper crystallographic convention for the axial lengths of the basic cells at room temperature.

The basic cell dimensions for $(NH_4)_2BeF_4$, at room temperature, are

$$a = 7{\cdot}49, \quad b = 10{\cdot}39, \quad c = 5{\cdot}89 \text{ Å} \quad \text{(Mukherjee, 1944)}\,.$$

The basic space group, with this axial designation, is *Pnam*. This follows from space-group extinctions and the absence of piezo- and pyroelectricity.

We use the term 'basic' cell because our re-examination of the $(NH_4)_2BeF_4$ structure reveals superstructuring, with the true room-temperature cell having the b and c dimensions doubled. This superstructuring does not obtain for all crystals of the K_2SO_4 type; and in order to emphasize the pseudo-isomorphism of these, we maintain the same axial designation for the basic cells of the entire family.

The symmetry of the true (superstructured) cell of $(NH_4)_2BeF_4$ at room temperature is *Acam* or *Aca*2; and we select the former because of the absence of piezo- and pyroelectricity. In addition to the weak superstructure lines, stacking disorder is revealed in the b direction.

$(NH_4)_2SO_4$ at room temperature sometimes shows a superstructure and sometimes does not. The axial lengths for the basic cell are

$$a = 7{\cdot}729, \quad b = 10{\cdot}560, \quad c = 5{\cdot}951 \text{ Å} \quad \text{(Wyckoff, 1951)}\,,$$

if we follow the convention $c < a < b$.

The ferroelectric phases of these two crystals are significantly different.

Below its Curie point, $(NH_4)_2BeF_4$ has its a dimension doubled. The basic ferroelectric cell has

$$a_f^b \simeq 2a,\; b_f^b \simeq b,\; c_f^b \simeq c\,,$$

and the symmetry is $Pn2_1a$. The true ferroelectric cell has a superstructure, and

$$a_f \simeq 2a,\; b_f \simeq 2b,\; c_f \simeq 2c\,.$$

Dielectric measurements confirm b as the polar (ferroelectric) axis.

$(NH_4)_2SO_4$ shows no changes in axial lengths or systematic absences in passing to its ferroelectric phase. The mirror symmetry of the room-temperature structure is lost, and the space group becomes $Pna2_1$. The establishment of c as the polar direction is confirmed by dielectric measurements. Thus the direction of the ferroelectric axis in $(NH_4)_2SO_4$ is at 90° to that in $(NH_4)_2BeF_4$.

Complete X-ray and neutron studies of the upper and lower phases of both crystals are in progress, and knowledge of the mechanisms of the transitions must await completion of these. Dielectric and thermal studies of the transitions are reported elsewhere (Hoshino, Vedam, Okaya & Pepinsky, 1958).

X-ray and thermal measurements have been made on a number of other crystals of the K_2SO_4 type, and on various mixed crystals in this class. It has been found, for example, that superstructure maxima appear in $(NH_4)_2(BeF_4, SO_4)$ at room temperature, and these resemble maxima in a fibre diagram. X-ray patterns of $(NH_4, Rb)_2SO_4$ reveal disorder in the (001) plane. We have observed new transitions and other anomalous properties in a very large number of simple, double and mixed anhydrous sulfates, selenates, fluoberyllates, chromates, etc. and these are presently under examination.

References

Donnay, J. D. H. & Nowacki, W. (1954). *Crystal Data*. New York: Geological Society of America, Memoir 60.

Groth, P. (1908). *Chemische Krystallographie*, vol. 2. Leipzig: Engelmann.

Hoshino, S., Vedam, K., Okaya, Y. & Pepinsky, R. (1958). *Phys. Rev.* In the Press.

Matthias, B. & Remeika, J. P. (1956). *Phys. Rev.* **103**, 262.

Mukherjee, P. L. (1944). *Indian J. Phys.* **18**, 148.

Pepinsky, R. & Jona, F. (1957). *Phys. Rev.* **105**, 344.

Wyckoff, R. W. G. (1951). *Crystal Structures*, vol. 2, chap. 8, table p. 47. New York: Interscience Publishers.

---

* Research supported by the Contract No. AF 18(603)-35 with the Air Force Office of Scientific Research, Contract No. DA-36-039-SC-72385 with the Army Signal Corps Engineering Laboratories, and Contract No. AT(30-1)-1516 with the Atomic Energy Commission.