Elastic Properties of Monoclinic Telluric Acid Ammonium Phosphate, 
\(\text{Te(OH)}_6 \cdot 2\text{NH}_4\text{H}_2\text{PO}_4 \cdot (\text{NH}_4)_2\text{HPO}_4\),

near the Paraelectric-Ferroelectric Transition

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Dedicated to Prof. Dr. H.E. Müser on the occasion of his 60th birthday

The elastic constants of \(\text{Te(OH)}_6 \cdot 2\text{NH}_4\text{H}_2\text{PO}_4 \cdot (\text{NH}_4)_2\text{HPO}_4\), TAAP, point symmetry \(m\), have been measured by ultrasonic resonance methods passing through the paraelectric-ferroelectric transition at ca. 320 K. In the range between 273 and 340 K the elasticity tensor exhibits only a slight anisotropy. No discontinuity of the elastic constants is observed. However, some temperature derivatives of the elastic constants show slight anomalies within the range 310 to 325 K. The strongest effect occurs with the longitudinal elastic resistance \(c_{22}\). The thermal expansion which varies only slightly between 263 and 340 K, is highly anisotropic in contrast to the thermoelastic behaviour. A strong negative thermal expansion is observed in a direction within the mirror plane, ca. 45° apart from the direction of spontaneous polarization. This effect is not accompanied by a corresponding thermoelastic anomaly. The interactions connected with the transition are of the totally symmetric type. Like many other properties the elastic and thermoelastic behaviour of TAAP resembles that of triglycine sulphate (TGS). Larger differences between TAAP and TGS are found in the pressure dependence of various properties. For example the pressure dependence of the transition temperature \(T\) is negative for TAAP (−3.8 K/kbar) and positive for TGS (3.9 K/kbar).

Introduction

At room temperature telluric acid forms various types of addition compounds with alkali or ammonium phosphates and arsenates. Some of the potassium and ammonium salts have been recently studied in respect to their structural properties [1]. Special interest has been devoted to the title compound TAAP which possesses a paraelectric-ferroelectric transition at ca. 320 K. Large single crystals have been grown by Nicolau from aqueous solutions at ca. 300 K employing a recirculation technique [2]. Dielectric, pyroelectric and optical properties have been reported by Gauthier et al. [3]. They found a surprising similarity to triglycine sulphate in all these properties. The aim of the present paper is to clarify whether also the elastic properties show such a similarity in the vicinity of the transition.

Experimental

Single crystals of optical quality with dimensions up to 50 mm were grown from non-stoichiometric aque-
ous solutions by the method outlined in detail by Nicolau [2]. The axes $e_i$ of our Cartesian reference system are related to the crystallographic basic vectors $a_i$ according to

$$e_i \parallel (a_i^* + a_j^*)$$

The setting as introduced by Averbuch-Pouchot and Durif [1] is characterized by $a_1 = 15.66 (5)$, $a_2 = 6.314 (5)$, $a_3 = 9.818 (5)$, $a_4 = 105.49 (5) \degree$, space group $Pn$. $a_i^* \parallel$ are the basic vectors of the corresponding reciprocal system. In our setting the vector $e_3$ coincides with the (101) face normal which runs nearly parallel to the direction of spontaneous polarization [3]. The specimens for the measurement of elastic wave velocities were cut as rectangular parallel-epipeds with dimensions of about $10 \times 10 \times 10$ mm. On each specimen at least one pair of faces was prepared plane-parallel with deviation from plane-parallelism less than 0.001 mm, yielding definite acoustic resonators with propagation vectors normal to those faces. The resonance frequencies of these plates were measured in the range between 6 and 40 MHz at different temperatures between 263 and 340 K.

The state of resonance was detected with the aid of diffraction of monochromatic light by the ultrasonic grating of the standing waves. The wave velocities $v$ are obtained from the $m$th and $n$th resonance frequency $f_m$ and $f_n$ employing the relation $v = 2D (f_n - f_m)/(n - m)$, where $D$ is the thickness of the plane-parallel plate. The velocities of each triple of elastic waves propagating in the directions $e_i$ and $(e_i \pm e_j)$, $(i, j = 1, 2, 3)$ were measured, yielding a set of 21 independent wave velocities.

Our raw crystals possessed a certain amount of macroscopic twinning, contact twins on $\{101\}$, as described by Nicolau [2]. Some specimens could not be prepared in monocrystalline form. In those cases a splitting of the resonances was observed. Due to the small orientational difference of the two possible domains, the influence on the accuracy was negligible. In all cases the errors of the wave velocities could be limited to less than 0.3%. The evaluation of the thirteen independent elastic constants $c_{ijkl}$ of our monoclinic crystal was achieved by employing a computer program which had been used earlier in the case of triclinic crystals by Haussi hl and Siegert [4]. For each wave velocity we obtain one determinant

$$-\rho v^2 \delta_{ik} + c_{ijkl} g_j / g_i,$$

which vanishes if the corresponding directional cosines $g_i$ of the propagation vector are introduced. $c_{ijkl}$ are the components of the elasticity tensor. If the set of propagation directions is chosen as given above, the results can easily be controlled by hand calculations except in the case of $c_{12}$, $c_{23}$ and $c_{25}$, where the hand calculation requires several steps of approximation. The piezoelectric coupling, which is present in crystals of point symmetry $m$, was neglected, as it is very small due to the small piezoelectric constants and the large dielectric constants in the vicinity of the transition temperature. The density used is $\rho = 2.121$ g cm$^{-3}$, determined on large single crystals by the buoyancy method at 293 K. The thermoelastic constants $T_{ij} = d \log c_{ij}/dT$, $T$ temperature, were derived from the values $d(pv^2)/dT$ which are obtained from observed temperature-induced shifts of the corresponding resonance frequencies according to

$$d \log(pv^2)/dT = d \log(p)/dT$$

The first and the second terms on the right hand side - temperature derivatives of density and thermal expansion, respectively - are calculated from the thermal expansion tensor which in advance has been determined from measurements of longitudinal thermal expansion in the directions $e_i$ and $(e_i \pm e_j)$ by the aid of an inductive gauge dilatometer in the range between 280 and 360 K (see Table 1). The values for $c_{ij}$ and $T_{ij}$ for some distinct temperatures are listed in Table 2.

In a second series of measurements the variation of the thermoelastic constants near the transition was investigated employing small temperature steps of ca. 1 K. All wave velocities showed an anomalous behaviour onsetting at ca. 310 K and ending at ca. 322 K. However, the wave velocities exhibit no discontinuity in that range. Certain derivatives of the type $d \log(pv^2)/dT$ possess a lambda-like behaviour, others only a slight extremum value within the transition range. $v_{ij}$ is the velocity of a wave propagating in direction $e_i$ for $i = j$ and in direction $(e_i + e_j)$ otherwise. The three velocities for each direction are designated by $v_{ij} \equiv v_{ij}' \equiv v_{ij}''$. These lambda-peaks and extrema, respectively, are obtained at 315.5 K, indicating the steepest slope of the $d \log(pv^2)/dT$-curve, whereas the ferroelectric Curie temperature is 321 K [3]. Examples for the largest lambda-like effects are $T_{22}$, $T_{13}$, $T_{33}$, $T_{13}$, $T_{23}$, $T_{33}$ with positive peak values and

### Table 1. Coefficients of thermal expansion $\alpha_{ij}$ of TAAP below and above the ferroelectric transition. $\alpha_i^\pm$ are the values in the principle axes system. Unit: 10$^{-6}$ K$^{-1}$. Estimated limits of error in parentheses.

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$\alpha_{11}$</th>
<th>$\alpha_{22}$</th>
<th>$\alpha_{33}$</th>
<th>$\alpha_{13}$</th>
<th>$\alpha_{11}^\pm$</th>
<th>$\alpha_{22}^\pm$</th>
<th>$\alpha_{33}^\pm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>7 (2)</td>
<td>23 (3)</td>
<td>20 (3)</td>
<td>-31 (4)</td>
<td>-18</td>
<td>23</td>
<td>45</td>
</tr>
<tr>
<td>340</td>
<td>25 (2)</td>
<td>53 (4)</td>
<td>33 (3)</td>
<td>-29 (4)</td>
<td>-0.3</td>
<td>53</td>
<td>58</td>
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