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Brillouin scattering studies of ferroic $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$ (DMACA)

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Abstract. High resolution Brillouin spectroscopy has been used to study the elastic properties of ferroic (i.e. ferroelectric and ferroelastic) $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$, otherwise known as DMACA. The experiments covered the temperature range from 170 to 300 K, and included the ferroelectric phase transition at about 240 K. The temperature dependence of Brillouin modes has been observed for the longitudinal phonons propagating in the four directions [100], [010], [101] and [111]. The relaxation times of the order parameter were determined and different types of coupling between polarization and strain are discussed.

1. Introduction

Crystals with general formula $[\text{NH}_2(\text{CH}_3)_2]_3\text{X}_2\text{Y}_9$ (with $\text{Y} = \text{Cl}, \text{Br}$ and $\text{X} = \text{Sb}, \text{Bi}$) are built of two-dimensional layers of corner sharing halogen octahedra. The cavities between the octahedra are occupied by the dimethyloammonium cations which form relatively weak hydrogen bonds with halogen atoms. The phase transitions observed in these materials are related to the motion of dimethyloammonium cations or reorientation of the anions [1–4].

The DMACA crystal exhibits an interesting phase sequence. It crystallizes at room temperature in the monoclinic system (space group $P2_1/a$, point group $2/m$) and shows ferroelastic properties. The ferroelasticity of the $2/m$ phase was postulated on the basis of the observations of an elastic domain wall movable under the action of uniaxial stress. The prototype symmetry for this phase could not be experimentally determined because the crystal decomposes at $T_d \sim 340$ K. The possible symmetry of the prototype phase has been discussed in detail [5] on the grounds of birefringence measurements and domain structure observations. The authors postulated the $\bar{3}m$ trigonal point group to be the ferroelastic prototype of DMACA.

At about 240 K, DMACA undergoes the phase transition to the polar phase. As it was found from the pyroelectric measurements [1] this transition is related to the onset of spontaneous polarization along the a and c crystallographical directions. This suggests the monoclinic point group 2 as the probable symmetry of the ferroelectric phase. From the dielectric studies of DMACA [3] it appears that the ferroelectric phase transition is of the order–disorder type with the macroscopic relaxation time of the order of 10^{-7} s. On the basis of the above mentioned features, the structural changes of DMACA can be summarized as in figure 1.

When analysing this diagram, the question arises about the elastic properties of such a system and possible interactions between the electric and elastic degrees of freedom. To date

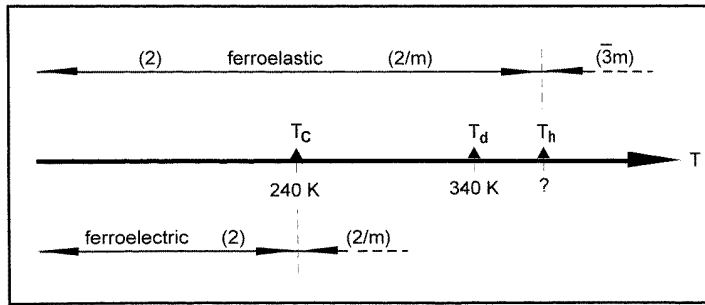


Figure 1. A schematic phase diagram for DMACA. Point group symmetries are shown in brackets. T_h indicates the ferroelastic phase transition that would be expected if the crystal did not decompose at T_d .

the only existing results on the elastic properties of the crystals from this family are those derived from Brillouin scattering studies of bromide analogue DMABA [6]. The authors reported a large anomaly in the velocity of the longitudinal phonon propagating in the c crystallographical direction, which was accompanied by a critical behaviour of the line width. However, these changes were not attributed to the ferroelectric phase transition.

In this work we report the results of Brillouin scattering studies of DMACA in the temperature range from 170 to 300 K. On the basis of the observed temperature behaviour of the four longitudinal phonons propagating in [100], [010], [101] and [111] directions, we discuss the possible coupling of the effective elastic constants with the ferroelectric order parameter. A single relaxation model is used to describe the influence of the ferroelectric phase transition on the sound attenuation.

2. Experimental procedure

Single crystals of DMACA were grown from the 10% solution of HCl at 290 K by the slow evaporation of the solvent. Colourless and transparent crystals of the density of $1.90 \times 10^3 \text{ kg m}^{-3}$ were obtained with the perfect cleavage plane perpendicular to the c axis.

Samples of the four different orientations were prepared to study the sound velocity propagation of the longitudinal [100], [010], [101] and [111] phonons. The typical size of the sample was $4 \times 4 \times 3 \text{ mm}^3$.

The Brillouin spectrometer has been described in detail elsewhere [7]. The incident light was provided by a stabilized single-mode argon-ion laser operating at 514.5 nm and polarized perpendicularly to the scattering plane. The scattered light was analysed at 90° using a piezoelectrically scanned triple pass Fabry–Pérot interferometer (Burleigh model RC-110) with free spectral ranges 20.20 and 25.40 GHz. With a normal finesse of about 60, the instrumental line width Γ_l did not exceed 0.3 GHz (for smaller FSR). Any drifts due to the laser, electronics or Fabry–Pérot interferometer were automatically compensated by a PC-based data acquisition and control system (FPDACS–MUN, Canada). Sound velocities v were deduced from the measured frequency shifts $\Delta\nu$ using the Brillouin equation

$$v = \lambda \Delta\nu (n_i^2 + n_s^2 - 2n_i n_s \cos \Theta)^{-\frac{1}{2}} \quad (1)$$

where λ is the wavelength of the incident light, n_i and n_s are refractive indices for the incident and scattered light respectively and Θ is the scattering angle. The refractive indices of DMACA were estimated for 514.5 nm at room temperature using the microscopic method. We found $n_a = 1.75$, $n_b = 1.77$ and $n_c = 1.74 \pm 0.01$.

Taking into account the results of linear birefringence measurements [5] from which the relative changes of refractive indices at the ferroelectric phase transition were found to be no bigger than 10^{-3} we assumed them constant when calculating the sound velocities.

The Brillouin scattering experiments on DMACA were performed from 170 to 300 K using the cryostat described in a previous publication [8]. The temperature of the sample was controlled with the stability of ± 0.02 K.

3. Experimental results and discussion

Usually, results of a Brillouin experiment permit determination of all non-zero components of the elastic stiffness tensor by solving the equation of motion $|c_{ijkl}q_jq_k - \rho v^2\delta_{il}| = 0$, where c_{ijkl} are the components of the elastic stiffness tensor, and q_j and q_k are direction cosines of the phonon propagating at velocity v in the crystal of density ρ . The success of this procedure depends, of course, on the detection of a sufficient number of longitudinal and transverse phonons as a function of the crystal orientation.

Because DMACA exhibits monoclinic symmetry ($2/m$ and 2) over the entire temperature region studied, there are 13 independent elastic stiffness coefficients to be considered [9]. Their determination is a particularly demanding task because the scattering power of transverse phonons is weak, the noise-to-signal ratio for phonons propagating perpendicular to the layers is high and there are elastic domains already present at room temperature. As an alternative it was consequently decided to concentrate on determining the temperature dependence for the velocities of selected longitudinal phonons only. For the longitudinal phonons the typical noise-to-signal ratio was of the order of 10^{-1} and the Brillouin shifts varied from 9 to 13 GHz. In figure 2 the typical spectrum of DMACA is presented. Only the longitudinal phonon with the energy of 9.86 GHz was observed. One can notice the asymmetry in the Rayleigh peak due

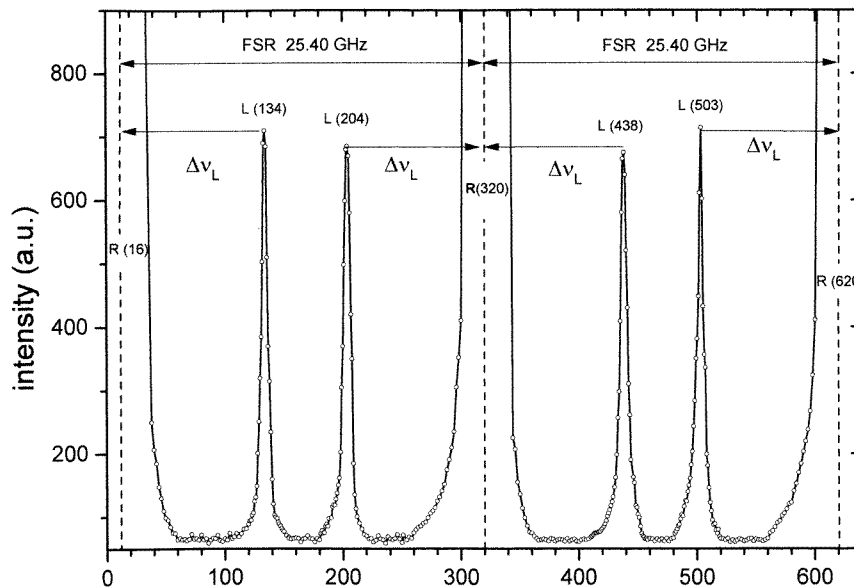


Figure 2. Brillouin spectra of DMACA. Phonon [101]; temperature 292.10 K; L and R state for positions of Brillouin and Rayleigh components respectively; FSR = 25.40 GHz; intensity of R components $\sim 7.6 \times 10^5$; accumulation time— 2.6×10^3 s; laser power 90 mW.

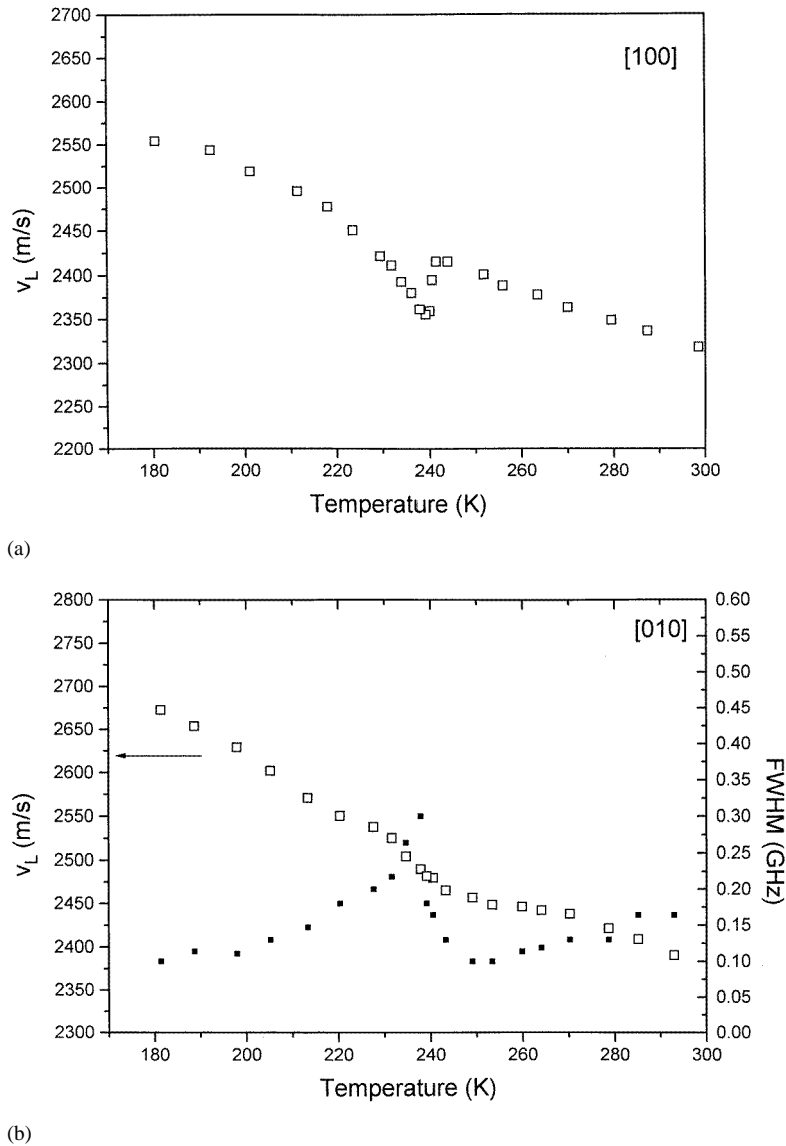
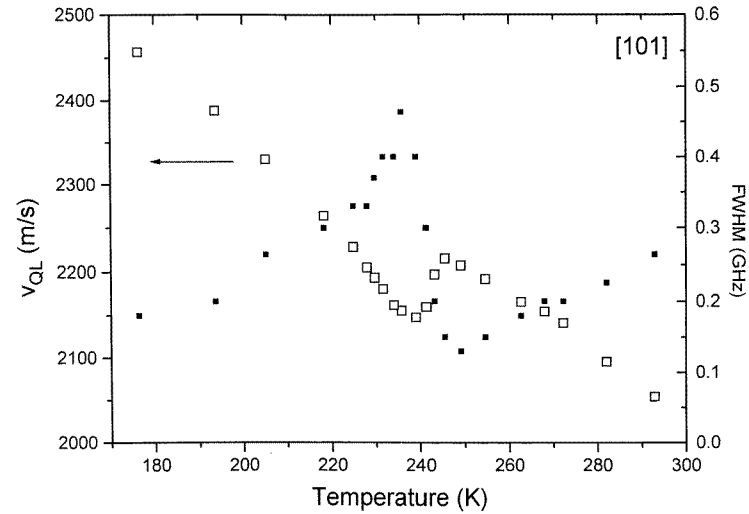


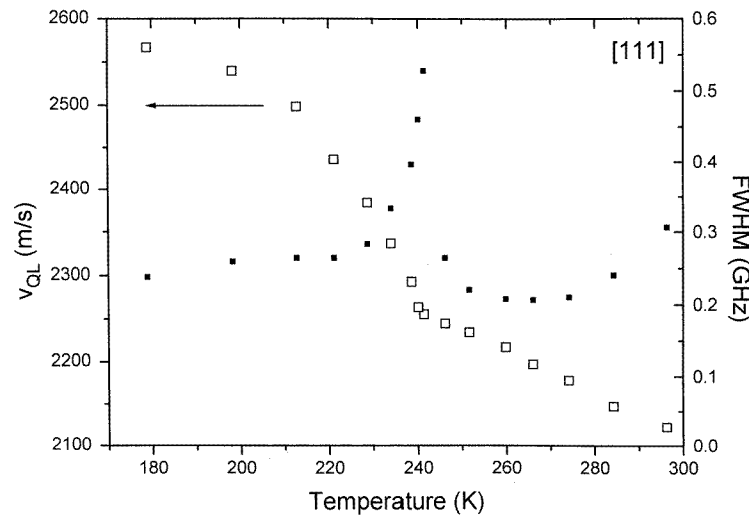
Figure 3. Temperature dependence of the longitudinal phonon velocities of DMACA and corresponding full width at half maximum: (a) [100], (b) [010], (c) [101], (d) [111]. Please note that all velocities are plotted in the same vertical scale.

to the presence of both elastic domains and layers in the sample. In some cases this asymmetric noise overlapped the Brillouin components.

The results obtained are presented in figures 3(a)–(d) where it can be seen that all selected modes are affected by the transition at 240 K but in different ways. Three types of behaviour can be distinguished for v versus T in the vicinity of T_C : (i) step-like changes of about 90 m s^{-1} ($v_{[100]}$ and $v_{[101]}$) which correspond to the shift change of about 0.4 GHz, (ii) changes proportional to the order parameter (for $v_{[111]}$) and (iii) relatively small depths not exceeding 30 m s^{-1} for the remaining phonons.



(c)



(d)

Figure 3. (Continued)

Because of the restricted selection of propagation directions, only the c_{22} elastic constant could be determined via the relationship $c_{22} = \rho v^2$. At 300 K the result is $c_{22} = 1.08 \times 10^{10} \text{ N m}^{-2}$.

The temperature dependence of the sound attenuation was investigated by approximate determinations of the 'true' full width at half maximum (FWHM), Γ , of the observed Brillouin lines. The procedure applied involved determination of the instrumental line width on the basis of an experiment with light scattering on a standard sample of fused silica. Using the same set of pinholes, the Rayleigh and Brillouin lines of the studied DMACA samples could be well fitted to the Lorentz function. Since no broadening of the instrumental line during temperature measurements was evidenced, a simplified procedure for determination of the 'true' width,

proposed in [10], was applied. The procedure was the simple subtraction of the instrumental contribution, Γ_I , from the observed FWHM value.

For Γ the largest T_C anomalies were for the phonons propagating in the [111] and [101] directions (see figure 3). For $v_{[100]}$ Γ was found to be independent of T in the entire range and the value was about 0.12 GHz.

Assuming that the single relaxation time, τ , is appropriate, it can be determined by combining two equations: the first expresses [11] the dependence of the sound velocity, v , on frequency, ω ,

$$v^2 = v_0^2 + (v_\infty^2 - v_0^2)\omega^2\tau^2(1 + \omega^2\tau^2)^{-1}. \quad (2)$$

Here, v_∞ is the limiting high-frequency velocity and v_0 is the sound velocity not affected by the transition. The second equation is a corresponding expression for the sound attenuation,

$$\alpha = (2v)^{-3}(v_\infty^2 - v_0^2)\omega^2\tau(1 + \omega^2\tau^2)^{-1}. \quad (3)$$

The relaxation time τ is then given by:

$$\tau = (2\alpha)^{-1}v^{-3}(v^2 - v_0^2) \quad (4)$$

and can be calculated from the true width of the Brillouin line.

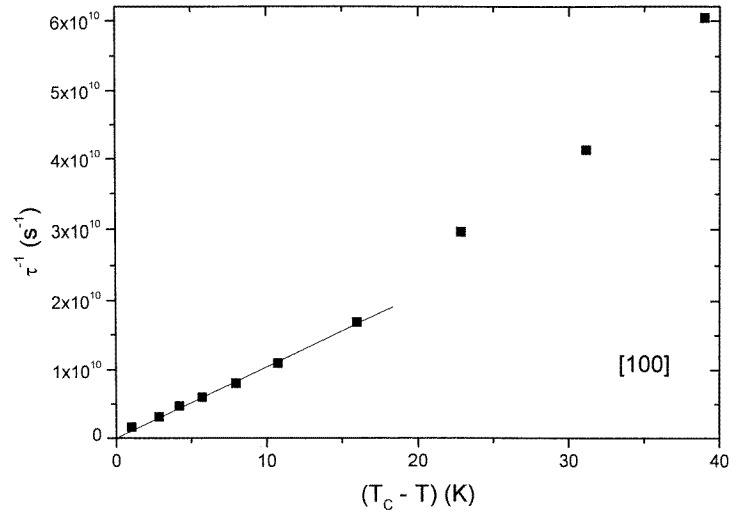
At temperatures close to T_C , the τ value was found to be 4.77×10^{-10} and 1.21×10^{-10} s for the [100] and [101] directions, respectively. According to the Landau theory [12] the relaxation time of polarization fluctuations in the vicinity of the phase transition is linearly proportional to the inverse temperature difference, i.e. $\tau = A(T_C - T)^{-1}$. For the sake of comparison we have plotted in figure 4 the temperature dependence of the inverse relaxation time τ^{-1} for the phonon velocities $v_{[100]}$ and $v_{[101]}$. The behaviour in these two cases is typical of that for the order–disorder transition in ferroelectrics, namely, they show step-like changes at T_C caused by the induced piezoelectric coupling in the ferroelectric phase. As evident in both cases, τ is a linear function of temperature with the slopes $A = (1.00 \pm 0.15) \times 10^{-11}$ K s and $(5.20 \pm 0.12) \times 10^{-9}$ K s for the directions [100] and [101], respectively.

As stated above, DMACA exhibits the spontaneous polarization in the *ac* crystallographic plane, so one could expect the largest elastic anomaly in the [010] direction. This is not evident in our results. The temperature dependence of $v_{[010]}$ is very small near T_C when compared to those in the other directions. Unfortunately, the [001] phonon could not be observed below T_C , because of the presence of a high level of parasitic light in all those samples that were oriented for this purpose. However, when analysing the character of temperature changes of the remaining phonons it seems that the T dependence of $v_{[001]}$ should be similar to that observed for the bromide analogue, DMABA [6]. If so, the nature of the two components of the spontaneous polarization (P_a and P_c) must be different in the terms of classical classification of ferroelectric materials. The P_c seems to have a clear order–disorder origin with the perpendicular fluctuations reflected in the temperature behaviour of the phonon [100]. The final determination of the origin of P_a will be possible when complementary data on elastic properties of DMACA in the z direction are available.

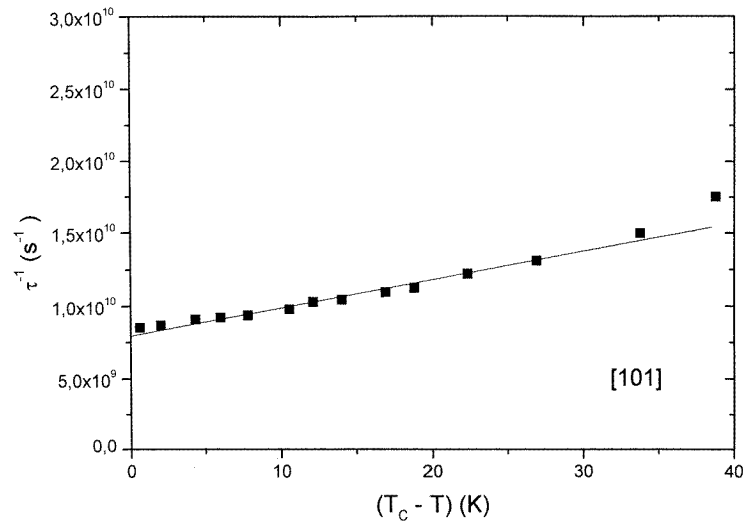
In order to provide a basis for the future description of the phase transition in DMACA we now consider the general types of coupling term between polarization P_i and the elastic strain ε_{ij} according to the Rehvald classification [13]. The interaction potential, F_{int} , contains various degrees of strain, and the polarization and crystal symmetry determine which coefficients are non-vanishing [14] in the following equation:

$$F_{int} = a_{ijk}P_i\varepsilon_{jk} + b_{ijkl}P_iP_j\varepsilon_{kl} + c_{ijklm}P_i\varepsilon_{jk}\varepsilon_{lm} + d_{ijklmn}P_iP_j\varepsilon_{kl}\varepsilon_{mn} + \dots \quad (5)$$

The first term in equation (5) is restricted for the crystals in which polarization and strain belong to the same irreducible representations or, in other words, for piezoelectrics (already in



(a)



(b)

Figure 4. Temperature dependence of the inverse relaxation time in the ferroelectric phase: (a) phonon [100], (b) phonon [101].

the paraelectric phase). When analysing our data given in figure 3 it appears that the dominant coupling term for DMACA is the quadratic electrostrictive (second) term in equation (5) which leads to the step-like changes in $v_{[100]}$ and $v_{[101]}$ at T_C given by $\Delta v = b_{ijkl}/(2A_4)^{1/2}$, where A_4 is the coefficient of P^4 in the Landau expansion.

In order to explain the temperature behaviour of $v_{[111]}$ it is necessary to consider the last two terms in equation (5). The nonlinear coupling described by the third term occurs only in ferroelectrics that exhibit a piezoelectric effect in the paraelectric phase, which is not the case here. According to the Thomas–Sloczewski equation [15] the quadratic coupling both in the strain and polarization (fourth term in equation (5)) gives rise to an increase of the

elastic constant in the ferroelectric phase that is proportional to the square of polarization, i.e. $\Delta c = 2dP^2$. This in turn leads to the linear correlation between v and P . According to the authors of [1], the spontaneous polarization changes like $(T_C - T)^\beta$ at temperatures close to T_C . They quoted the value $\beta = 0.5$ for polarized samples with self-biasing field removed. For other cases β may be much higher. In the present case it was found that $v_{[111]}$ just below T_C was consistent with $\beta = 0.75$.

4. Summary

Our preliminary results of the elastic properties of DMACA crystal obtained by the Brillouin scattering method indicate the different character of the two components of spontaneous polarization. Since no distinct anomaly was found in the temperature dependence of $v_{[010]}$ phonon velocity perpendicular to the polar ac plane, we attribute the changes of $v_{[100]}$ velocity to a lattice stiffening due to the onset of component P_c below T_C . The relaxation times $\tau_{[100]}$ and $\tau_{[010]}$ were found to be the inverse function of temperature, but the temperature dependences are small when compared with those for other ferroelectric systems [16]. We conclude that the dominant terms in the interaction part of the free energy are those of the type $bP^2\varepsilon$ and $dP^2\varepsilon^2$ and should be included in the total energy expansion in order to account for the coupling between the elastic and electric degrees of freedom. A detailed theoretical analysis of the ferroelectric phase transition in DMACA is in progress and will be presented in the near future.

Acknowledgments

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