Dielectric and Pyroelectric Properties
of Ammonium Hydrogen-DL-Malate Monohydrate,
\( \text{NH}_4\text{(C}_4\text{H}_5\text{O}_4\text{)}\cdot\text{H}_2\text{O} \)
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The dielectric and pyroelectric properties of ammonium hydrogen-DL-malate monohydrate
\( \text{NH}_4\text{(C}_4\text{H}_5\text{O}_4\text{)}\cdot\text{H}_2\text{O} \) were studied as a function of temperature and crystallographic
direction. The components of the dielectric tensor at room temperature are within the
limits \( 5.9 \leq \varepsilon \leq 8.6 \). The pyroelectric coefficient \( |p| \) increases from \( \varepsilon \approx 18 \text{ \mu C m}^{-2}\text{K}^{-1} \) at
\( T = 100 \text{ K} \) to \( 32 \text{ \mu C m}^{-2}\text{K}^{-1} \) at room temperature. The angular variation of \( p \) in the ac-plane of
the crystal with symmetry Cc is \( \approx 10^\circ \).

Using an INDO procedure which includes crystal field effects in a self-consistent way (SCEF)
the charge distribution in the solid was calculated. With the therefrom resulting dipole moment
and together with the dielectric measurements the pyroelectric coefficient \( p \) and the change of
\( |p| \) with temperature was calculated. Experiment and theoretical result agree satisfactorily.

Introduction

Ammonium hydrogen-DL-malate monohydrate, \( \text{NH}_4\text{(C}_4\text{H}_5\text{O}_4\text{)}\cdot\text{H}_2\text{O} \) (AMAL)
crystallizes in the monoclinic space group \( C_2\text{H}_2 \) [1] with only one symmetry element, a glide
plane. In contrast, ammonium hydrogen L-malate, \( \text{NH}_4\text{(C}_4\text{H}_5\text{O}_4\text{)}\), crystallizes in the
orthorhombic space group \( D_2\text{-P}_{2\text{I}}\text{2}_1_2 \) [2, 3]. The two structures are substantially different, e.g. even
the geometrical parameters of the malate ion differ in important details.

The lacking center of symmetry in the title compound is responsible for its interesting physical
properties like optical anisotropy. Betzler et al. [4] have shown that AMAL can be used for phase-
matched second harmonic generation. Other physical properties, which can be observed in the
monoclinic domatic space group are piezoelectricity and pyroelectricity. For crystals with the space
group Cc the problem arises that the spontaneous polarization can have any direction within the
symmetry plane, in contrast to symmetry classes with a unique polar axis which fixes the direction of
the spontaneous polarization. A well studied sub-stance with the space group Pm is for example the
ferroelectric compound lithium trihydromalate, \( \text{LiH}_3(\text{SeO}_3) \), and its deuterated analogue [5, 6]. In
the following we report an investigation of the pyroelectric coefficient and the dielectric constant of
AMAL and its temperature dependence.

Experimental

Preparation

Ammonium hydrogen-DL-malate monohydrate
was prepared from commercial components in
stoichiometric amounts (DL-malic acid and ammo-
nium hydroxide). The composition of the crystals
was determined by chemical analysis (calculated
values in brackets): C: 28.12% (28.41%), H: 6.53%
(6.56%), and N: 8.32% (8.28%).

Large single crystals, \( 30 \times 20 \times 15 \text{ mm}^3 \), can be
grown by slow cooling of a seeded aqueous solution
from \( T = 305 \text{ K} \) to 295 K. Identification of the
crystal axes and faces was made by comparison of
the optical measurements with the crystal structure
data [1]. The habitus of the crystal is shown in
Figure 1.

For the measurement of the dielectric constant
\( \varepsilon = \varepsilon' - i \varepsilon'' \) and the pyroelectric coefficient \( p \), different
oriented crystal plates were cut in slices with a wire saw. The actual orientation of the
crystal has been checked by optical measurements.

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* Part of the Dr.-Ing. Dissertation S. Fleck, Darmstadt.
Fig. 1. Habitus of ammonium hydrogen-DL-malate monohydrate, NH$_4$((OOCCHOHCH$_2$COOH) • H$_2$O.

The two opposite faces of the crystal plates were polished and painted with air drying silver paste. By this method single crystal capacitors with an area $15 \leq A/mm^2 \leq 60$, thickness $0.4 \leq d/mm \leq 0.8$ and filled with a single crystal dielectricum were obtained.

Measurement of the Dielectric Constants and the Pyroelectric Coefficient

The impedance of the different oriented single crystal capacitors was measured in a temperature range from 200 K to the decomposition temperature, $T_d$, using the bridge method described in [7]. The measurement of the actual temperature at the sample site was accurate to $\pm 0.5$ K and the dielectric measurements were limited in accuracy by the determination of the crystal area and its thickness to 3%. Only $\varepsilon = \varepsilon'$ is given in the following. $\varepsilon''$ is very small and values $\varepsilon'' > 0.1$ are found near $T_d$.

The pyroelectric coefficient $p$ at constant stress was measured on different oriented single crystal capacitors in the temperature range $100 \leq T/K \leq T_d$. As earlier [7, 8], the method of constant temperature variation was used, employing a temperature variation rate of $0.5 \leq T \cdot t^{-1}/(K \min^{-1}) \leq 2$. For each crystal direction investigated, the measurements of $\varepsilon$ and $p$ were repeated using different plates. An accuracy for the pyroelectric coefficient of $\pm 8\%$ was achieved.

In the range $245 \leq T/K \leq T_d$ the pyroelectric voltage was also measured with the low frequency sinusoidal temperature oscillation method. The temperature oscillations were created by a Peltier element with a frequency of 0.01 Hz and temperature amplitudes of $0.5 \leq T/K \leq 3$ [7, 8]. The accuracy of the temperature determination was in this case $\pm 0.3$ K, and that of the pyroelectric coefficient was $\pm 5\%$.

Calculation of Dipole Moments in Solids

In order to discuss the temperature dependence of the pyroelectric coefficient in terms of molecular properties, it is necessary, to calculate the dipole moment of AMAL. This was done by two methods. At first, the dipole moment $\mu$ was determined using dipole moment increments for each bond or group [9, 10] and the known value of $\mu$ for H$_2$O [11], respectively. There are some uncertainties in this method. For example, the dipole moment for the group $-C\equiv O$ found by summing up the values of the bond increments given in literature [10] differs appreciably from the dipole moment increment reported for this group. Also the variation of the dipole moment of the C–H bonds due to the neighbouring groups is not included in the increment method. Furthermore, to calculate the total resulting dipole moment on the basis of the method of increments, the partial dipole moment has to be found which results from the charge separation between the NH$_4$ ion and the group $(-C\equiv O)^\circ$.

The data gained from the empirical increment method are somewhat arbitrary and not satisfactory. The solid state effect is completely neglected.

Calculation of the Dipole Moment by Semiempirical Methods of Quantum Chemistry

The basis for a theoretical determination of electric dipole moments in solids is the calculation of charge distributions. We have studied the electronic structure of AMAL on the basis of a semiempirical LCAO MO model of the INDO-type (intermediate neglect of differential overlap) [12], using an improved modification [13]. Solid state effects have been simulated by means of a self-consistent electrostatic field (SCEF) approach [14, 15] which leads to an approximative expression for the interaction energy between a preselected reference molecule and its neighbours. Dispersion energies and exchange interactions are neglected in the present SCEF formalism [16]. The perturbational approach is thus suitable for the investigation of intermolec-
ular interactions that are largely determined by electrostatic (Coulomb) terms while covalency effects due to the kinetic energy of the electrons are small in comparison to the former interaction potential. This condition should be fulfilled in the title compound where the solid state arrangement is built up via hydrogen bonds between adjacent molecular units; the atomic centers forming the hydrogen bonds show always large charge separations.

The basis of the employed model is the fragmentation of the total solid into a reference molecule (R), whose electronic structure is treated explicitly, and environment molecules (N). The coupling between both units is handled in the frame of the mean field approximation. The partitioning scheme is sketched in Figure 2. The corresponding mean field operator $\hat{F}$ is given by an operator $\hat{F}_0$ associated to a single molecular unit and by the operator $\hat{F}_{\text{ef}}$, which describes an electrostatic coupling between the reference molecule and the environment,

$$\hat{F} = \hat{F}_0 + \hat{F}_{\text{ef}}.$$  

(1)

For the numerical approach it is necessary to take into account the coupling between the reference unit R and the external ones N; the coupling between external units is thereby neglected:

$$\hat{H}_{RN} \neq 0; \quad \hat{H}_{NN} = 0.$$  

(2)

The perturbational Hamiltonian $\hat{H}_{\text{ef}}$ is defined by

$$\hat{H}_{\text{ef}} = \sum_{\mu=1}^{n} \sum_{j} Z_j \left( \sum_{j=1}^{n} B_{\mu v} \frac{\nu(2) \cdot \nu(2)}{r_{\mu v}} \right).$$  

(3)

The first term in (3) corresponds to the core contribution from the external field, the second one to the two electron part of $\hat{H}_{\text{ef}}$, with

$\mu = \mu$-th AO in the reference unit,

$Z_j = $ atomic core charge of the $j$-th atom in the $N$-th external unit,

$r_{\mu j} = $ distance vector between $j$-th atom in $N$-th external unit and $\mu$-th AO in R,

$r_{\mu v} = $ distance between the $v$-th AO in N and the $\mu$-th AO in R,

$B_{\mu v} = $ is the $v$-th diagonal element of the bond order matrix.
By means of a simple central field monopole approximation it is possible to reduce $\hat{H}_{ef}$ to an operator of the one-electron type [17, 18]

$$\hat{H}_{ef} = \sum_{\mu=1}^{n} \sum_{N} \sum_{j} \frac{q_{j}}{r_{\mu j}}$$  \hspace{1cm} (4)

with $q_{j}$ = atomic net charge of the $j$-th centre in the $N$-th neighbouring unit. The matrix elements of the perturbational Fock operator are defined below: diagonal terms are given in (5) and the off-diagonal terms in (6). The off-diagonal elements are found by means of the Mulliken approximation [19]

$$F_{\mu \nu, \epsilon \sigma} = \sum_{N} q_{j} V_{\mu \nu}$$  \hspace{1cm} (5)

$$F_{\mu \nu, \epsilon \sigma} = \frac{1}{2} S_{\mu \nu} (F_{\mu \nu, \epsilon \sigma} + F_{\nu \epsilon, \mu \sigma})$$  \hspace{1cm} (6)

with $V_{\mu \nu}$ = electron core interaction and $S_{\mu \nu}$ = overlap integral.

The equations show the necessary computational steps. i) A trial collection of atomic net charges $q_{j}$ is determined for the isolated molecule. These $q_{j}$ numbers are used to construct the external field. ii) Diagonalization of the complete Hartree-Fock operator leads to a new collection of $q_{j}$ numbers, which are iterated up to SCEF convergence $\Delta E = 10^{-4}$ a.u.

**Results**

**Dielectric Constant**

Ammonium hydrogen-DL-malate monohydrate crystallizes with the space group $\text{Cc}$ and the dielectric tensor has the form: $(\varepsilon_{ij})$; $i, j = 1, 2, 3$; $\varepsilon_{ij} = \varepsilon_{ji}$; $\varepsilon_{12}, \varepsilon_{23} = 0$. $\varepsilon_{22}$ is obtained directly from measurements of dielectric constant on a (010)-crystal plate (curve IV in Figure 3). The other components of the dielectric tensor, $\varepsilon_{11}, \varepsilon_{13}, \varepsilon_{33}$, describe an ellipse in the ac-plane of the crystal. They can be calculated from measurements of the dielectric constant in more than three directions within the (010)-plane by a formalism given by Nye [20]; the principles of this method are summarized below. If $A_{i}$ is the value of the dielectric constant in the selected direction characterized by $\theta$, $\theta$ = angle between the selected direction and the [100]-axis, $A_{i}$ is given by

$$A_{i} = (\sin \theta \cdot \cos \theta) \begin{pmatrix} \varepsilon_{11} & \varepsilon_{13} \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \sin \theta \\ 0 \end{pmatrix}$$

$$\varepsilon = (\theta_{i} \cdot \theta) \varepsilon_{ij}$$  \hspace{1cm} (7)

$\varepsilon$ can be calculated by solving the equation

$$\varepsilon = (\theta_{i} \cdot \theta) \varepsilon_{ij} \cdot A_{i}$$  \hspace{1cm} (9)

The tensor of the dielectric constant obtained for $T = 200$ K and $T = 300$ K in the crystallophysical system $a, b, z$, with $z$ perpendicular to $a$ and $b$, reads

$$\varepsilon(200 \text{ K}) = \begin{pmatrix} 5.57 & 0 & 0.41 \\ 0 & 5.60 & 0 \\ 0.41 & 0 & 7.26 \end{pmatrix}$$

$$\varepsilon(300 \text{ K}) = \begin{pmatrix} 5.35 & 0 & 0.47 \\ 0 & 5.95 & 0 \\ 0.47 & 0 & 8.34 \end{pmatrix}$$

Fig. 3. Components of the dielectric constant in the ac-plane characterized by $\theta$ = angle between the direction of measurement and a preferred crystallographic vector. I–V: $\theta_{i}$ = angle between the direction of $\varepsilon_{i\ldots\varepsilon_{V}}$ and the axis [100]. I) $\theta_{i} = 142.1^\circ$; here the direction of the measurement corresponds to the normal of the plane (101). II) $\theta_{ii} = 52.1^\circ$. III) $\theta_{III} = 30.6^\circ$; here the direction of measurement corresponds to the normal of the plane (100). IV) $\theta_{IV} = 120.6^\circ$. V) $\theta_{V} = 90^\circ$; this direction corresponds to the normal of the plane (001). $\theta_{V}$ corresponds to the measurement on a plate cut parallel to the plane (010).
Using the circle construction of Mohr [20] the angle $\Phi$ between the principle axis of the ellipse and the axis [100] can be found. The experiment gave $\Phi = 77^\circ$ and $81.3^\circ$ for $T = 200$ K and $T = 300$ K, respectively. Therefrom the dielectric tensor in the principal coordinate system is

$\varepsilon(200 \text{ K}): \varepsilon_{11} = 5.55; \varepsilon_{22} = 5.60; \varepsilon_{33} = 7.29$;

$\varepsilon(300 \text{ K}): \varepsilon_{11} = 5.34; \varepsilon_{22} = 5.95; \varepsilon_{33} = 8.36$.

**The Pyroelectric Coefficient**

AMAL belongs to the only one symmetry class, where the pyroelectric coefficient is not fixed in a preferential crystallographic direction, but its orientation can change within a certain plane, here within the (010)-plane. The pyroelectric vector has the form $p(T) = (p_1, 0, p_3)$. It can be obtained by measurements in two perpendicular directions within the (010)-plane. The absolute value and the direction of the pyroelectric vector simply result from the vector sum of the measured quantities. For an unambiguous assignment of the direction of the pyroelectric vector a measurement in a third direction has to be done. We have performed two measurements in orthogonal directions, but rotated against the first set by an angle of $21.5^\circ$. Thereby magnitude and direction variations of $p$ are found, the sign being still undetermined.

In Fig. 4 the components of the pyroelectric vector, $p_z$, are given as a function of temperature. Figure 5 shows the absolute value of the pyroelectric vector as a function of temperature, and the direction is given by the angle $\psi$ between the pyroelectric vector and the crystallographic [100]-axis. A slight maximum in the absolute value of the pyroelectric vector = pyroelectric coefficient, $|p|$, at about 259 K is observed while the angle, characterizing the direction, decreases in the temperature range investigated from $\psi = 77^\circ$ (100 K) to $\psi = 66^\circ$ (320 K). This behaviour can be compared with lithium trihydrogen selenite [5] and lithium trideuteroselenite [6], where the direction of the spontaneous polarization varies by about $4^\circ$ in the temperature range $180 \leq T/K \leq 360$. The dielectric ellipse and the direction of the pyroelectric coefficient for 200 K and 300 K are shown together with the calculated dipole moment $\mu$ in Figure 6.

**Electric Dipole Moment; Method of Increments**

Using the method of bond increments for the calculation of the dipole moment, the charge separation between the ammonium ion and the COO$^-$ group was treated in two ways. At first the part of the dipole moment resulting from $d$(NH$_4^+$ ... COO$^-$) was calculated by assuming point charges at the sites of the nitrogen N$^+$ and the
Fig. 5. Absolute value (upper part) of the pyroelectric vector, $|\mathbf{p}|$, and direction (lower part) of $\mathbf{p}$. $\psi$ symbolizes the angle between $\mathbf{p}$ and the axis [100]. The full symbols are deduced from the curves I) and II) and the open symbols from the curves III) and IV) in Figure 4.

Fig. 6. Dielectric ellipse $\varepsilon(\delta)$ and pyroelectric vector $\pm \mathbf{p}$ (the sign of $\mathbf{p}$ is unknown) at $T = 200$ K and $T = 300$ K, together with the calculated dipole moment (INDO-SCEF) $\mu$ and the electric field of the neighbouring molecules $E_N$.

Fig. 7. Schematic display of the reference unit R (dashed) and the directions of the hydrogen bonds to the neighbours.

oxygen, O(1)$^\circ$ (see Figure 7). This leads to the total dipole moment $\mu_1$. In a second approach the negative point charge was located at the center of O(1) and O(2) ($\mu_2$). From the symmetry of the space group it follows that, due to the glide plane, there is no component of $\mu$ in the [010]-direction. The values found for $\mu$ and for the angle $\varphi$ between the dipole moment and the axis [100] are:

$$
\mu_1 = 30.2 \cdot 10^{-30} \text{ Cm}, \quad \varphi_1 = 198^\circ,
$$

$$
\mu_2 = 40.5 \cdot 10^{-30} \text{ Cm}, \quad \varphi_2 = 203^\circ.
$$

It is obvious that direction and value of the dipole moment are mainly fixed by the charge separation...
between the NH$_4^+$ and the COO$^-$ group. The direction of $\mu$ is defined $\Theta \rightarrow \Phi$.

**Electric Dipole Moment and Net Charges from the SCEF-INDO Calculations**

In the numerical INDO (SCEF) calculations we adopted the experimental structure parameters [1] for the unperturbed molecule NH$_4^+$(OOCCCHOHCH$_2$COOH)$\cdot$H$_2$O in the vacuum and in the solid state. The formula unit R and the atomic numbering scheme are displayed in Figure 7. The external field has been build up in two types. In the first approach of approximation only eight external units have been employed. We have selected those neighbours N which are coupled to the reference system via hydrogen bonds. In the second calculation we constructed a spherical external field by means of 16 neighbouring molecules, i.e. an approximation beyond the nearest neighbour’s scheme was used (Figure 2). It turned out that the additional external units had no significant influence on the calculated charge distribution, showing that modifications in the electronic structure of the title compound in the solid state are rather local effects caused by hydrogen bonded neighbours. Interactions beyond the nearest neighbour’s are important only if lattice (Madelung) energies are calculated.

In Table 1 we have summarized the atomic net charges $q_j$ of the title compound in the vacuum and in the external field created by 16 adjacent molecules. A comparison of the charge distribution in the vacuum and the solid shows large electronic reorganizations at those atomic sites that form hydrogen bonds to adjacent molecules. These redistributions are pronounced for O(2), O(3), O(4) as well as for the hydrogen atoms H(O3), H(1, N), H(2, N) and for the H atoms of the H$_2$O molecule. The charge separation between three atomic centers forming a hydrogen bridge is always enlarged. It leads to increasing electrostatic interactions that allow for a stabilization in the crystal.

Furthermore are given in Table 1 the dipole moment of the formula unit and the angle $\varphi$ between the dipole moment and the axis [100]. Magnitude and direction of the dipole moment are comparable in both states, the vacuum and the solid. It is obvious, that the direction and magnitude is mainly fixed by the geometry of the molecule and the crystal lattice.

**Table 1. Atomic net charges in one molecule (formula unit) of AMAL (see Figs. 2 and 7).**

<table>
<thead>
<tr>
<th></th>
<th>Isolated molecule</th>
<th>Solid-state environment (16 molecules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)</td>
<td>-0.81</td>
<td>-0.83</td>
</tr>
<tr>
<td>O(2)</td>
<td>-0.75</td>
<td>-0.82</td>
</tr>
<tr>
<td>O(3)</td>
<td>-0.49</td>
<td>-0.65</td>
</tr>
<tr>
<td>O(4)</td>
<td>-0.63</td>
<td>-0.65</td>
</tr>
<tr>
<td>O(5)</td>
<td>-0.54</td>
<td>-0.60</td>
</tr>
<tr>
<td>O(6)</td>
<td>-0.65</td>
<td>-0.76</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.71</td>
<td>0.74</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>C(3)</td>
<td>-0.30</td>
<td>-0.34</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.73</td>
<td>0.79</td>
</tr>
<tr>
<td>H(O3)</td>
<td>0.35</td>
<td>0.52</td>
</tr>
<tr>
<td>H(O5)</td>
<td>0.30</td>
<td>0.33</td>
</tr>
<tr>
<td>H(1, O6)</td>
<td>0.30</td>
<td>0.37</td>
</tr>
<tr>
<td>H(2, O6)</td>
<td>0.33</td>
<td>0.39</td>
</tr>
<tr>
<td>H(C2)</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>H(1, C3)</td>
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<td>0.17</td>
</tr>
<tr>
<td>H(2, C3)</td>
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<td>0.19</td>
</tr>
<tr>
<td>N</td>
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<td>-0.10</td>
</tr>
<tr>
<td>H(1, N)</td>
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<td>0.29</td>
</tr>
<tr>
<td>H(2, N)</td>
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<td>0.30</td>
</tr>
<tr>
<td>H(3, N)</td>
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<td>0.19</td>
</tr>
<tr>
<td>H(4, N)</td>
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<td>0.21</td>
</tr>
<tr>
<td>$\mu$/C$\cdot$m</td>
<td>$44.7 \cdot 10^{-30}$</td>
<td>$44.1 \cdot 10^{-30}$</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>200.0°</td>
<td>199.6°</td>
</tr>
</tbody>
</table>

**Discussion**

AMAL belongs to the group of substances with a pyroelectric coefficient, which can vary its direction with temperature within a symmetry plane. In this case the direction of $p$ is an additional independent parameter in the calculation of $p = f(T)$ compared to substances with a polar crystal axis.

The temperature dependence of the polarization $P$ of AMAL is described by the model introduced in [7]. The crystal is treated as a dielectric medium, composed of dipoles with a permanent moment $\mu$, with a dielectric constant $\varepsilon$, and a polarizability $\alpha$. The internal field at the site of a dipole is built up by the Lorentz field $E_l$ plus the electric field $E_N$ of the neighbouring dipoles N, which are treated as point charges. The field $E_N$ was calculated at the site of the reference unit R, using the atomic net charges determined by the SCEF approach, $q_j$, and the structure data from [1]

$$E_N(x, y, z) = \frac{1}{4\pi \varepsilon_0 \sum N_j} \sum_j q_j \frac{r_j}{|r_j|^3} \equiv \frac{1}{4\pi \varepsilon_0} S_N(x, y, z),$$

(10)
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with \( r_j \) = radius vector from atom \( j \) in the external molecule \( N \) to the reference unit \( R \) and \( S_N \) = abbreviation for the summation. The volume of the reference unit \( V_R \) was divided into volume elements \( dV \) of about \( 4 \times 10^{-32} \text{ m}^3 \). For each volume element \( E_N(x,y,z) \) was calculated and in a further step \( E_N \) was averaged over \( V_R \):

\[
\langle E_N \rangle = \frac{1}{V_R} \sum E_N(x,y,z) \ dV \equiv \frac{1}{4\pi\varepsilon_0} \langle S_N \rangle. \tag{11}
\]

By this method the mean electric field \( \langle E_N \rangle \) of the neighbouring molecules \( N \) averaged over the volume of the reference unit \( V_R \) is obtained. The direction of \( \langle E_N \rangle \) is characterized by \( \Omega = \angle ([100], \langle E_N \rangle) \) (Figure 6).

Using the abovementioned physical parameters the polarization \( P \) of a crystal can be described \([7]\) by

\[
P = \frac{N_A}{3V} (\varepsilon_p + 2) |\mu| \cos \delta + \frac{1}{4\pi} (\varepsilon_p - 1) |\langle S_N \rangle| \cos \beta. \tag{12}
\]

with \( 1/V = \rho/M \) = number of molecules per unit volume, \( \rho = \text{density} = 1.50 \text{ Mg/m}^3, M = \text{molar mass} = 169.13 \text{ g/mol}, N_A = \text{Avogadro number} = 6.022 \times 10^{23} \text{ mol}^{-1}, |\mu| = \text{dipole moment} = 44.06 \times 10^{-30} \text{ C m}, |\langle S_N \rangle| = 0.547 \text{ C m}^{-2}, \varepsilon_p = \text{dielectric constant in the direction of} \( P \), \( \delta = \text{angle between} \mu \text{ and} P \), \( \beta = \text{angle between} \langle E_N \rangle \text{ and} P \). Differentiation of (12) leads to an expression for the temperature dependence of the pyroelectric coefficient:

\[
p = \frac{dP}{dT} = -\frac{N_A}{3V} (\varepsilon_p + 2) |\mu| \cos \delta \frac{\partial V}{\partial T} \tag{13}
+ \frac{N_A}{3V} (\varepsilon_p + 2) |\mu| \frac{\partial \cos \delta}{\partial T} \\
+ \frac{1}{4\pi} (\varepsilon_p - 1) |\langle S_N \rangle| \frac{\partial \cos \beta}{\partial T} \\
+ \left( \frac{N_A}{3V} |\mu| \cos \delta + \frac{1}{4\pi} |\langle S_N \rangle| \cos \beta \right) \frac{\partial \varepsilon_p}{\partial T}.
\]

The first term can be set equal to zero as the temperature dependence of the volume can be neglected in the temperature range considered. \( \varepsilon_p \) and \( \partial \varepsilon_p/\partial T \) are temperature dependent quantities, which can be extracted from the curves of Figure 3. Below \( T = 200 \text{ K} \) extrapolated values have been used.

The direction of the polarization \( P \) which is necessary for the estimation of \( \delta(T) \) and \( \beta(T) \) can be approximated under the assumption that \( dP/dT = 0 \) for \( T \rightarrow 0 \text{ K} \), e.g. the pyroelectric coefficient \( \varepsilon_p \) and the polarization \( P \) are parallel at \( T = 0 \text{ K} \). An extrapolated value of the angle between the [100]-axis and \( P \) at \( T = 0 \text{ K} \) from Fig. 5 is \( \psi = 80^\circ \). With this, \( |P| \) can be obtained from (12), \( |P| = 0.143 \text{ C m}^{-2} \). Using the direction and value of \( P \) the variation of \( P(T) \) is described by

\[
P(T) = \int p(T) \ dT. \tag{14}
\]

The changes of \( \delta \) and \( \beta \) with temperature are deduced directly from the angular variation of \( P(T) \), because the calculated dipole moment \( \mu \) and the electric field \( \langle E_N \rangle \) are assumed to be fixed over the whole temperature range.

The temperature dependence of the pyroelectric coefficient can be obtained using (13) and introducing the following: The measured values for \( \varepsilon_p \) and \( \partial \varepsilon_p/\partial T \), the values for \( \cos \delta \) and \( \cos \beta \) deduced as described above, and the calculated values for \( \mu \) and \( \langle E_N \rangle \). Introducing all constants and temperature-independent coefficients, (13) reduces to

\[
p = 0.0784 (\varepsilon_p + 2) \frac{\partial \cos \delta}{\partial T} + 0.0436 (\varepsilon_p - 1) \frac{\partial \cos \beta}{\partial T} \\
+ 0.0784 \cdot \cos \delta + 0.0436 \cos \beta \frac{\partial \varepsilon_p}{\partial T} \tag{15}
\]

\[= \text{p(1)} + \text{p(II)} + \text{p(III)}.\]

In Table 2 the values for \( \varepsilon_p \) and \( \partial \varepsilon_p/\partial T \) are given for selected temperatures, together with the cos \( \delta \) and cos \( \beta \). Additionally the data for \( |p| \) (calc) = \( |p| \) (1) and \( |p| \) (exp) are listed. The resulting curve \( |p| \) (1) = \( \sum p(1,i) \) with \( i = \text{I, II, III} \) in Fig. 8 follows the trend of the measured one, \( |p| \) (exp), as there is an increase in the temperature range \( 100 \leq T/\text{K} \leq 280 \). But the maximum in \( |p| \) (exp) is not found and the increase of \( |p| \) with \( T \) is heavily over-estimated, reaching a value of the pyroelectric coefficient which is three times as large as \( |p| \) (exp). In Fig. 8 the components \( |p| \) (1, I) to \( |p| \) (1, III) of \( |p| \) (1) corresponding to the three terms in (15) are given, too. \( p \) (1, I) has the opposite sign of \( p \) (1, I) and \( p \) (1, III). It is easily seen that the main part of the temperature dependence of \( p \) (1) is due to \( p \) (1, III), e.g. the temperature dependence of the dielectric constant \( \varepsilon_p \).
Table 2. Compilation of the different physical parameters either measured or calculated, which have been used in the calculation of the pyroelectric coefficient $|p|$ (see text). For comparison the calculated values $|p| (1) - |p| (3)$ are given together with $|p| (\text{exp})$.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>120</th>
<th>160</th>
<th>200</th>
<th>240</th>
<th>280</th>
<th>320</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_p$</td>
<td>7.20</td>
<td>7.31</td>
<td>7.46</td>
<td>7.70</td>
<td>8.14</td>
<td>8.70</td>
</tr>
<tr>
<td>$\varepsilon_p / \partial T \cdot 10^3$</td>
<td>2.25</td>
<td>3.25</td>
<td>4.50</td>
<td>8.30</td>
<td>12.10</td>
<td>14.70</td>
</tr>
<tr>
<td>$\cos \delta$</td>
<td>0.4942</td>
<td>0.4947</td>
<td>0.4958</td>
<td>0.4970</td>
<td>0.4986</td>
<td>0.5005</td>
</tr>
<tr>
<td>$\partial \cos \delta / \partial T \cdot 10^5$</td>
<td>1.0</td>
<td>1.4</td>
<td>2.5</td>
<td>3.5</td>
<td>4.4</td>
<td>4.75</td>
</tr>
<tr>
<td>$\cos \beta$</td>
<td>0.7850</td>
<td>0.7854</td>
<td>0.7861</td>
<td>0.7869</td>
<td>0.7881</td>
<td>0.7894</td>
</tr>
<tr>
<td>$\partial \cos \beta / \partial T \cdot 10^5$</td>
<td>1.12</td>
<td>1.37</td>
<td>1.87</td>
<td>2.5</td>
<td>3.12</td>
<td>3.25</td>
</tr>
<tr>
<td>$</td>
<td>p</td>
<td>(1) / (\mu \text{C m}^{-2} \text{K}^{-1})$</td>
<td>14.8</td>
<td>22.7</td>
<td>34.5</td>
<td>58.3</td>
</tr>
<tr>
<td>$</td>
<td>p</td>
<td>(2) / (\mu \text{C m}^{-2} \text{K}^{-1})$</td>
<td>6.8</td>
<td>10.2</td>
<td>18.2</td>
<td>29.1</td>
</tr>
<tr>
<td>$</td>
<td>p</td>
<td>(3) / (\mu \text{C m}^{-2} \text{K}^{-1})$</td>
<td>2.7</td>
<td>7.0</td>
<td>13.4</td>
<td>18.3</td>
</tr>
<tr>
<td>$</td>
<td>p</td>
<td>(\text{exp}) / (\mu \text{C m}^{-2} \text{K}^{-1})$</td>
<td>19.3</td>
<td>23.1</td>
<td>26.6</td>
<td>30.4</td>
</tr>
</tbody>
</table>

From the values used in the calculations, the dipole moment $\mu$ and the field $|\langle E_N \rangle|$ arising from the neighbouring molecules $N$ at the site of the reference unit $R$ introduce the largest uncertainty. It is known that semiempirical LCAO-calculations describe dipole moments not better than to about 20% [13]. For the electric field $|\langle E_N \rangle|$, which arises from the semiempirically calculated charge distribution, unfortunately the same is true. Therefore $|\langle E_N \rangle|$ was varied within the limits of error to test the dependency of $p(T)$.

Using values of $1.1 \cdot |\langle E_N \rangle|$ and $1.15 \cdot |\langle E_N \rangle|$ in the calculations of the pyroelectric coefficient, curves $|p| (2)$ and $|p| (3)$ in Fig. 8 are obtained. Obviously curve $|p| (2)$ is in better accordance with $|p| (\text{exp})$, while curve $|p| (3)$, e.g. the curve calculated with a deviation of $+15\%$ in $|\langle E_N \rangle|$, shows already a smaller value. The curvature of $|p| (\text{exp})$ is represented best by the calculated curve $|p| (3)$ while the magnitude is in the order of $|p| (2)$.

The used variation of $|\langle E_N \rangle|$ causes a drastic change of the value of the third term in (15), while the first and second terms remain almost unchanged. This change is due to the difference of the dipole field and the internal field in the third term. $(a \cdot \cos \delta + b \cdot \cos \beta)$ is practically independent of $T$ and therefore acts as a scaling factor for the influence of the temperature dependence of the dielectric constant upon the pyroelectric coefficient. The employed model shows a sensitive response upon small disturbances. Nevertheless the measured pyroelectric coefficient can be represented within the limits of error of the used parameters. It is noted that only physical relevant values are employed in the calculations and no free parameters fitted to the experimental curve have been introduced into it.

**Acknowledgement**

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