Monte Carlo study of a compressible pseudospin model for $(CH_3NH_3)_5Bi_2Cl_{11}$

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A two-sublattice peudospin model with distance-dependent interaction parameters is constructed for the ferroelectric phase transition at 307 K and for the isomorphous anomaly at 180 K in pentakis (methylammonium) undecachlorodibismuthate (III) $(CH_3NH_3)_5Bi_2Cl_{11}$. A series of Monte Carlo simulations involving continuous degrees of freedom of deformation is performed for the model. The critical temperatures turn out about 23% lower than those resulting from the mean-field treatment for the three-dimensional fcc lattice in the absence of coupling with strain. An upward shift in the critical temperature then is found due to the coupling with the strain. The multiple histogram method is used to obtain the theoretical predictions for the temperature dependence of the spontaneous polarization, dielectric susceptibility, and specific heat. The existence of a narrow peak in the specific heat and the ratio of the Curie constants close to 4 are confirmed. Evidence is given of the usefulness of the Monte Carlo method with fairly small simulation boxes for the studies of isomorphous anomalies.

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I. INTRODUCTION

Pentakis (methylammonium) undecachlorobismuthate (III) of chemical formula $(CH_3NH_3)_5Bi_2Cl_{11}$, abbreviated PMACB, undergoes under ambient pressure a ferroectric phase transition at $T=307$ K. By further cooling, a smooth isomorphous anomaly marked by a significant increase in the spontaneous polarization at about $T=180$ K has been found.[1] Detailed crystallographic studies[2] have indicated a direct relation between macroscopic properties of the crystal and a gradual orientational ordering of the dipolar methylammonium (MA) cations. Thus, the ordering of a sublattice, called MA(1), of the methylammonium cations is responsible for the ferroelectric phase transition. In turn, the isomorphous anomaly has its origins in the subsequent ordering of another sublattice MA(2) in the field created by the cations of the sublattice MA(1) already ordered.[3] The dilatometric studies[4] revealed a strong coupling of the spontaneous polarization to mainly the ''pancake'' strain,

$$\varepsilon = -\frac{1}{\sqrt{6}}(2\varepsilon_{33}-\varepsilon_{11}-\varepsilon_{22}). \quad (1)$$

Based on these observations, a two-sublattice compressible pseudospin model has been proposed[5] and its parameters have been fitted to the ensemble of the existing experimental data in the mean-field approximation. Two results of those fits are noteworthy: (i) a fairly weak direct coupling of both sublatticies, and (ii) the strength of the coupling of the sublattice MA(1) to the strain [Eq. (1)] indicating a tricritical point at 307 K. Concomitants of the tricritical point in the mean-field description are: the factor of -4 of the slopes of the inverse susceptibilities as functions of temperature (or factor 4 of the Curie constants)[6] and a sharp peak, in addition to a step, in the temperature dependence of the specific heat. The above hypotheses are still worth being checked experimentally. On the other hand, it is interesting to know, how far they are inherent in the model and not just a consequence of its mean-field treatment. To cast a light on this problem we have performed a series of Monte Carlo (MC) simulations for a model analogous to that treated by the mean-field theory in Ref. 5. To the best of our knowledge this is the first MC study of a phase transition where, apart from discrete pseudospin degrees of freedom, continuous deformation is explicitly taken into account. In Sec. II we give the definitions of the geometry and of the interactions in the present model. This is the simplest possible microscopic model, which in the mean-field approximation is equivalent to the one of Ref. 5. The treatment of the numerical data obtained in the simulations and the resulting predictions for the behavior of physical quantities are described in Sec. III. The physical significance of the results and prospectives for further investigations are summarized in Sec. IV.

II. COMPRESSIBLE PSEUDOSPIN MODEL FOR MC SIMULATIONS

Whereas it is enough to make the pseudospin-pseudospin interaction parameters formally dependent on the relevant

strain component ε in the mean-field approximation,[5] it is necessary to explicitly define all the force constants and all the distance dependencies of the pseudospin interaction parameters to meet the needs of the Monte Carlo simulations. Following the assumptions made in Ref. 5 we consider two sublattices of pseudospins $\sigma_i \in$ MA(1) and $\vartheta_i \in$ MA(2). An insight into the real structure of PMACB [Refs. 1–3] indicates that both sublattices may be putatively approximated by a distorted face-centered cubic (fcc) structures arranged in the manner characteristic for the NaCl crystal. Each pseudospin $\sigma_i \in$ MA(1) and $\vartheta_i \in$ MA(2) is supposed to take two possible orientations $\sigma_i, \vartheta_i = \pm 1$ along the crystallographic direction (001). This lowers the initial cubic symmetry to a tetragonal one even in the disordered phase. Further lowering of symmetry implied by the orthorhombic structure of PMACB is irrelevant at the level of the present approximations.

To place ourselves at the opposite limit with respect to the inherently infinite-range treatment of the mean-field theories we have restricted the inter and intrasublattice interactions to the nearest neighbors only. Therefore, the total energy of the system at a given configuration is a sum

$$H = H_{el} + H_s \tag{2}$$

with the following purely elastic part H_{el},

$$\begin{aligned} H_{el} = & \frac{1}{2} \sum_{i \in \{\sigma\}} \sum_{j \in \langle i \rangle_\sigma} K^\sigma (r_{ij} - r_\sigma)^2 \\ & + \frac{1}{2} \sum_{k \in \{\vartheta\}} \sum_{l \in \langle k \rangle_\vartheta} K^\vartheta (r_{kl} - r_\vartheta)^2 \\ & + \sum_{i \in \{\sigma\}} \sum_{l \in \langle i \rangle_\vartheta} K^{\sigma\vartheta} (r_{il} - r_{\sigma\vartheta})^2. \end{aligned} \tag{3}$$

The parameters K^σ, K^ϑ, and $K^{\sigma\vartheta}$ are the displacive force constants for the nearest-neighboring sites within the sublattices σ, ϑ and for the nearest neighbors belonging to different sublattices, respectively. The distances $r_\sigma = r_\vartheta = a/\sqrt{2}$ and $r_{\sigma\vartheta} = a/2$ are the equilibrium separations between the corresponding neighbors in the lattice, whereas r_{ij} are the instantaneous distances between the pseudospins. The quantity a is the lattice constant, i.e., the edge of the initial cube of the NaCl structure. The notation used for the summation ranges is the following: $i \in \{\alpha\}$ denotes the sites belonging to the sublattice $\alpha = \sigma, \vartheta$; the sign $j \in \langle i \rangle_\alpha$ represents those sites, which belong to the sublattice α and are at the same time the nearest neighbors of the site i. The form of the purely elastic part of the lattice energy [Eq. (3)] implies the following ''bare''[7] elastic constants counted per crystallographic asymmetric unit, i.e., per pair of sites (σ, ϑ):

$$\begin{aligned} c_{11} &= \frac{2}{a}(K^\sigma + K^\vartheta + K^{\sigma\vartheta}), \\ c_{12} &= c_{44} = \frac{1}{a}(K^\sigma + K^\vartheta). \end{aligned} \tag{4}$$

Consequently, the ''bare'' bulk modulus and the elastic constant conjugated with the ''pancake'' strain ε of Eq. (1) are as given by Eq. (5) and Eq. (6), respectively,

$$c_{11} + 2c_{12} = \frac{1}{a}(4K^\sigma + 4K^\vartheta + 2K^{\sigma\vartheta}), \tag{5}$$

$$c_{11} - c_{12} = \frac{1}{a}(K^\sigma + K^\vartheta + 2K^{\sigma\vartheta}). \tag{6}$$

The contribution H_s to the energy of Eq. (2) describes the pseudospin-pseudospin interactions.

$$\begin{aligned} H_s = & -\frac{1}{2} \sum_{i \in \{\sigma\}} \sum_{j \in \langle i \rangle_\sigma} J^\sigma(r_{ij}) \sigma_i \sigma_j - \frac{1}{2} \sum_{l \in \langle k \rangle_\vartheta} J^\vartheta(r_{kl}) \vartheta_k \vartheta_l \\ & - \sum_{i \in \{\sigma\}} \sum_{l \in \langle i \rangle_\vartheta} J^{\sigma\vartheta}(r_{il}) \sigma_i \vartheta_l . \end{aligned} \tag{7}$$

The conventions of the summation over the neighbors in Eq. (7) are the same as in Eq. (3). The quantities $J^\alpha(r); \alpha = \sigma, \vartheta, \sigma\vartheta;$ are the interaction parameters of the pseudospins. Their dependence on the instantaneous distance between the interacting pseudospins ensures coupling with strain. It has been shown in the mean-field approximation,[5] that the experimental temperature dependence of the spontaneous polarization in PMACB can be satisfactorily fitted with the pseudospin interaction parameters given as third-order polynomials of the strain ε [Eq. (1)]. We retain this kind of dependence in the present study by assuming the following third-order expansion of the interaction parameters as functions of the separation vector r of the pseudospins

$$J^\alpha(r) = J_0^\alpha + f(\hat{r})[J_1^\alpha(r - r_\alpha) + J_2^\alpha(r - r_\alpha)^2 + J_3^\alpha(r - r_\alpha)^3], \tag{8}$$

for all $\alpha = \sigma, \vartheta, \sigma\vartheta$. The equilibrium distances r_α are the same as in the purely translational part of the energy [Eq. (3)]. To ensure a coupling with the pancake strain of Eq. (1) we introduce a factor $f(\hat{r})$ depending on the spatial orientation of the vector r linking the instantaneous positions of the corresponding pseudospins, where $\hat{r} = r/|r|$. In the present study the factor is

$$f(\hat{r}) = 1 - |\cos\theta| 3\sqrt{2}/4, \tag{9}$$

where θ is the angle between the separation vector r and the crystallographic direction (001). The angular dependence of the function Eq. (9) assures a tendency to contraction in the direction (001) and to simultaneous expansion in the perpendicular directions as required by the pancake strain Eq. (1).

From among all the conceivable models giving rise to the same mean-field as in Ref. 5, the one discussed above involves the least number of microscopic parameters. In general, there are as many pseudospin-interaction parameters J as there are crystallographically inequivalent pairs of pseudospins in the crystal. The mean-field approximation neglects any distance dependence of these interactions and, moreover, imposes their infinite spatial range. Only if the initial range of interactions is infinite, is the mean-field treat-

ment correct. Therefore, the present restriction of the pseudospin interactions to the nearest neighbors amounts to studying the opposite-limit case with respect to the mean-field approximation. With this simplification the number of deformation-dependent interaction parameters $J(\mathrm{r})$ equals 3, i.e., the number of the parameters used in the mean-field approximation.

The elastic interactions are also the simplest possible here. The intersublattice force constants K^{σ} and K^{ϑ} assure the stability of the crystal with respect to all the macroscopic strains (one force constant per sublattice is sufficient in the present case of the fcc sublattice whereas at least two force constants are needed for a simple cubic lattice). The intersublattice force constant $K^{\sigma\vartheta}$ is needed to describe a resistance of the structure with respect to mutual displacement of sublattices also called inner strain.[8] In contrast to the mean-field approach there is no possibility of defining a one deformation to be coupled with ferroelectric order parameters in three dimensions.

Despite its simplicity the model is expected to describe all the electric and thermodynamic phenomena related to the spontaneous polarization and to its reaction to an external field applied parallel to the polar axis. More parameters would be needed to account for dielectric and elastic anisotropy of the material. However these are not the subject of the present study.

III. NUMERICAL PROCEDURES AND RESULTS

The presence of the continuous degrees of freedom related with the displacements of the pseudospins increases considerably the computation time of the MC simulations in comparison with the usual Ising-type models on rigid lattices.[9] Thus, effective algorithms for fitting the parameters of the model to the known experimental data are of crucial importance in this case. On the other hand, being not particularly interested in the very vicinity of the critical point, we could legitimately restrict our calculations to relatively small simulation boxes.

The first step of the fitting was the estimation of the interaction parameters J_0^{α}, $\alpha=\sigma,\vartheta$ for both sublattices without mutual coupling and without coupling with the strain, i.e., for all the remaining parameters equal to zero. As the estimate of the parameters J_0^{α}, $\alpha=\sigma,\vartheta$ we have used the fixed point of the reduced Binder cumulant $U_L=1-\langle e^4\rangle_L/(3\langle e^2\rangle_L^2)$,[9] where $\langle e^n\rangle_L$ is the average of nth power of the lattice energy, obtained in a simulation run at the box size L. The lengths La of the edges of the cubic simulation box involved the multiples $L=2$, 4, 8, and 10 of the lattice parameter $a=14$ Å. With the number 8 of the pseudospins per elementary cell, the number of the particles in the above simulation boxes amounted to 64, 512, 4096, and 8000, respectively. The periodic boundary conditions were applied in all the cases. The resulting ratio k_BT_c/J_0^{σ} turned out to be equal to 9.731. The corresponding ratio in the mean-field approximation amounts to the number of the nearest neighbors in the fcc lattice, i.e., $k_BT_c^{MF}/J_0^{\sigma}=12$. Thus, the mean-field approximation over-rates the critical temperature by about 23% in the case of the $3d$ fcc lattice (see Ref. 9 for analogous values for $2d$ and $3d$ simple cubic lattices). Knowing the temperature of the ferroeletric phase transition $T_c=307$ K and the temperature of the isomorphous anomaly $T_a=180$ K we could obtain $J_0^{\sigma}/k_B=31.55$ K and $J_0^{\vartheta}/k_B=18.50$ K.

With the above starting values we introduced the force constants $K^{\sigma}=K^{\vartheta}=K^{\sigma\vartheta}=K=1000$ K/Å^2 that have been held invariable throughout all the computations. These values assure the fluctuations of the strain comparable with the experimental longitudinal elastic constants c_{ii} [see Eqs. (5) and (6)] in PMACB.[10] The shear elastic constants c_{44} and $c_{11}-c_{12}$ are not known experimentally in this material. No information on the reaction of the material onto inner strain is available either. This justifies the use of equal values for all the force constants. In fact all the results presented here do not change if we multiply all the force constants by a factor keeping constant the ratios J_2^{σ}/K and $J_1^{\sigma 2}/K$. The statement is valid for a whole class of such models with $J_3^{\sigma}=0$ (see below). We present its proof in the Appendix.

As it is known from the mean-field approach,[5] the coupling parameters J_1^{σ} and J_2^{σ} play the decisive role in the determination of the actual shape of the temperature-dependent spontaneous polarization just below the ferroelectric phase transition. Indeed, the ascent of the spontaneous polarization obtained in the simulations with those parameters equal to zero turned out to be much too weak in comparison with the experimental data.[11] A similar effect was observed in the phenomenological theory.[12] To estimate the values of the coupling constants J_1^{σ} and J_2^{σ} needed to obtain the desired shape of the temperature-dependent spontaneous polarization in the present simulations we chose a temperature $T=297$ K below the T_c and progressively increased the coupling constant J_1^{σ} in each simulation run so as to obtain the value $\langle\sigma\rangle$ corresponding to the experiment. The coupling between the sublattices σ and ϑ being expected weak, we neglected the contribution of the sublattice ϑ to the polarization at this temperature. The ratio $J_2^{\sigma}/J_1^{\sigma}$ was held constant. Its value was deduced from the analogous ratio obtained in the mean-field theory.[5] The third-order coefficient J_3^{σ} was put zero. The number of the Metropolis Monte Carlo steps in each run was equal to 1000. To save the computation time we performed the calculations for the size $L=4$ of the simulation box and used the last configuration obtained for a given value of J_1^{σ} as the starting configuration for the subsequent value. This made the thermalization of the system faster. Once a satisfactory agreement with the experimental polarization had been reached we performed a longer simulation for the box size $L=8$. The resulting values were $J_1^{\sigma}=4298.1$ K/Å and $J_2^{\sigma}=9210.0$ K/Å^2. The remaining coupling constants have been chosen by keeping the proportionality to the corresponding values in the mean-field theory: $J_1^{\vartheta}=614.0$ K/Å, $J_2^{\vartheta}=0$ K/Å^2, and $J^{\sigma\vartheta}=2.0$ K.

Using these values we performed series of simulations in the temperature range from $T=100$ K to $T=450$ K every 5 K. Again, to save the computation time and to speed up the thermalization we used the final configuration from each temperature as the starting configuration for the simulation in the next temperature. Whereas the resulting curve of the

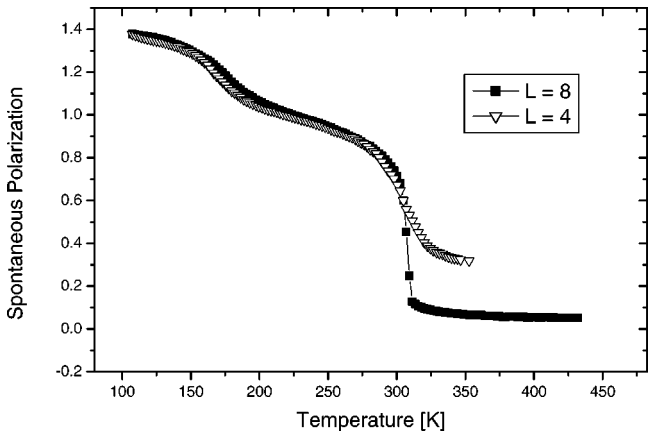

FIG. 1. Temperature dependence of spontaneous polarization $P=\langle\sigma+\gamma\vartheta\rangle$ in present model for PMACB with box sizes $L=4$ and $L=8$. Coefficient $\gamma=0.37$ represents the ratio of permanent dipole moments associated with sublattices MA(2) and MA(3). See text for parameters of the model.

temperature-dependent polarization for $L=4$ was decidedly too smooth close to the ferroelectric phase transition point, the corresponding shape for $L=8$ turned out to be close to the experimental data. However, the critical temperature was shifted up to about 350 K. To finally get the correct critical temperature we multiplied all the constants of the energy of Eqs. (3) and (7) and specified above by a common factor 307/350 = 0.877. This is equivalent to enlarging of the temperature scale by the inverse of this factor. At each temperature a histogram in energy as well as in the polarization has been collected. This allowed us to improve the statistics by using at each temperature the reweighted probability distributions from several neighboring temperatures.[13] The same reweighting technique allowed us to generate the probability distributions at the bridging points so as to obtain the final results every 2.5 K. The set of histograms selected for the multihistogram analysis at each temperature encompassed those histograms that had the most significant overlaps with the histograms originally simulated at the temperature closest to the temperature under consideration. The selection was made by ascribing to each histogram a Gaussian weight as a function of the inverse of the overlapping areas. All the effective histograms were additionally smoothed with the use of the convolutional smoothing technique.[14]

The resulting spontaneous polarization $P=\langle\sigma+\gamma\vartheta\rangle$ with the ratio of the dipole moments of both sublattices $\gamma=0.37$ estimated from the experimental results[11] is shown in Fig. 1 for the box sizes $L=4$ and $L=8$. The curve obtained with the box size $L=8$ resembles reasonably well the experimental results.

Figure 2 represents the simulated specific heat calculated with the use of the average fluctuations of the energy $c=(\langle e^2\rangle-\langle e\rangle^2)/k_BT^2$. The values obtained agree with those given by the formally equivalent expression $c=\partial\langle e\rangle/\partial T$. The behavior of the specific heat for both box sizes is very similar close to the isomorphous anomaly $T\approx 180$ K. A large maximum resembles the experimental curve obtained in the adiabatic calorimetry experiment.[13] In the vicinity of the ferroelectric phase transitiion at $T=307$ K only the curve for

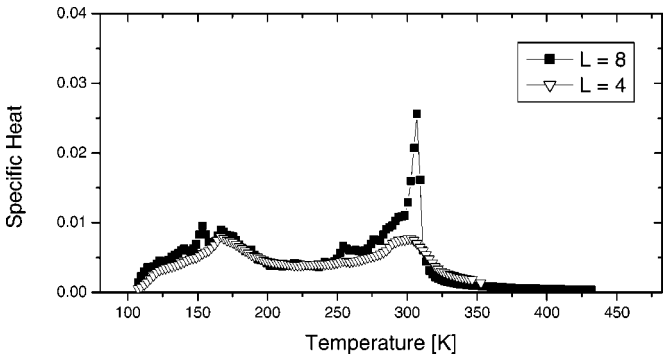

FIG. 2. Temperature dependence of excess specific heat for PMACB obtained with box sizes $L=4$ and $L=8$.

$L=8$ is comparable to the experiment.[15] Similar to the mean field fit[5] the steplike behavior, characteristic for the second order phase transition in the Landau theory, is accompanied by a narrow peak.

The behavior of the dielectric susceptibility $\chi=\{\langle(\sigma+\gamma\vartheta)^2\rangle-\langle\sigma+\gamma\vartheta\rangle^2\}/k_BT$ obtained in the present simulations is shown in Fig. 3. Two curves for each box size are related to the effect of domain switching. In particular, when the simulation is started from the ordered state: $\sigma_i=1$ and $\vartheta_i=1$ at a sufficiently low temperature, the system stays close to this state during the whole simulation time. However, close to the phase transition the system may jump to the other domain where $\langle\sigma\rangle\approx\langle\vartheta\rangle\approx-1$. Such an effect can be interpreted in two ways: (i) either as a result of domain switching in the ordered phase or (ii) as a result of a fluctuation whose spatial extent surpasses the box size in the disordered phase. In case (i) one has to put $\langle|\sigma+\gamma\vartheta|\rangle$ instead of $\langle\sigma+\gamma\vartheta\rangle$ that amounts to the hypothesis of equal probability of each domain, whilst the quantity of interest concerns one of the domains only. In case (ii) the average $\langle\sigma+\gamma\vartheta\rangle$ should be taken as it follows from the simulation because averaging over fluctuations then is a physical effect. The curves marked in Fig. 3 as ltp. (low-temperature phase) correspond to the case (i) and the curves htp. (high-temperature phase) to the treatment (ii). The susceptibility htp. becomes very high in

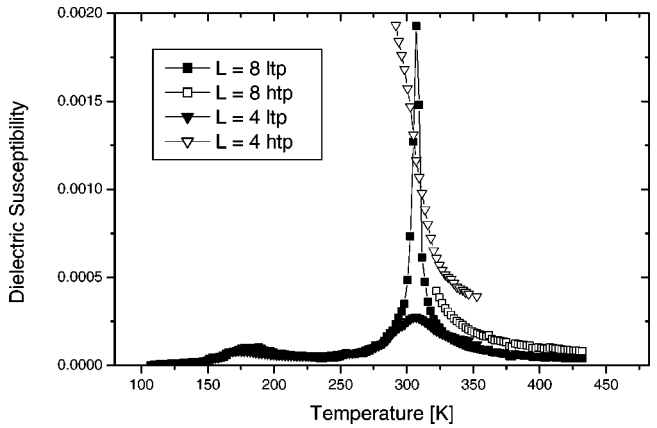

FIG. 3. Dielectric susceptibility in the present model of PMACB. ltp. (low-temperature phase), htp. (high-temperature phase). See text for precise meaning.

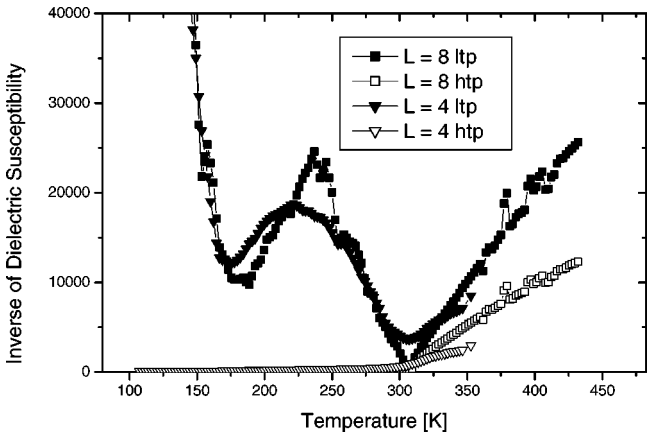

FIG. 4. Inverse of dielectric susceptibility of Fig. 3.

low temperatures so that the corresponding parts of the curves are not visualized in Fig. 3. The behavior of the curves ltp. and htp. shows a hysteresis: the maximum in the htp. curve lies lower than the maximum in the ltp. curve. Figure 3 shows that the hysteresis diminishes with increasing box size as it should be in a second-order phase transition. Of course, for comparison with experiment one should take those parts of htp. and ltp. curves that correspond to the phase actually existing in the given temperature. The general shape of the curve for $L=8$ fits well the measured static susceptibility.[16] A particularity of the dielectric results is the factor about -4 between the slopes of the temperature-dependent inverse susceptibilities below and above the ferroelectric phase transition at $T=307$ K.[6] Figure 4 shows the inverse of the susceptibility of Fig. 3. The interesting ratios fitted to the linear parts of the curves are equal -4.6 and -3.1 for $L=4$ and $L=8$, respectively.

IV. DISCUSSION

The results described in the previous section show that the Monte Carlo method is particularly well adapted for studies of isomorphous anomalies, where no infinite-range fluctuations develop. The results of simulations for PMACB near $T=180$ K agree with experiment even for relatively small sizes of the simulation box.

The upwards shift of the critical temperature as a result of the direct coupling with strain is a new effect which was not observed in a similar system, where the translational degrees of freedom were eliminated at the expense of introduction of four-body interactions.[17] This problem will be treated in more detail in future.

A precise distinction between the first- and second-order phase transition was not possible with the box sizes tractable in the present study. Much larger sizes would be needed to allow one to find the sharp dip in the temperature-dependent Binder cumulant U_L, which is a signature of the phase-equilibrium temperature.[18] However, we conclude on the second order of the phase transition in the present set of parameters on the basis of the narrowing hysteresis in the dielectric susceptibility.

The problem, whether a strictly continuous phase transition is at all possible in a model where the square of the order parameter is coupled with a strain, relates to an old hypothesis of fluctuation-induced first-order phase transition. It was shown by renomarlization-group methods that a first-order phase transition would occur in a simple cubic lattice in which the square of the Isinig-order parameter was coupled with isotropic volume expansion $\varepsilon_{11}+\varepsilon_{22}+\varepsilon_{33}$.[19] The phase transition then was of first order irrespective of the strength of the coupling except for some degenerate choices of the bare elastic constants. It seems that similar reasoning would produce analogous results in our case despite the different strain symmetry [Eq. (1)]. This is all the more plausible that a coupling of the square of the order parameter with an elongation ε_{11} [Ref. 20] resulted in a first-order phase transition for the parameters, which in the mean-field approximation would correspond to a tricritical point. The coupling constant J_1^{σ} resulting from the present study being smaller than the one obtained in the mean-field fit[5] corroborates this finding. The above short review of theoretical predictions contradicts numerous experimental results, which show a clear continuous phase transition with a well-determined coupling of the type discussed. The reason for the effective continuity of these phase transitions may lie in a suppression of the fluctuations by long-range interactions as indicated in Ref. 20. On the other hand the limitations of the present simulations may paradoxically correspond to the real experimental situation where smearing out of the phase transition eventually leading to an apparent continuity may be caused by structural imperfections, textures etc. Now a question arises whether a tricritical point can at all occur in the models discussed. This problem will be studied in future.

The present study confirms that the ratio of the Curie constants below and above the transition is markedly greater than 2. Although a very precise estimate cannot be reached with the box sizes applied, it is now clear that the model parameters deduced from those yielding the tricritical point in the mean-field approximation (see Sec. III) lead to similar effect of increasing this ratio. The existence of a sharp peak in the specific heat in addition to a step visible in Fig. 2 is one more evidence that the features found in the mean-field theory are rather inherent to the model than a result of the approximation although the peak is also predicted in fluctuation-induced first-order phase transition.[19,20] A possible nonexistence of the tricritical point in this kind of models indicates that ratios of the Curie constants different from 2 are not *a priori* excluded in the kinds of models.

APPENDIX

Consider a class of models with the third-order terms in expansion Eq. (8) vanishing as done in Sec. III. The set of displacements $u_{\kappa}=u_{\alpha i\gamma}$ in direction $\gamma=x,y,z$, of an atom at the ith site belonging to sublattice α will be abbreviated by vector $\vec{u}$. Then the energy of Eq. (2) can be written as a second-order polynomial in variables $\vec{u}$.

$$H=-\frac{1}{2}\{s_\alpha J_{0\alpha\alpha'}s_{\alpha'}+s_\alpha \vec{J}^{T}_{1\alpha\alpha'}s_{\alpha'}\vec{u}$$

$$+\vec{u}^{T}s_\alpha \overleftrightarrow{J}_{2\alpha\alpha'}s_{\alpha'}\vec{u}-\vec{u}^{T}\overleftrightarrow{K}\vec{u}\}. \quad \text{(A1)}$$

Here α and α' label the pseudospins; summation is understood over repeated indices. The quantities with an arrow are vectors, and with double arrows are matrices labeled with the index κ. The superscript T stands for matrix or vector transpose. It is clear from Eqs. (3), (7), and (8) that the elements of the matrices $\overleftrightarrow{J}_{2\alpha\alpha'}$ and $\overleftrightarrow{K}$ are proportional to the coefficients of second order in Eq. (8) and to the force constants of Eq. (3). Similarly the vector $\vec{J}_{1\alpha\alpha'}$ is proportional to the linear coefficients in Eq. (8).

$$H=-\frac{1}{2}\{s_\alpha J_{0\alpha\alpha'}s_{\alpha'}-(\vec{u}-\vec{u}_0)^{T}[\overleftrightarrow{K}-s_\alpha \overleftrightarrow{J}_{2\alpha\alpha'}s_{\alpha'}]$$

$$\times(\vec{u}-\vec{u}_0)+\vec{u}_0^{T}[\overleftrightarrow{K}-s_\alpha \overleftrightarrow{J}_{2\alpha\alpha'}s_{\alpha'}]\vec{u}_0\}. \quad \text{(A2)}$$

where

$$\vec{u}_0=[\overleftrightarrow{K}-s_\alpha \overleftrightarrow{J}_{2\alpha\alpha'}s_{\alpha'}]^{-1}s_\alpha \vec{J}_{1\alpha\alpha'}s_{\alpha'} \quad \text{(A3)}$$

The Boltzmann factor $\exp(-H/k_BT)$ then is a multidimensional Gaussian in variables $\vec{u}$ for every configuration s of the pseudospins. One can see that when the matrices $\overleftrightarrow{J}_{2\alpha\alpha'}$ and $\overleftrightarrow{K}$ are multiplied by a common factor and the vectors $\vec{J}_{1\alpha\alpha'}$ by the square root of this factor, then the width of the Gaussian will be multiplied by the same factor and the displacements $\vec{u}_0$ corresponding to the relaxed state at given configuration s will be multiplied by the square root. Consequently, the partition function $Z=\Sigma_s\int \exp(-H/k_BT)d\vec{u}$ will only change by a factor. Any average value of a product $\langle \Pi_\alpha s_\alpha\rangle$ representing dielectric properties of the material then will stay constant by such a transformation.

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[1] P. Carpentier, thesis, University of Lille I, France, 1995.
[2] J. Lefebvre, P. Carpentier, and R. Jakubas, Acta Crystallogr., Sect. B: Struct. Sci. **47**, 228 (1991).
[3] P. Carpentier, J. Lefebvre, and R. Jakubas, Acta Crystallogr., Sect. B: Struct. Sci. **51**, 167 (1995).
[4] R. Jakubas, P. Francois, and J. Lefebvre, Acta Phys. Pol. A **85**, 579 (1994).
[5] P. Carpentier, J. Lefebvre, R. Jakubas, W. Zając, and P. Zieliński, Phase Transitions **67**, 571 (1999).
[6] R. Jakubas, L. Sobczyk, and J. Lefebvre, Ferroelectrics **100**, 143 (1989).
[7] K.H. Michel and J. Naudts, Phys. Rev. Lett. **39**, 212 (1977); J. Chem. Phys. **67**, 547 (1977); K.H. Michel and J.M. Rowe, Phys. Rev. B **32**, 5818 (1985); K. Żabińska and P. Zieliński, Z. Phys. B: Condens. Matter **58**, 173 (1985).
[8] C.G.S. Cousins, J. Phys. C **11**, 4867 (1978); **11**, 4881 (1978); **15**, 1857 (1982).
[9] K. Binder, Z. Phys. B: Condens. Matter **43**, 119 (1981); Phys. Rev. Lett. **47**, 693 (1981).
[10] R. Jakubas, J. Lefebvre, H. Fontaine, and P. Franǫis, Solid State Commun. **81**, 515 (1992).
[11] J. Mróz and R. Jakubas, Ferroelectrics **118**, 29 (1991).
[12] P. Carpentier, P. Zieliński, J. Lefebvre, and R. Jakubas, Z. Phys. B: Condens. Matter **102**, 403 (1997).
[13] A.M. Ferrenberg and R.H. Swendsen, Comput. Phys. **1988**, 101.
[14] M.P. Seah, W.A. Dench, B. Gale, and T.E. Groves, J. Phys. E **21**, 351 (1988), and references given therein.
[15] B.A. Strukov, R. Poprawski, S.A. Taraskin, and J. Mróz, Phys. Status Solidi A **143**, K9 (1994).
[16] R. Jakubas and J. Lefebvre, Ferroelectrics **108**, 115 (1990).
[17] Z. Łodziana, W. Schranz, and A. Fuith, J. Phys.: Condens. Matter **11**, 2449 (1999).
[18] W. Janke in *Computer Simulation Studies in Condensed-Matter Physics*, edited by D.P. Landau, K.K. Mon, and H.-B. Schüttler (Springer, Berlin, 1994), Vol. VII, p. 29.
[19] D.J. Berman and B.I. Halperin, Phys. Rev. B **13**, 2145 (1976).
[20] A.P. Levanyk, S.M. Minyukov, and M. Vallade, J. Phys.: Condens. Matter **5**, 4419 (1993).