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Temperature Dependence of Spontaneous Polarization in Order−Disorder Pyridinium Periodate Extracted from ²H NMR Data

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On the basis of occupancy factor data for nitrogen atoms in the pyridinium cation obtained from the structural study of PyHIO$_4$ by neutron diffraction,[4] the shape of the potential for cation reorientation about the axis perpendicular to its plane was found. The ²H NMR spectra of d$_5$PyHIO$_4$ taken over a wide range of temperatures have allowed the determination of potential minima populations. These data were used to obtain the temperature dependence of spontaneous polarization. The agreement between the spontaneous polarization calculated in this way and the measured values is very good and indicates that the ferroelectric crystal is of the order−disorder type.

Introduction

Ferroelectrics recently have been the subject of extensive studies because of their possible applications in nanodevices.[1] One of the most promising applications is FERAM (ferroelectric random access memory).[2,3] Hence, looking for new ferroelectric materials and studying their physical properties, such as spontaneous polarization, seems to be reasonable and desired. Particular interest is focused on the ferroelectrics, of whose Curie points are higher than room temperature.

In general, ferroelectric crystals can be divided into two types: the displacive type and the order−disorder type. In displacive crystals, the spontaneous polarization appears as a result of a relative shift of ions and molecules. In the order−disorder crystals, the spontaneous polarization is a result of ordering of electric dipoles of ions or molecules. The spontaneous polarization can be determined experimentally from measurements of pyroelectric effects or from hysteresis loop parameters. As yet, only a few attempts at calculations of spontaneous polarization have been made.[5−12] The problem is not easy, but the calculation of spontaneous polarization seems to be the best way to understand the nature of ferroelectricity in the compounds studied.

Pyridinium salts belong to a family of molecular-ionic crystals with interionic hydrogen bonds. The ferroelectric properties have been found in salts whose anions have a tetrahedral symmetry (i.e., BF$_4$, ClO$_4$, ReO$_4$, and IO$_4$).[13−16] A characteristic feature of these ferroelectrics is that they undergo a sequence of two phase transitions, out of which that at higher temperatures takes place at the Curie point. According to the symmetry of the high-temperature phase (prototype), the family can be divided into two groups. The first includes PyHBF$_4$ and PyHClO$_4$, which crystallize in the trigonal system. The second group whose prototype phase has an orthorhombic symmetry includes PyHReO$_4$ and PyHIO$_4$. Figure 1a presents the arrangement of ions in the elementary cell of PyHBF$_4$ (space group $R\bar{3}m$) projected in the direction perpendicular to the [111] direction.[17] The pyridinium cations occupying the vertices of the elementary cell are coplanar, and the center of the cell is occupied by the anion
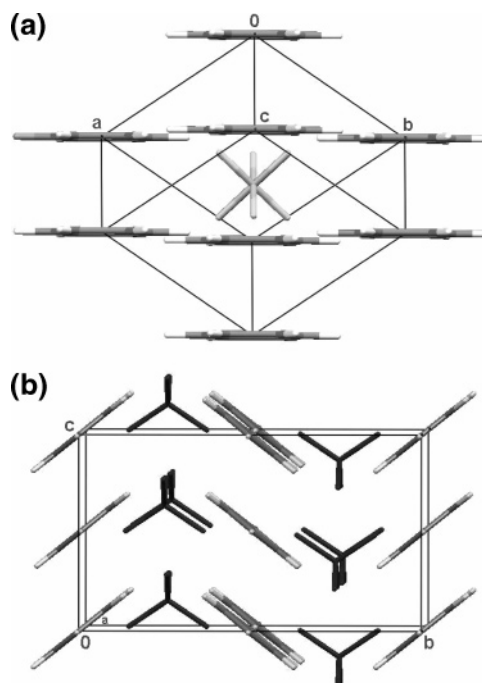
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Figure 1. (a) Arrangement of ions in the PyHBF$_4$ crystal in the [111] direction (high-temperature phase).[17] (b) Arrangement of ions in PyHIO$_4$ along the [100] axis (high-temperature phase).[4]

BF$_4$. Both ions are disordered. Figure 1b presents the arrangement of ions in the elementary cell of PyHIO$_4$ (space group *Cmcm*) along the [100] axis.[18] The cations and anions form columns along the *y*-axis. The pyridinium plane makes an angle of ∼39° with the *xz*-plane. The pyridinium cations are disordered, while the anions are ordered.

As follows from the NMR study, in all pyridinium salts, the cation undergoes reorientations about the axis perpendicular to its plane.[13−16] In PyHBF$_4$ and PyHClO$_4$, in their high-temperature phases (I), the reorientations take place between the equivalent minima of potential energy, while in the intermediate phases (II) and the low-temperature phases (III), the reorientations take place between the minima of different values.

The ^{1}H NMR measurements performed as a function of temperature and pressure for PyHIO$_4$ have shown that in the ferroelectric phases (the intermediate (II) and low-temperature (III)), the cation reorientations take place between the potential energy minima of different values and have suggested that in the paraelectric phase (the high-temperature phase (I)), the pyridinium cation undergoes reorientations through equivalent potential barriers.[18,19]

In the attempts at calculating the spontaneous polarization of the crystals of PyHBF$_4$ and PyHClO$_4$, the model potential was used.[9−12] On the basis of the known dynamics of the cation, a model of the 6-fold potential energy barrier with minima of different values in the ferroelectric phases was assumed. The populations of particular minima of the potential energy were calculated from the ^{2}H NMR line shape determined as a function of temperature, and these data were used for the calculation of polarization as a function of temperature. Unfortunately, the polarization determined in this way was inconsistent with the experimental data, in particular, in the intermediate phase (II). There are three possible reasons for this disagreement: (1) the neglect of the anion dipole moment, (2) the neglect of the contribution due to the dipole moment produced by the shift of the ions, and (3) the inadequacy of the model used. Unfortunately, the complex domain structure of the crystals prevents accurate determination of their structure in the ferroelectric phases, so identification of the reasons for this disagreement is rather impossible.

For the crystal of PyHIO$_4$, the situation is different as its structures in all three phases were determined by X-ray methods[18,20,21] and by neutron diffraction methods.[4] According to the single-crystal neutron diffraction study (at T = 350, 300, and 100 K), the high-temperature (I) and intermediate (II) phases are orthorhombic while the low-temperature (III) phase is monoclinic and correspond to the space groups *Cmcm*, *Cmc2$_1$*, and *C112$_1$*, respectively. The elementary cell parameters in the low-temperature phase are a is 8.25 Å, b is 7.11 Å, and c is 12.80 Å, and the γ angle is equal to 90.5°. The neutron diffraction study has permitted determination of the nitrogen atom occupancy factor in the pyridinium cation in all phases.

In view of the previous statements, an attempt was made to determine the shape of the potential energy for the reorientation of the pyridinium cation. To find the population of particular potential minima as a function of temperature, the ^{2}H NMR spectra of d$_5$PyHIO$_4$ were recorded in a wide temperature range. The final aim of the study was the determination of the temperature dependence of the spontaneous polarization for PyHIO$_4$ on the basis of the shape of the potential obtained from the neutron diffraction study and the occupancy data obtained from ^{2}H NMR.

Experimental Procedures

The compound d$_5$PyHIO$_4$ was obtained by allowing perdeutero-pyridine to react with ortho-periodic acid. The salt was twice recrystallized from alcohol, dried, ground to powder, degassed, and sealed off for NMR experiments.

DSC measurements were made with a Thermal Analysis Q2000 type calorimeter. The DSC study of the sample d$_5$PyHIO$_4$ revealed two phase transitions at the same temperatures as for the fully protonated sample (210 and 323 K).

The ^{2}H NMR absorption line was recorded using a Bruker DSX 400 spectrometer operating at 61.4 MHz. A standard phase cycled quadrupole echo sequence was used with quadrature detection. The $\pi/2$ pulse was 2.4 μs, and τ was 15−40 μs. The recorded echo signals were subjected to fast Fourier transform.
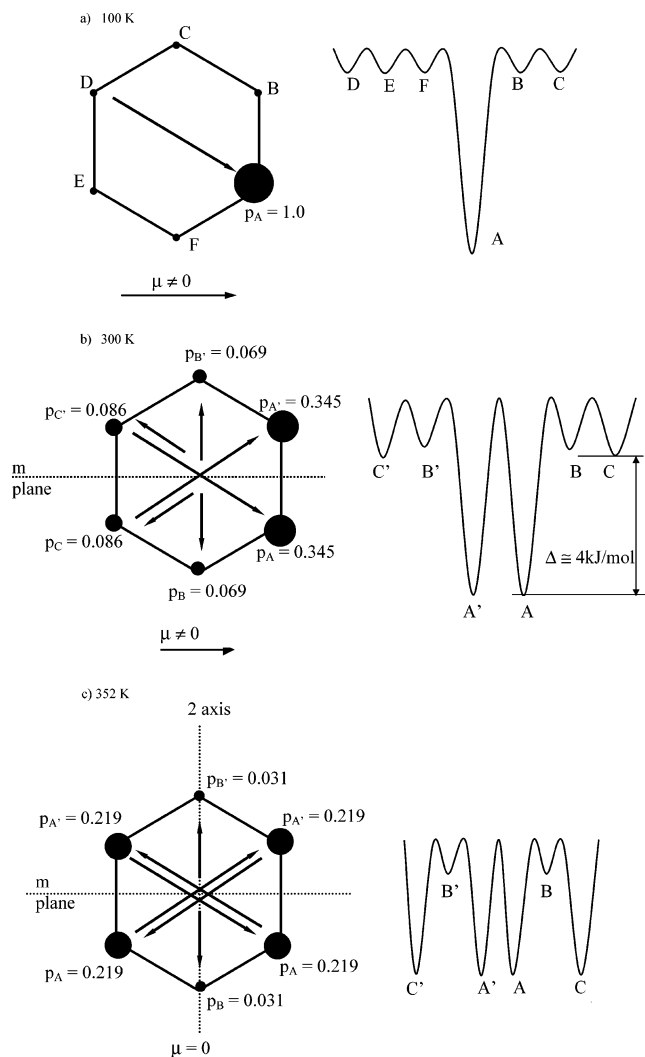

Figure 2. Occupancy of the nitrogen atom of the pyridinium cation at 100, 300, and 352 K and the shape of the potential energy function.

Results and Discussion

Potential Shape. Results of the ^{1}H NMR study[18] have shown that the pyridinium cation in the low-temperature phase (III) and in the intermediate phase (II) undergoes reorientation through nonequivalent barriers of potential energy. On the basis of the spin−lattice relaxation time T_1 as a function of temperature and pressure, the activation barrier for the pyridinium cation reorientation was calculated assuming the model with one minimum deeper than the other two.[18,19] The height of the energy barrier between the deepest minimum and the maximum E_A value obtained from the experimental measurements was close to 17 kJ/mol in the low-temperature phase (III) and the intermediate phase (II), while the difference between the deepest and the two shallow minima in the intermediate phase (II) was 4 kJ/mol.

Figure 1b presents the arrangement of ions in the elementary cell of the crystal in the high-temperature phase (I). This arrangement is very similar in all three phases. The cations and anions are interconnected by the N−H···O hydrogen bonds. In the low-temperature phase (III), the cation has no elements of symmetry, while in the intermediate (II) phase, the cation site symmetry is m, and in the high-temperature (I) phase, it is $2/m$ (Figure 2). Because of the lack of cation symmetry elements in the low-temperature phase (III), it is possible to discern six independent nitrogen atom positions denoted as A−F, which

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are distanced by 60°. The occurrence of the *m* plane in the intermediate phase (II) implies that only three independent positions are possible A = A′, B = B′, and C = C′. In the high-temperature phase (I), the presence of a 2-fold axis besides the *m* plane means that position C becomes equivalent to A (A = A′ = C = C′) and that only two independent positions are possible.

As follows from the neutron diffraction study, the population of the six positions in the cation by the nitrogen atom is nonequivalent. In the low-temperature phase (III), the nitrogen atom position is well-determined, and its occupancy factor is 100%. In the intermediate phase (II), the nitrogen atom occupancy factor at position A is 34.5%, at position B it is 6.9%, while at position C it is 8.6%. In the high-temperature phase (I), the nitrogen atom occupancy factor at position A is 21.9%, and at position B it is 3.1%.

Analysis of particular populations may help to reproduce the shape of the potential energy in individual phases. We considered six minima at 60° intervals. In the low-temperature phase (III), there is only one deep minimum (position A) and five shallow ones. In the intermediate phase (II), there are two deep minima (positions A and A′), two shallow ones (C and C′), and two even shallower ones (B and B′). In the high-temperature phase (I), there are four deep minima (positions A, A′, C, and C′) and two shallow ones (B and B′). It should be emphasized that even in the high-temperature phase (I), the positions are nonequivalent, so the potential is not symmetrical, in contrast to the situation in PyHBF$_4$ and PyHClO$_4$.

Making use of the population ratio of the potential energy minima, it is possible to estimate the difference between the minima Δ from the Boltzmann equation

$$p'/p = \exp(-\Delta/RT)$$

where p' and p are the populations of the higher and lower energy levels, T is the temperature, and R is the Boltzmann constant.

In the intermediate phase (II) at 300 K for the population ratio $p_B/p_A = 69:345 = 0.2$, the value of Δ is 4.0 kJ/mol, and for $p_C/p_A = 86:345 = 0.25$, the value of Δ is lowered to 3.5 kJ/mol. These values calculated on the basis of the structural data are in good agreement with the value of Δ obtained from the NMR measurements.[18] It should be emphasized that the NMR experiment does not allow us to determine the potential shape for the pyridinium cation reorientation, but the interpretation of the NMR data requires the assumption of a certain model of potential for the reorientation considered. The NMR results have provided information on the height of the energy barriers, while the neutron diffraction data have permitted the reproduction of the potential shape. The shape of the potential found from the neutron diffraction results has been used for further interpretation of the ^{2}H NMR results.

Analysis of the potential shape in all phases and the populations of all positions permitted us to explain as to why the low-temperature phase (III) and the intermediate phase (II) are ferroelectric, while the high-temperature phase (I) is paraelectric. It is known that the pyridinium cation is endowed with a dipole moment and directed along the axis joining the nitrogen atom and the opposite carbon atom. Spontaneous polarization depends on the sum of the contributing dipole moments of all cations in the elementary cell projected on the polar axis (the *z*-axis). The cell contains four cations, but to understand the results, it is enough to analyze just one of them. As shown in Figure 2, both in the low-temperature phase (III) and in the intermediate phase (II), the resultant dipole moment

along the *z*-axis is different from zero, while in the high-temperature phase (I), it is zero.

^{2}H NMR. Analysis of the neutron diffraction results has permitted conclusions about the shape of the potential energy function, which has qualitatively explained the appearance of ferroelectricity in the low-temperature phase (III) and in the intermediate (II) phase. The calculation of spontaneous polarization requires the knowledge of the populations of the potential energy minima as a function of temperature. NMR spectra of the crystal d$_5$PyHIO$_4$ were recorded on deuterons in the range of 140−360 K. In the lowest temperatures, the line is the Pake doublet, with the characteristic frequencies $\Delta\nu_{zz} = 253.5$ kHz, $\Delta\nu_{yy} = 136.7$ kHz, and $\Delta\nu_{xx} = 120$ kHz. The quadrupole coupling constant Q_{cc} calculated for the frequencies is 169 kHz and is a bit lower (about 5%) than the analogous values determined for other pyridinium salts: d$_5$PyHI,[22] d$_5$PyHBF$_4$,[9,10] d$_5$PyHClO$_4$,[11,12] and d$_5$PyHNO$_3$.[23] The asymmetry parameter η is 0.066 and is a bit higher than the values obtained for the other pyridinium salts. Figure 3 shows the ^{2}H NMR line shape characteristic of each of the phases, while Figure 4 shows the temperature dependence of the width of these lines. The width of the line $\Delta\nu_{zz}$ decreases with increasing temperature over the whole temperature range studied and does not reveal any jump changes at the phase transition temperatures. The width of the line $\Delta\nu_{xx}$ also decreases with increasing temperature and at 300 K reaches zero. Above this temperature, the width of this line begins to grow but also does not reveal any jump changes at the phase transition points. The width of the line $\Delta\nu_{yy}$ does not change with temperature in the range studied.

The width of the lines $\Delta\nu_{ii}$ ($i = x, y, z$) is proportional to the relevant components of the electric field gradient V_{ii}. As the $\Delta\nu_{yy}$ component does not change with temperature and the earlier study of the pyridinium cation dynamics has shown that the cation performs reorientations only in its plane, the component V_{yy} must be perpendicular to this plane. Thus, the component V_{zz} coincides with the C−D bond, and the component V_{xx} is perpendicular to this bond.

The ^{2}H NMR line shape of d$_5$PyHIO$_4$ studied in the low-temperature phase (III) and the intermediate phase (II) is similar to that observed for d$_5$PyHBF$_4$.[9,10] However, in the high-temperature phase (I), the ^{2}H NMR line shape is essentially different from that observed for d$_5$PyHBF$_4$. In the latter compound, in its phases (I as well as III), a similar line shape is observed, namely, the Pake dublet with $\Delta\nu_{zz}^{\mathrm{I}} = \Delta\nu_{xx}^{\mathrm{I}} = 1/2\Delta\nu_{xx}^{\mathrm{III}}$. This means that the pyridinium cation undergoes reorientations about the axis perpendicular to its plane, between the equilibrium potential energy minima. For d$_5$PyHIO$_4$ in the high-temperature phase (I), $\Delta\nu_{zz}^{\mathrm{I}}$ does not equal $\Delta\nu_{xx}^{\mathrm{I}}$, which proves that cation reorientation takes place between the nonequivalent potential energy minima, similar to phases (III) and (II). Hence, the analysis of the ^{2}H NMR line shape has qualitatively confirmed the shape of the potential energy determined from the structural investigation and shown that in the high-temperature phase, the cation reorientations occur through the nonequivalent potential energy minima.

Assuming the potential energy shape obtained in this study and the populations of the potential energy minima found from structural investigations, we performed simulations of the ^{2}H NMR line at 140, 303, and 353 K, with the use of the software described in detail in ref 9. The results are presented in Figure 3. The simulated line was in good agreement with that obtained in the experiment.

In the next step, the potential energy minima populations at the previous temperatures were assumed to be the starting
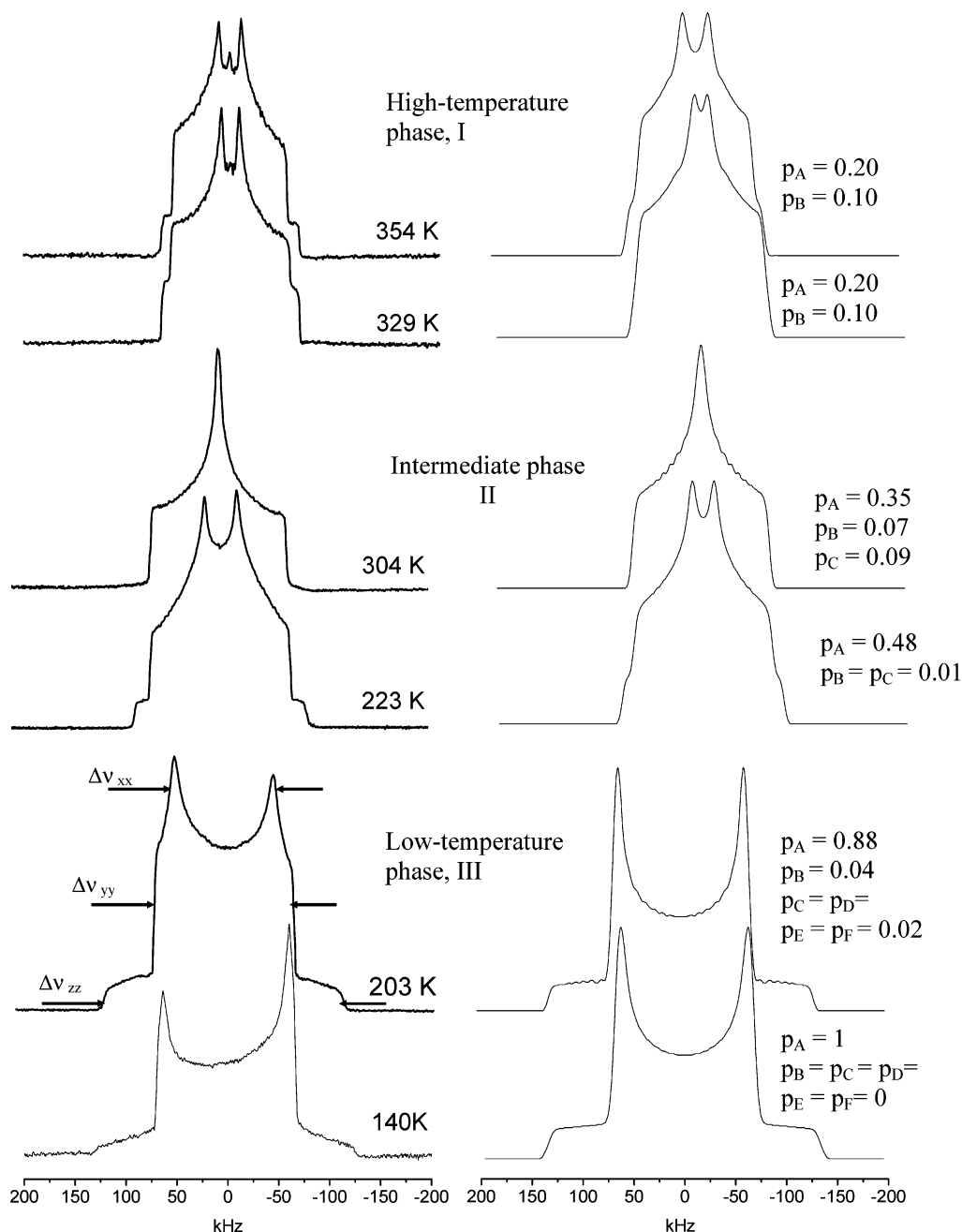
Figure 3. Shape of the ^{2}H NMR line at selected temperatures (on the left −are measured lines, and on the right −are simulated lines).

parameters and from the best fit of the simulated line to the experimental one, the populations of the minima at the other temperatures were found. The results are presented in Figure 5. Taking into account the symmetry of the intermediate phase (II), Figure 5 presents the probabilities of populations of the three potential energy minima p_A, p_B, and p_C (Figure 2). In the low-temperature phase (III) at 140 and 160 K, minimum A is populated 100%. With increasing temperature, its population decreases, and at 203 K, it is 90%. The other minima at 203 K are populated 2% each. In the intermediate phase (II) at 213 K, minima A and A′ are populated 48%, and at 323 K, their population decreases to 21%. The populations of minima B and B′ and C and C′ are the same to 293 K. Above this temperature, the population of minima C and C′ increases faster than that of minima B and B′. In the high-temperature phase (I), minima A and A′ and C and C′ are populated to the same degree of 20%, while minima B and B′ are populated 10% each. In phase I, the populations of the minima do not depend on temperature.

Spontaneous Polarization. Having determined the populations of the potential energy minima to such accuracy, an attempt was made at calculating the spontaneous polarization from the formula

$$P_{Sz} = \frac{Z\mu}{V} \cos\theta \sum_i p_i \cos\varphi_i$$

where V is the elementary cell volume, Z is the number of cations in the elementary cell, μ is the dipole moment of the cation, p_i is the probability of population of the ith potential energy minimum, φ_i is the angular position of the minimum, and Θ is the angle made by the cation plane with the xz-plane of the crystal.

The value of μ calculated for the pyridinium cation structure at 100 K by the Gaussian 98 packet in the 6−-51G* base is 1.97 D.[4] Knowing the positions of the potential energy minima, their populations, and the volume of the elementary cell as a
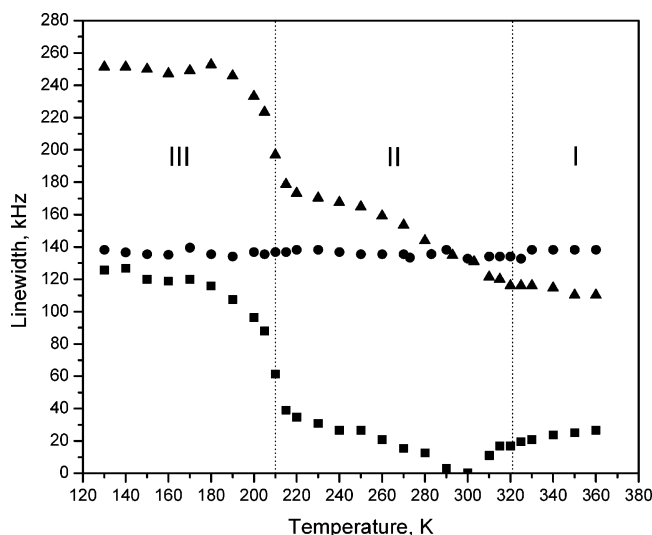
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Figure 4. Temperature dependence of the ^{2}H NMR linewidth (▲) $\Delta\nu_{zz}$, (●) $\Delta\nu_{yy}$, and (■) $\Delta\nu_{xx}$. The vertical dotted lines indicate the phase transitions.
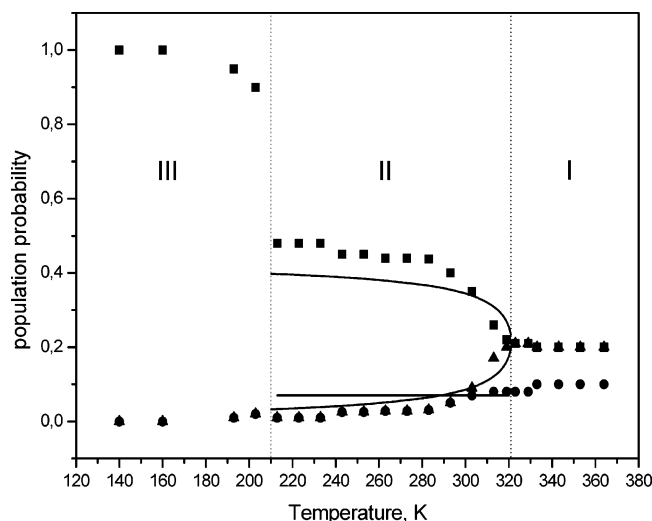

Figure 5. Potential energy minima populations as a function of temperature: (■) p_A, (●) p_B, and (▲) p_C. The solid lines denote populations calculated in ref 21. The vertical dotted lines indicate the phase transitions.

function of temperature,[19] it was possible to calculate the temperature dependence of spontaneous polarization.

To be able to compare our results with the experiment in which the spontaneous polarization was measured along the polar axis z,[4] the polarization calculated was projected on this axis. The angle Θ made by the cation plane with the xz-plane of the crystal depends weakly on temperature and takes the values of 38.5, 39.17, and 38.95° at 100, 300, and 352 K, respectively.[4] The calculations were performed for an angle of 38.9°, and the results are presented in Figure 6. The character of the temperature dependence of spontaneous polarization obtained in the experiment is very similar to that of the calculated dependence; however, in the ferroelectric phases, the measured spontaneous polarization is greater than the calculated one. Figure 6 shows the difference in these values. In a wide range of temperatures (up to room temperature), the difference is constant and of 0.97 μC/cm^2.

Recently, a structural study of the crystal in the intermediate phase as a function of temperature was reported.[21] On the basis of the known occupancy factor of the six positions in the cation by the nitrogen atom, the authors of this paper showed that with
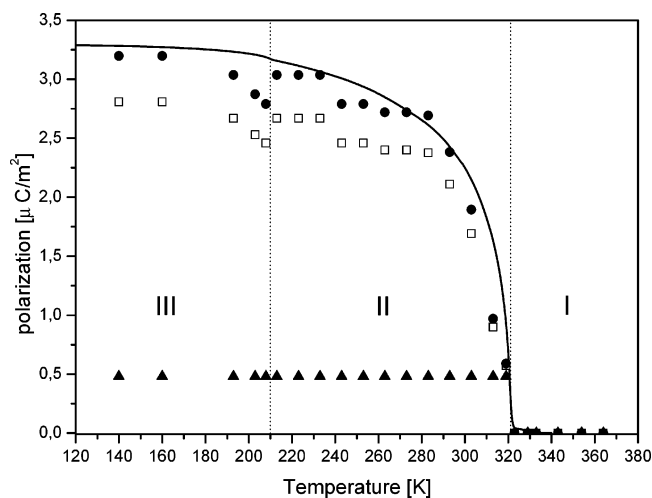

Figure 6. Measured[4] (solid line) and calculated temperature dependence of the spontaneous polarization: (▲) anion contribution, (□) anion and cation contribution (assuming $\mu = 1.97$ D), and (●) anion and cation contribution (assuming $\mu = 2.3$ D). The vertical dotted lines indicate the phase transitions.

increasing temperature, the anion performs a small rotation about the a-axis, which leads to the elongation of the interionic hydrogen bond N—H···O.[21] To obtain the temperature dependence of population, these authors used the measured spontaneous polarization value[4] and assumed that only the cation was the source of polarization and that the population of position C was temperature independent. The values of the populations of the potential energy minima they obtained were compared with our results (Figure 5). As follows from the comparison, the assumption of the constant population of position C is incorrect. The population of position A is lower than the experimental population up to room temperature, while the population of position B is in good agreement with the experimental results. This comparison shows that the assumption about the cation being the only source of the dipole moment is also wrong.

In the Introduction, we specified three possible sources of disagreement between the measured and the calculated polarization. The third of them, which is the inadequacy of the potential, should be rejected because the calculations were performed with the use of the experimentally determined potential and not the model one. The second source, the contribution of the dipole moment generated by the shift of ions, also can be rejected because the elementary cell parameter c, along the polar axis, is practically temperature independent.[19] Of course, with increasing temperature, the elementary cell volume increases but only because of the changes in the lattice parameters a and b.

Thus, the most probable source of the disagreement is the contribution of the dipole moment of the anion. The projection of μ onto the polar axis calculated for the shape of the periodate anion at 100 K with the help of Gaussian 98 with the 6−51G* basis set was 0.27 D.[4] This value of the anion dipole moment leads to participation in the spontaneous polarization of 0.48 μC/cm^2. The total value of the spontaneous polarization resulting from both the cation and the anion dipole moments also is shown in Figure 6.

The fact that the tetrahedral anion can have a dipole moment as a result of its deformation and its participation in the mechanism of ferroelectricity generation is well-justified; it has been confirmed in the structural studies. Besides, it is known that pyridinium halogens do not show ferroelectric ordering, while the pyridinium salts with pseudo-tetrahedral anions FSO$_3$

and $FCrSO_3$ show such an ordering.[24,25] However, even taking into account the dipole moment of the anion, the spontaneous polarization is approximately 0.5 $\mu C/cm^2$ lower than the measured value.

Let us analyze the possible reasons for this difference. The uncertainty of the spontaneous polarization measurement can stem from two factors. The first one is the imperfect cutting out of the crystal, at a certain deviation from the polar axis. Each deviation from the polar axis results in a decrease in the spontaneous polarization value. The second factor is the uncertainty in the determination of the sample surface. Taking these two factors into account, the uncertainty of the spontaneous polarization measurement is estimated to be ±10%, and even for this uncertainty, the calculated value is still a bit lower than the experimental one.

The most probable reason for this disagreement is the method of determination of the dipole moment of the ions. The dipole moment was calculated by using the X-ray structural data of the ion, however, neglecting its environment, which could lead to slightly incorrect charge distribution in the ion considered. An illustration of the previous phenomenon can be the charge distribution calculated for the inclusion compound of thiourea with pyridinium nitrate.[26] The pyridinium cations occupy the channel of a square cross-section made by the thiourea molecules and nitrate anions. The charge distribution was calculated for the cluster containing 16 thiourea molecules, 16 nitrate anions, and three pyridinium cations (altogether, 228 atoms). The dipole moment values obtained for the pyridinium cation in such a cluster varied from 1.9 to 2.8 D, depending on the character of the nearest neighbor. Therefore, assuming in the calculations a dipole moment of the pyridinium cation in $PyHIO_4$ of 2.3 D, instead of 1.97 D calculated for the isolated ion, and taking into account the dipole moment of the anion (by 1 order of magnitude lower), a very good agreement with the experimental results was obtained. This agreement supports the assumption that the ferroelectric $PyHIO_4$ crystal is of the order−disorder type.

Conclusion

(1) On the basis of the occupancy factor determined for the nitrogen atom in the pyridinium cation from the neutron diffraction study,[4] the shape of the potential energy function for the pyridinium cation reorientation was determined. It has been found that in all three phases, the cation performs reorientations about the axis perpendicular to its plane, between the nonequivalent potential energy minima. (2) On the basis of the ^{2}H NMR line measurements, the populations of the potential energy minima as a function of temperature were calculated. (3) Given the potential energy minima populations, it was possible to calculate the spontaneous polarization. A good agreement between the calculated and the measured values of spontaneous polarization permits classification of the ferroelectric $PyHIO_4$ crystal as the order−disorder type.

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