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Brief Reports

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Optical study of the successive phase transitions of *n*-alkyl ammonium dihydrogen phosphate crystals

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Measurements of the birefringence and indicatrix rotation in a family of ammonium dihydrogen phosphate (ADP) related ferroelastic crystals $C_nH_{2n+1}NH_3H_2PO_4$ (abbreviated as C_nADP), with $n=1-9$ and 12, reveal successive phase transitions depending on the lengths of the alkyl ammonium chains. This, taken together with the results of investigations of the dielectric constant, thermal expansion, and elastic modulus in C_7ADP, shows that intercalated layered structures are realized in this case with different packing of the chains for odd and even n between layers of PO_4 tetrahedra linked two dimensionally by H bonds.

The phase transitions in layered crystals like the well-known layered perovskites (see Ref. 1 and references cited therein) are due to rotational ordering or collective conformational transformations of the chains, the inorganic matrix (layers of the corner sharing octahedra in that case) remaining rather unchanged. Such a system provides, e.g., a model for a lipid bilayer embedded in a crystalline matrix.[2] We present in this paper results of investigations of ten crystals with the chemical formula $C_nH_{2n+1}NH_3H_2PO_4$, which can be considered as relatives to the well-known ammonium dihydrogen phosphate (ADP) ($NH_4H_2PO_4$), where the ammonium ions are substituted by alkyl ammonium chains of various lengths. The compounds may crystallize in layers of PO_4 tetrahedra linked by H bonds alternating with layers of alkyl ammonium; proton ordering within the anorganic layers should be similar to the ordering in ADP. The results of our investigations can be therefore compared with the characteristic behavior of similar layered systems.

The substances, with $n=1-9$ and 12, were prepared by mixing stoichiometric amounts of the particular *n*-alkyl amin (purum, Fluka) with H_3PO_4. Single crystals were grown from a methanol solution using a thermal gradient method. The samples obtained were typically thin plates of several mm^2 area and 0.1–0.5 mm thick. Some problems occurred with C_1ADP, which is rather hygroscopic, and with C_{12}ADP, where only very small samples were obtained. All crystals showed a dense ferroelastic lamellar domain structure (which can be changed by pressing the samples) when observed under the polarizing microscope. In all cases the direction perpendicular to the plates (denoted as the *c* direction here) coincides with the acute bisectrix, with different indicatrix orientation in the neighboring domains. This means that the symmetry of the crystals is not higher than monoclinic. The chemical composition of the samples was controlled by elementary organic analysis (for C, N, P, and H contents). In all cases checked so far (for $n=3$, 4, 7, 8, and 9) the chemical formula given above was confirmed.

The orientation of the optical indicatrix in the two neighboring domains is schematically illustrated for the various samples in Fig. 1, where φ denotes the angle between the domain walls (which was usually the only well-defined direction in the samples) and the fast axis of the indicatrix section. The birefringence Δn_{ab} is typically of about 4×10^{-3} and even smaller in C_3ADP and C_5ADP. The temperature dependence of the indicatrix rotation angle φ measured during the first heating of the as grown samples are shown in Fig. 2. At the ferroelastic transition φ goes to zero (or 90°) either continuously in crystals with short chains ($n=1-4$) or by a jump (for $n\geq5$) and the domain structure, which becomes very dense closely below the transition, disappears. A certain inhomogeneity of the samples (slightly disoriented blocks) is, however, observed between crossed polarizers even above the transition. It slowly disappears on further heating. Note that for crystals with longer ($n\geq5$) chains the behavior of φ differs in the samples with odd and even number of carbons in chains.

A more complete picture of phase transitions is obtained from measurements of the birefringence, performed again using the polarizing microscope (in a single domain in the ferroelastic phase) either manually with a Berek compensator (rotating in the same time the sample according to the indicatrix rotation) or with an automatic

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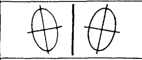
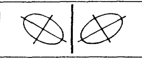
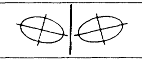
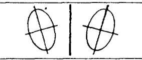
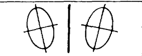
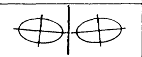
n	indicatrix orientation	φ(°)	optic sign	Δn
1		80	+	3.4
2		77	+	3.9
3		30	+	1.6
4		12	—	4.2
5		65	—	2.7
6		13.5	—	3.4
7		75	—	4.2
8		11.5	—	4.1
9		78	—	4.3
12		~5	—	

FIG. 1. Optical indicatrix orientation in C_nADP, $n=1-9$ and 12 in the neighboring domains. The birefringence Δn_{ab} is given in units 10^{-3}. $C_{12}ADP$ samples were too small for Δn determination.

Senarmont compensator[4] (with manual rotation at the transition only). The results are summarized in Fig. 3. For the crystals with $n \geq 5$ we find further phase transitions above the ferroelastic one, all of strongly first order. The hysteresis effects are again different in crystals with odd and even numbers of carbons in the chain. In the former case, the stability of the room-temperature phase decreases with the increasing length of the chain. In C_9ADP after cooling from the high-temperature phase a different phase (probably similar to the normal room-temperature phase of the even crystals) remain stable. In the crystals with $n=4$, 5, and 6 the strains at the ferroelastic transition are so large (compare also the indicatrix rotation in Fig. 1) that the samples become opaque at room temperature after they were once heated above the ferroelastic transition. At high temperatures the birefringence becomes very low in all samples.

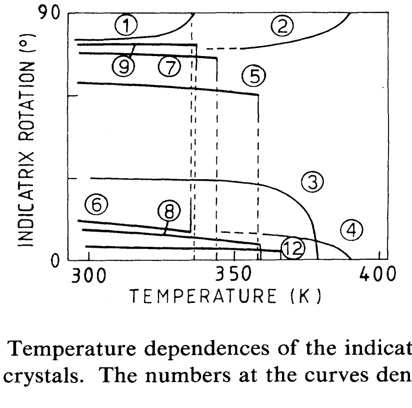


FIG. 2. Temperature dependences of the indicatrix rotation in C_nADP crystals. The numbers at the curves denote the particular n.

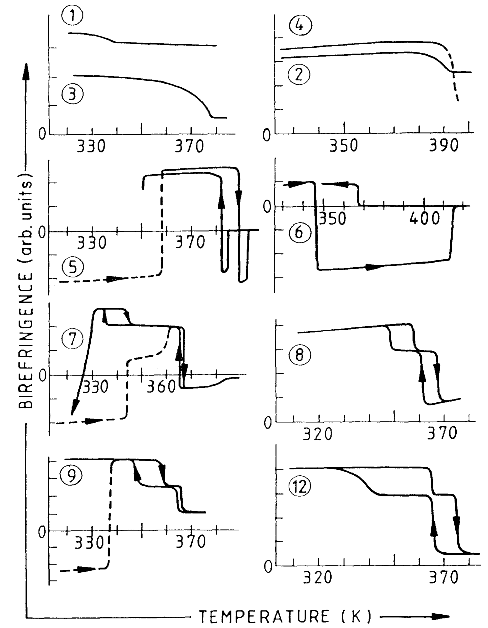


FIG. 3. Temperature dependences of the birefringence in C_nADP crystals. The dashed curves for $n=5$, 7, and 9 show the first heating of the virgin samples. For $n=4-6$ no measurement we more possible below the ferroelastic transition on cooling.

To obtain additional informations about the nature of the transitions we have also studied dielectric and mechanical properties of several crystals. In Fig. 4 preliminary results for C_7ADP are shown. The thermal expansion and the elastic modulus were measured along the

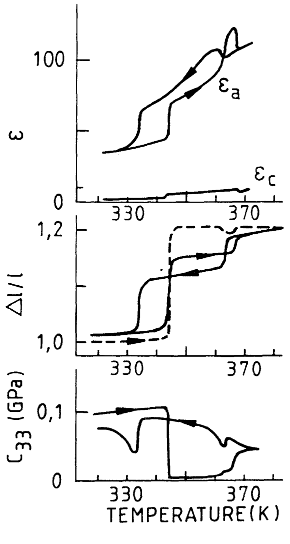


FIG. 4. Temperature dependences of the dielectric constants ϵ_a and ϵ_c and of the thermal dilatation and elastic modulus along c axis in C_7ADP. The dashed line shows the thermal dilatation on the first heating the sample.

c axis using a Perkin-Elmer DMA7 system. We observe large (but still reversible, and well reproducible after the first heating) changes of the thermal expansion at the transitions and a very large decrease of the elastic modulus above the ferroelastic transition on heating. The temperature dependence of the dielectric constant is similar to the one in the layered perovskites,[3] but in our case we have an appreciably larger dielectric anisotropy. The dielectric constant ϵ_a in the direction parallel to the layers (measured on the sample cut perpendicularly to the plate and to the domain walls) is more than one order of magnitude larger then ϵ_c. Similar results were obtained for the crystals with $n=3$, 4, and 8. In these crystals small jumps of the dielectric constant reveal additional phase transitions within the ferroelastic low-temperature phase, which only very slightly influences the optical behavior.

In C_nADP crystals the anorganic layers can be easily modified either by substitution of P by As atoms or by deuteration. We have prepared samples of alkyl ammonium dihydrogen arsenates C_n ADA and deuterated phosphates d-ADP with $n=7$ and 8. In the latter case D_3PO_4 and normal alkyl ammonium were used for the crystallization from heavy-water solution. Because especially the deuterated samples were rather small and not yet satisfactory for quantitative measurements, we shall mention here only some qualitative results. In the arsenates the ferroelastic transition is shifted to higher temperatures. In C_7ADA its temperature is increased by about 20 K with respect to the corresponding phosphate, while in C_8ADA the ferroelastic phase is stable up to the melting point. The deuteration has an important effect in d-C_7ADP, where no domains are present at room temperature and only a transition similar to the 369-K transition in normal C_7ADP (the chains melting) occurs at 360 K. An additional first-order transition appears at 220 K, but no ferroelastic domains are seen even below it.

A detailed report on our investigations will be published elsewhere.[5] However, the main features of the behavior of the C_nADP crystals presented here make it possible to draw certain conclusions concerning the structure and the nature of the (main) phase transitions: First our data confirm the presence of an intercalated layered structure, with the layers of the PO_4 tetrahedra linked by a two-dimensional network of the H bonds. The trans-trans[3] chains conformation at room temperature leads to different packing for odd and even n, as in some other intercalated systems.[6] The crossover from the continuous behavior at the ferroelastic transition in the crystals with short chains (to $n=4$) to the discontinuous jumps at lower temperatures in the crystals with longer chains (Fig. 2) is characteristic for the layered structures. In the former case the key-hole interaction (i.e., the interaction of the NH_3 end of the chain with the layer) is important, while the interchain interaction increases its role with increasing lengths of the chains and different structures (and chains packings) may be realized. The behavior of the thermal expansion with the total (and reversible) change of more than 20% in C_7ADP demonstrates again essential changes of the chain system; probably an orientational ordering of the chains at the first transition and the chains melting at the second one.[6] The assumption of an H-bond network connecting the PO_4 tetrahedra is supported by the observed dielectric anisotropy. The proton ordering within the layers may be influenced by transformations of the chains due to the chain-layer coupling. The deuteration has strong effect in some of the crystals. It is probably caused by a modification of the crystal structure. The nature of the additional transitions within the ferroelastic phase in most of the crystals, connected with small dielectric anomalies, remains unclear.

We may conclude that we introduce a new group of ferroelastic crystals with intercalated layered structure and various phase transitions within the chain system. Very interesting questions for further work concern the proton ordering within the layers and its interaction with the chains. However, for better insight into the nature of the phase transformations in these compounds structural data are needed. X-ray investigations and the growth of the larger crystals for dielectric and elastic studies are now in progress.

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[1] R. Kind, Ferroelectrics **24**, 81 (1980).

[2] R. Blinc, M. I. Burgar, V. Rutar, B. Zeks, R. Kind, H. Arend, and G. Chapuis, Phys. Rev. Lett. **43**, 1679 (1979).

[3] R. Kind, S. Plesko, H. Arend, R. Blinc, B. Zeks, J. Seliger, B. Lozar, J. Slak, A. Levstik, C. Filipic, V. Zagar, G. Lahajnar, F. Milia, and G. Chapuis, J. Chem. Phys. **71**, 2188 (1979).

[4] M. Zimmermann and W. Schranz, Meas. Sci. Technol. **4**, 186 (1993).

[5] J. Kroupa and A. Fuith (unpublished).

[6] G. Chapuis, K. Schenk, and J. Zuniga, Mol. Cryst. Liq. Cryst. **114**, 113 (1984).