Multilevel genetic-algorithm optimization of the thermodynamic analysis of the incommensurate phase in ferroelectric $Sn_2P_2Se_6$

S. V. Berezovsky, V. Yu. Korda, and V. F. Klepikov*
Scientific and Technological Center of Electrophysics, National Academy of Sciences of Ukraine, 28 Chernyshevsky St., P.O. Box 8812, UA-61002 Kharkov, Ukraine

(Received 27 April 2000; revised manuscript received 9 February 2001; published 20 July 2001)

Interesting experimental properties of the incommensurate phase in ferroelectric $Sn_2P_2Se_6$ are explained in the framework of Landau-type phenomenological theory. The unique procedure of multilevel genetic-algorithm optimization is implemented to find parameters of the thermodynamic potential. It is shown that the temperature dependence of the polarization wave number in the incommensurate phase can be correctly described simultaneously with the anomalous heat capacity only when the nonlinear properties of the order parameter distribution are taken into account.

DOI: 10.1103/PhysRevB.64.064103 PACS number(s): 77.80.Bh, 61.44.Fw, 02.60.Pn, 64.70.Kb

I. INTRODUCTION

$Sn_2P_2Se_6$ ferroelectric is of great interest at the moment (see the review in Refs. 1 and 2 and references therein). It belongs to the family of $Sn_2P_2(Se_zS_{1-z})_6$ solid solutions for which the Lifshitz point[3] is not only predicted, but actually observed experimentally in the concentration diagram at the point $z=0.28$.

The incommensurate (IC) phase in uniaxial proper $Sn_2P_2Se_6$ ferroelectric appears under normal pressure at the temperature $T\equiv T_I=221\,\mathrm{K}$ as a result of the second-order phase transition from the high-temperature paraelectric state with $P2_1/c$ symmetry. The order parameter (OP) $\varphi(x)$ is one dimensional and corresponds to the component of the spontaneous polarization P. In the IC phase the polarization $P(x)$ is modulated along the wave vector $\mathbf{k}$ lying in the crystal symmetry plane perpendicular to the [010] axis. The long-period IC structure is 12–14 times larger than the initial crystal cell. With cooling, the modulation wave number $k=|\mathbf{k}|$ continuously decreases and abruptly becomes equal to zero at $T\equiv T_L\approx 193\,\mathrm{K}$. At this point, $Sn_2P_2Se_6$ undergoes a first-order phase transition into a ferroelectric (commensurate) state with Pc symmetry.

According to the classification introduced in Ref. 4, $Sn_2P_2Se_6$ belongs to the so-called type-II ferroelectrics for which the phenomenological approach[5,6] is applicable for theoretical description of the IC phase properties. Experiments show[7] that polarization modulation in $Sn_2P_2Se_6$ does not essentially differ from a sinusoidal one even in the vicinity of the phase transition from the IC into the commensurate (C) phase. That is why the one-harmonic approximation is widely used for a description of the OP spatial distribution[2,8–10]:

$$\varphi(x)=a\sin(bx). \tag{1}$$

At the same time, dielectric, birefringence, and dilation measurements clearly reveal an ''anomalous,'' from the viewpoint of one-harmonic predictions, low-temperature behavior of several important characteristics of the system (such as integrated satellite intensity, susceptibility, heat capacity, etc.), which seems quite natural because high harmonics are expected to manifest themselves near the lock-in transition. More peculiar is that the model (1), being applied to the full set of experimental data, fails to qualitatively predict the sign of the curvature of the temperature dependence of the wave number in the full range of IC phase stability.[10,11]

These data motivate one to question the applicability of one-harmonic approximation in the case under study. In our previous paper[12] we have developed a mathematical procedure which allows one to generate the families of nontrivial and essentially nonlinear spatial distributions of the OP in the IC phase. We have argued that in the case of type-II ferroelectrics, a more correct approximation for the equilibrium order parameter in the incommensurate phase is the elliptic Jacobi sinus

$$\varphi(x)=a\,\mathrm{sn}[bx,\mu],\quad 0\leqslant\mu^2\leqslant 1, \tag{2}$$

which gives a deeper global minimum to the thermodynamic potential (TP), as against the model (1).

In the framework of this approach,[12] high harmonics of the OP modulation are consistently taken into account and their contribution to various thermodynamic characteristics can be estimated.[12–14] One of the features of the model[12] is that, in comparison with the one-harmonic approach, the dependence of the wave number on temperature is unique (''nonlinear''). It is remarkable that these properties of the model (2) are generated by a single additional variation parameter μ, unlike the large set of additional optimization parameters arising when a harmonic series is used.[5] Therefore, we may hope that our model will succeed in describing the mentioned experimental anomalies.

Unfortunately, the model (2) does not allow one to estimate analytically the equilibrium parameters of the IC phase at arbitrary temperature (except for the limiting cases $\mu\rightarrow 0,1$). Thus, in Refs. 12–14, the grid method was applied for numerical minimization of the TP with respect to the model parameters a, b, and μ. In order to analyze the experimentally measured data for $Sn_2P_2Se_6$, we should additionally make an optimization of the TP parameters. So the general

optimization procedure becomes two level: for every trial set of TP parameters, we must find the equilibrium set of OP ones.

Therefore, in general, the parameter space of our problem is highly dimensional, highly nonlinear, and has unknown and unpredictable topography. The grid methods can explore an arbitrary search space with evidently arbitrary precision, but take for that eventually infinite time. The gradient methods are much quicker than the grid ones, but often become stuck in a local minimum. Besides, such methods can accumulate the errors of function evaluations because each new test point in the parameter space depends on the previous one. Random search methods are stable against the mentioned disadvantage and can ''hop'' from one minimum to another, but are very time intensive.

The approach proved to perform efficiently on such complicated problem spaces is a genetic algorithm (GA).[15–17] The GA treats the optimization problem as a selection of the fittest set of parameters under the optimization. But the GA does not simply use the Darwinian idea of biological evolution by the selection of the fittest: it even mimics the details of mechanisms via which that evolution occurs: the mutation and heredity. From the evolutionary point of view, the gradient methods of optimization are totally hereditive because each new function evaluation is wholly determined by the previous one. At the same time, random search approaches are absolutely mutative because any consequent function evaluations are totally independent. Following the biological example, the GA encapsulates mutation and heredity in a way which can be easily tuned to fit almost any optimization problem.[18–20]

GA's are best performing on problems which admit the use of a satisfactory solution instead of a perfect one because it cannot guarantee to produce the latter (the inherent nondeterminism of the GA itself). On the one hand, this is an advantage because the GA can quite quickly find a ''good'' solution where the traditional search for a perfect one would take years of computing time on a supercomputer. But on the other hand, this feature can substantially reduce the field of possible applications of GA's.

For instance, if the problem implies a multilevel optimization, where the results of optimization on the ith level are considered as input data for $(i+1)$th one (as in our case), then the errors of optimization will have a tendency to accumulate and the final result will be unpredictable. Unfortunately, such optimization problems are not rare. Describing the state or behavior of complex systems (industrial, physical, biological, social, etc.), we usually implement mathematical models which have a number of variation parameters. The search for solutions may appear to be so complicated that we will be forced to substitute the ''exact'' solution by the model one with its own set of optimization parameters (as in our case). Therefore, in order to predict and control such a complex system, we should carry out a multilevel optimization.

The situation can be partially improved by performing a set of optimization runs with different initial populations and different population sizes, but it is difficult to predict how many runs, generations, and individuals would be needed. Besides, one can combine GA's with gradient and other deterministic methods, but these hybrids are still more of an art than a science.

Therefore, application of the model (2) to the thermodynamic analysis of the IC phase in ferroelectric $Sn_2P_2Se_2$ faces the general problem of correct implementation of a multilevel GA optimization.

The structure of the present paper is as follows.

In Sec. II we briefly formulate the thermodynamic theory of structural phase transitions in ferroelectric $Sn_2P_2Se_6$. A detailed description of the unique multilevel GA scheme, without which the application of the model (2) to the analysis of experimental data would not be possible, is presented in Sec. III. Results and a discussion are given in Sec. IV. Conclusions are summarized in Sec. V.

II. PHENOMENOLOGICAL ANALYSIS OF THE INCOMMENSURATE PHASE IN $Sn_2P_2Se_6$

The phase transition sequence from disordered to IC and C states in $Sn_2P_2Se_6$ can be described in the framework of the phenomenological approach proposed in Refs. 5 and 6. The TP for type-II ferroelectrics has the form

$$\Phi=\frac{1}{L}\int_0^L\left[\frac{\xi}{2}(\varphi'')^2+\frac{\eta}{2}(\varphi\varphi')^2+\frac{\delta}{2}(\varphi')^2+\frac{\alpha}{2}\varphi^2+\frac{\beta_0}{4}\varphi^4+\frac{\gamma}{6}\varphi^6\right]dx, \tag{3}$$

where $\varphi(x)\equiv P(x)$ is the OP; $\varphi'(x)\equiv\partial\varphi/\partial x$. The OP is modulated along the Ox axis, and L is the crystal length in the Ox direction. The material parameters $\xi>0$, $\eta>0$, $\delta<0$, $\beta_0<0$, and $\gamma>0$ are not assumed to depend on the temperature T, but $\alpha=\alpha_T(T-T_0)$, where α_T and T_0 are some constants.

Analysis of the experimental data shows that in $Sn_2P_2Se_6$ the parameter β_0 must be negative, and the direct (virtual) phase transition from the paraelectric state into the C phase is to be of first order.[1] As a consequence, a positive φ^6 term should be added in the expression (3), providing global system stability.[6,21]

The stable IC phase originates from competition and compromise between the $(\varphi'')^2$, $\xi>0$, and $(\varphi')^2$, $\delta<0$, gradient invariants in Eq. (3).[5,21] The gradient term $(\varphi\varphi')^2$, $\eta>0$, provides coupling of the wave number k with the order parameter amplitude a and is of great importance when describing the temperature dependence of the wave number and the low-temperature behavior of susceptibility.[5,11,12] Moreover, in the case of $Sn_2P_2Se_6$ (as well as for $NaNO_2$), the $(\varphi\varphi')^2$ invariant causes the paraelectric-IC phase transition to be of second order, although a direct transition from the paraelectric to the ferroelectric state is of first order (remember $\beta_0<0$).[1,6,11]

Long-range elastic forces play an important role in structural phase transitions (see, e.g., Ref. 11 and references therein). Taking into account the elastic interactions leads to a simple renormalization of β_0 coefficient in Eq. (3):

$$\beta_0\rightarrow\beta. \tag{4}$$

Renormalization is different for homogeneous strain (the case of the C phase) and for inhomogeneous deformation (the case of the IC state). In the isotropic approximation, the difference (''gap'')

$$\Delta = \beta_{\rm inc} - \beta_{\rm com} \tag{5}$$

between the coefficient $\beta_{\rm inc}$ for the IC phase and the parameter $\beta_{\rm com}$ for the C state depends only on the electrostrictive constant, bulk, and shear elastic module.[9,11]

As mentioned in the Introduction, the description of the IC phase in type-II ferroelectrics requires taking into account the deviation of the OP modulation from the pure one-harmonic wave (1). A way to consider higher harmonics is proposed in Ref. 12. Detailed descriptions of this approach are given in Refs. 12–14 and 22. Here it is important to emphasize that the OP (2) is an approximate solution of the variational equation for the functional (3). Therefore, the amplitude *a*, coefficient *b*, and elliptic modulus μ in the formula (2) should be defined by minimizing the TP with respect to them.

Our analysis aims to search for the set of TP and equilibrium OP parameters which reproduce as good as possible the following experimentally measured data: the temperature range of the IC phase stability $\Delta T = T_I - T_L = 28\,{\rm K}$,[1] the temperature dependences of the OP and wave number k,[2,7] and the anomalous heat capacity $\Delta C_p = -T\partial^2\Phi/\partial T^2$.[1,8] As a first step in our study, we have decided to use the experimentally measured value of $\Delta C_p(T_I)$ because, first, this value is derived with high precision and, second, we would like to estimate the abilities of our approach to describe, at least, some anomalous data.

The search process consists of two levels. On the first of them, for the given set of TP parameters, we look for the set of equilibrium OP parameters *a*, *b*, and μ generating the global minimum of the function $\Phi_{\rm inc}$ which is the TP of the IC phase in the model (2).[12] On the second level, by varying the TP parameters we find their set (and the corresponding set of equilibrium OP parameters) which minimizes a χ magnitude in the form

$$\chi = \chi_{\Delta T} + \chi_k + \chi_{\Delta C_p}, \tag{6}$$

$$\chi_{\Delta T} = \left| \frac{\Phi_{\rm inc} - \Phi_{\rm com}}{\Phi_{\rm com}} \right|, \tag{7}$$

$$\chi_k = \frac{1}{N}\sum_{n=1}^{N} \chi_k^{(n)}, \quad \chi_k^{(n)} = \left| \frac{k_{\rm theor}(T_n) - k_{\rm expt}(T_n)}{k_{\rm expt}(T_n)} \right|, \tag{8}$$

$$\chi_{\Delta C_p} = \left| \frac{B_{\rm theor} - B_{\rm expt}}{B_{\rm expt}} \right|, \tag{9}$$

where $\Phi_{\rm com}$ is the TP of the C phase (see, e.g., Ref. 11), $k_{\rm theor}(T_n)$ and $k_{\rm expt}(T_n)$ are the calculated and measured wave numbers at the experimental temperature points T_n, and $B_{\rm theor}$ and $B_{\rm expt}$ are the theoretical and experimental values of the magnitude $B = \beta_{\rm inc} + \frac{2}{3}\eta k^2(T_I)$.[11] The magnitude B is correlated with the anomalous heat capacity in the IC phase at the point $T = T_I$: $\Delta C_{p,{\rm inc}}(T_I) = T_I \alpha_T^2/(3B)$. The value of B can be obtained from the experimental data;[1,8] in our calculations, it is used to characterize the quality of the theoretical description of ΔC_p.

The choice of the goodness-of-fit parameter χ in the form (6)–(9) is conditioned by the following two reasons. First, the linear dependence of χ on the values of $\Phi_{\rm inc}$, $k_{\rm theor}$, and $B_{\rm theor}$ makes the problem space smoother, which is important because this space has unpredictable topography. Second, the values of ΔT, $k_{\rm expt}$, and $B_{\rm expt}$ are measured with different techniques in separate experiments; thus, if we want all these data to be fitted simultaneously, we should add all χ magnitudes (7)–(9) together.

III. MULTILEVEL MODIFICATION OF THE GENETIC ALGORITHM

The essentials of the traditional GA are as follows. Every parameter under optimization is represented by a 16-bit string called a gene, so that the parameter range is divided into 2^{16} parts, which is usually sufficiently precise. A set of genes representing optimization parameters is called a genome (an individual). Selective quality of an individual is called fitness. The population consists of a fixed number of individuals. Evolution begins from the initial population filled with randomly chosen genomes. For each individual the function under optimization is evaluated and the fitness is attached. Two individuals (parents) are chosen randomly according to their fitnesses to produce offsprings. Mating of parents uses two key GA operators: the mutation and crossover. Mutation means the inversion of a gene's bits, while crossover is the exchange of portions of bits between offsprings. After replication, offsprings are tested to acquire fitness. If the given offspring has a better fitness than the worst individual in the population, then the latter is substituted by the former to keep the population size. Next, a pair of parents is chosen and so forth. The algorithm terminates when the best fitness of the population is found to be equal to the worst one so that no further improvement should be expected.

Implementation of the multilevel GA faces two general problems: (i) the inherent nondeterminism of the GA, meaning that using it we cannot count on obtaining a perfect solution, which may make the final result incorrect; (ii) the number of function evaluations increases approximately as n^l where n is the mean number of function evaluations on a single level and l is the number of optimization levels (if $n \sim 10^4$ and $l=2$, then we have to make $\sim 10^8$ function evaluations and application of the GA appears impractical).

To handle the problem (i), we have to take care of the so-called ''hamming cliffs'' phenomenon (see, e.g., Ref. 23), which is a characteristic feature of the binary encoding widely used in the majority of GA applications in natural sciences. The matter is that the configurations of bits of two randomly chosen nearest-neighbor integer numbers (genes, the values of which differ by unity) can appear so diverse that the transformation of them into each other can require a number of highly correlated bit inversions made simultaneously. To ameliorate this problem, gray codes are used. These have the (desirable) property that for any two adjacent

integers they differ by exactly 1 bit (so no hamming cliff exists). They do not have further potentially desirable properties such as that changing any single bit in a gray code produces an integer within some small distance from the original one, etc. In fact, there is no possible encoding which can possess this desired sort of property. To avoid the problem with hamming cliffs, so-called ''phenotypic mutation'' operators are also used. Mutation of integers is commonly done using uniformly or normally distributed changes in the integer domain, with various methods for preventing overflow from the boundaries of the finite integer domain of the problem.

To fix the problem with hamming cliffs within the raw binary codes, we have implemented a rebuilding of the binary configuration of a gene as a first stage of the mutation operation. The problem usually appears if the given gene has its n lowest bits as units or zeros so that the increase or decrease of the gene value by 1 takes $(n+1)$-bit inversions made at once. Thus, before the conventional inversion of bits, it is worthwhile randomly shifting the value of gene by -1, 0, and $+1$. Our comparative tests on the minimization of simple functions show that the binary code with corrected mutation procedure improves the gray code for small populations and maintains its performance for large ones.

In order to efficiently deal with the problem (ii), we have to find a way of reducing the number of function evaluations needed on a single level of optimization. In other words, we should optimize the basic GA parameters and operators with respect to the number of function evaluations, keeping the quality of optimization along with that.

Mutation is a major GA operator making the evolution possible. Without crossover the GA usually works well, but without mutation it does not work at all. The frequency of mutation determines the degree of inheritance: if it is too high, the heredity is almost absent and the GA becomes one of the stochastic methods; if it is too low, the heredity is almost total and the GA appears to be one of the deterministic approaches. The maximum speed of evolution (minimum number of function evaluations) occurs when the frequency of mutation acquires some optimum value at the middle. This value cannot be estimated in general for any problem. Hence we treat it as a parameter under optimization, as well as we do with the problem parameters.

In our approach the frequency of mutation is implemented as a number of replicated genes, one of which, on average, has only 1 bit flipped. That number is allowed to be a gene having an initial value of 1 (every gene in the genome would be changed). During replication, the mutation genes of the parent and its offspring are randomly changed by -1, 0, and $+1$. Efficiency of the approach is conditioned by the following two advantages.

(a) For real problems it is impossible to predict the optimum population size. Thus we should admit that it is always smaller than the optimum one. If the frequency of mutation is low and constant, then the actual search space is strongly reduced. On the contrary, if the frequency of mutation is floating, then its high value at the initial stage of evolution, where the pressure of selection is weak yet, allows one to explore the whole search space, while its low value at the final stage, where the pressure of selection is very strong, gives an opportunity to approach the minimum close enough.

(b) Real problem spaces are usually highly dimensional and have complex landscapes. Efficient exploration of such spaces implies that the GA is able to change a number of optimization parameters at once. If the frequency of mutation is low, then the probability of simultaneous bit inversions in several genes is very small. On the contrary, a high frequency of mutation automatically guarantees a multipoint mutation event.

Unfortunately, the higher mutation rate, the smaller number of offsprings survives. To minimize harmful consequences of highly inexact replication, we have modified the bit inversion procedure itself. Traditional mutation operation assumes that the probability of inversion of a bit in a gene is distributed uniformly, so that the probability of a drastic change is equal to the probability of a slight one. By altering the shape of that distribution, we can, in principle, decrease the probability of lethal changes even if the mutation rate in the genome is very high. In biological genetics a similar alteration is called degeneracy of the genetic code and leads to similar results.[24] It is impossible to calculate or predict the distribution in closed form. Therefore, we introduce 16-bit-inversion-weight genes (one gene for every bit in a 16-bit string). These genes are incorporated in a genome and treated as optimization parameters as the problem parameters are. The initial values of the weight genes provide a uniform distribution of the mutation probability in a gene. Our experiments show that under a high frequency of mutation the weight genes rapidly adapt and the final number of function evaluations substantially reduces. In other words, we observe a dynamic degeneration of the binary code, meaning that during evolution the magnitude of changes caused by mutations substantially decreases. As we have mentioned above, there is no possible encoding which possesses the property that changing any single bit in a code produces an integer within some small distance from the original one. But now we see that the binary, gray, or any other possible encodings, being equipped with the dynamic degeneration technique proposed, acquire that property.

Crossover is a GA operator which is usually considered to improve the convergence of algorithm, i.e., to reduce the number of function evaluations. However, investigating the joint action of the new mutation operator described above and the traditional crossover procedure, we have found the latter not improving the convergence, but even making it worse. The following reason for this is possible. In biology, crossing over does not change genes: it only makes different versions of the same gene able to replace each other (to drift) in the population. The existence of a gene as a self-replicative unit of selection is possible just because crossing over does not destroy its internal structure. (More precisely, the probability of cutting the gene by crossover is very small because the mean distance between genes substantially exceeds the mean length of gene itself.) On the contrary, in the GA crossover always changes the gene value: thus, it can be treated as a special kind of mutation. Since the frequency of mutation in our approach is much higher than that in the traditional GA, the crossover-caused ''mutation'' additionally

increases the actual frequency of mutation, making it higher than the optimum one and therefore decreasing the number of offsprings surviving. Hence we do not use the crossover operator in our approach.

Further reduction of the number of function evaluations is conditioned only by the decrease of the population size. The smaller population size, the faster evolution and, unfortunately, the higher error percentage along with that.

In our problem, on the first level of optimization we derive the set of equilibrium OP parameters which gives the global minimum to $\Phi_{\rm inc}$. On the second level, the temperature T_L of the IC-C phase transition is obtained as a point of the closest approach of $\Phi_{\rm inc}$ and $\Phi_{\rm com}$. If $T>T_L$, then $\Phi_{\rm com}>\Phi_{\rm inc}$, but when $T<T_L$, then $\Phi_{\rm com}<\Phi_{\rm inc}$. The error on the first level means that the derived $\Phi_{\rm inc}$ is greater than the equilibrium one. When this error occurs at $T<T_L$, it has no harmful consequences, but if it happens at $T>T_L$, the $\Phi_{\rm inc}$ value becomes wrongly closer to $\Phi_{\rm com}$, $\chi_{\Delta T}$, Eq. (7) becomes mistakenly small and, as a result, the evolution becomes infinite. Similar problems arise when calculating χ_k, Eq. (8).

To find and fix errors automatically, we have devised the following very simple algorithm. If on the second level of optimization the parent and its offspring are clones (all TP genes match), they must be clones on the first level too (all OP genes must match). If this requirement is not fulfilled, then the OP genes corresponding to higher $\Phi_{\rm inc}$ are substituted by the ones generating lower $\Phi_{\rm inc}$. This recipe is used to correct calculations of both the temperature range of the IC phase and the values of wave numbers at experimental temperatures. In our experiments this algorithm has shown excellent performance (convergence) even under conditions when the percentage of the first-level unsuccessful runs is close to 50% regardless of the magnitude of the deviation from the true minimum. This observation has allowed us to substantially reduce the population size and, consequently, to additionally shorten the number of function evaluations. The error correction procedure proposed is a quite general and easily applicable key operator of any multilevel GA implementation.

IV. ANALYSIS OF EXPERIMENTAL DATA FOR $Sn_2P_2Se_6$: RESULTS AND DISCUSSION

In this section we apply the developed technique to reproduce the temperature dependences of the OP $\varphi(x)$ and wave number k, and the anomalous heat capacity $\Delta C_p(T_I)$ for ferroelectric $Sn_2P_2Se_6$.

It should be noted that critical fluctuations are not taken into account in the theory under consideration. It means that phenomena which have a fluctuation nature (such as nonzero values of ΔC_p in the paraelectric state in a close vicinity of the point of the transition into the IC phase) will not be discussed.

To calculate the thermodynamic characteristics of $Sn_2P_2Se_6$ in the IC phase, we must know the values of the TP parameters α_T, T_0, $\beta_{\rm com}$, Δ, γ, δ, ξ, and η. Some of these magnitudes can be found from analysis of the $Sn_2P_2Se_6$ behavior in the paraelectric or ferroelectric state[8,25]: $\alpha_T=1.6\times10^6\ \mathrm{J\,m\,C^{-2}\,K^{-1}}$, $\gamma=8.5\times10^{10}\ \mathrm{J\,m^9\,C^{-6}}$, $\beta_{\rm com}=-4.8\times10^8\ \mathrm{J\,m^5\,C^{-4}}$, and $\Delta=1.7\times10^8\ \mathrm{J\,m^5\,C^{-4}}$. The others, i.e., δ, ξ, and η, should be optimized. Note that the procedure of extracting $\beta_{\rm com}$ in Refs. 8 and 25 is not quite reliable; thus, we have decided to vary $\beta_{\rm com}$ as well. When the values of δ and ξ are known, the parameter T_0 is given by the relation

$$T_0=T_I-\frac{\delta^2}{4\xi\alpha_T} \tag{10}$$

This formula follows from the expression for effective temperature of the paraelectric-IC phase transition $\alpha_I\equiv\alpha(T_I)=\frac{1}{4}\delta^2/\xi$.[12]

The results of optimization are as follows: $\xi=2.35\times10^{-29}\pm1.53\times10^{-34}\ \mathrm{J\,m^5\,C^{-2}}$, $\eta=2.30\times10^{-9}\pm1.53\times10^{-14}\ \mathrm{J\,m^7\,C^{-4}}$, $\delta=-4.52\times10^{-11}\pm1.53\times10^{-16}\ \mathrm{J\,m^3\,C^{-2}}$, $\beta_{\rm com}=-4.43\times10^8\pm1.53\times10^{-3}\ \mathrm{J\,m^5\,C^{-4}}$. The temperature T_0 is equal to 207.4 K. The quality of the fit is $\chi_{\Delta T}=10^{-7}$, $\chi_k=9.4\times10^{-3}$, $\chi_{\Delta C_p}=3.1\times10^{-7}$, and $\chi=9.4\times10^{-3}$.

The errors in the fitted parameters are determined by dividing the range of variation of a given parameter by the number of grid points, which is equal to $2^{16}=65\,536$ (for the 16-bit genes).

We see that χ_k dominates the goodness-of-fit parameter χ. The following reasons for that are possible. First, the values of ΔT and $B_{\rm expt}$ are extracted in Refs. 1 and 8 with high precision, while the values of $k_{\rm expt}$ are measured in Refs. 2 and 7 with an average error per point up to 10%. Second, this fact can appear as the feature of our model (2) (note the twist of the solid curve in Fig. 2), which needs further investigation.

In order to estimate the reasonableness of the fit, we should note that the values of parameters found are typical of type-II ferroelectrics TP's which contain a φ^6 term.[11] Alongside with that, we should emphasize the substantial differences between our parameters and those obtained in Refs. 8 and 25 and further used in Ref. 10 for the attempt to describe the full set of data on ferroelectric $Sn_2P_2Se_6$: $\xi=4.4\times10^{-27}\ \mathrm{J\,m^5\,C^{-2}}$, $\eta=1.2\times10^{-8}\ \mathrm{J\,m^7\,C^{-4}}$, and $\delta=-4.0\times10^{-10}\ \mathrm{J\,m^3\,C^{-2}}$. The origin of this discrepancy is the following. The experimental data on the temperature behavior of the modulation wave number in the full range of stability of the IC phase, used in our study, are more up to date.[2,7] In determining the temperature range of the existence of the IC phase ΔT, we have not used any additional simplifying assumptions. In particular, unlike Refs. 8 and 25, we have not suggested the validity of the one-harmonic approximation in the full range of the IC phase and in the vicinity of the transition point to the ferroelectric state as well.

Figure 1 shows the spontaneous polarization P_0 in the ferroelectric state and the amplitude $|P_k|$ of the first Fourier harmonic of the OP modulation wave. The magnitude $|P_k|$ is expressed through the OP amplitude a in Eqs. (1) and (2) by the formula $|P_k|=\frac{1}{2}a$. At the lock-in transition point, the elliptic modulus is $\mu_L\equiv\mu(T_L)=0.755$. Using the technique described in Refs. 14 and 22, we find that for such μ_L the ratio of the amplitude $|P_{3k}|$ ($|P_{5k}|$) of the third (fifth) harmonic to the fundamental harmonic $|P_k|$ is $|P_{3k}|/|P_k|$

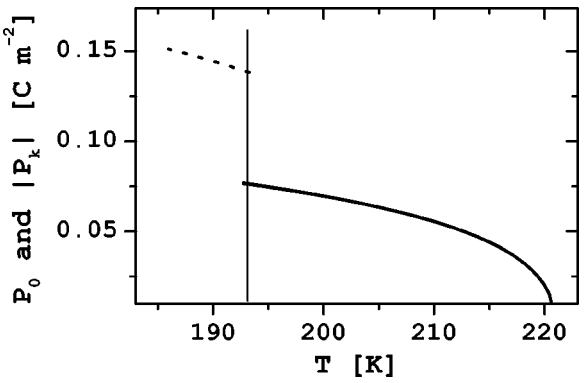

FIG. 1. Temperature dependences of the spontaneous polarization P_0 in the polar state (dotted curve) and the amplitude $|P_k|$ of the first harmonic of the order parameter $\varphi(x)$ in the IC phase for the models (2) and (1) (solid and dashed curves, respectively; they lie very close to each other). The vertical line indicates the location of the lock-in transition.

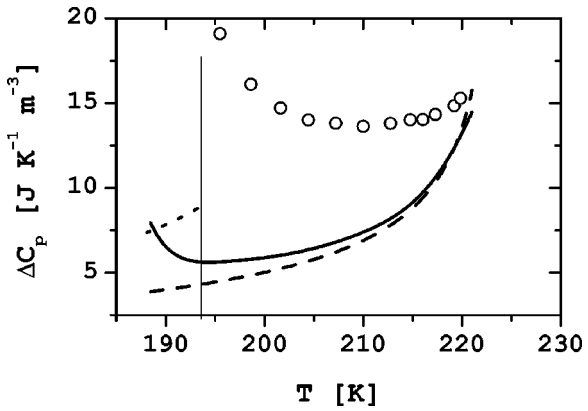

FIG. 3. Anomalous heat capacity ΔC_p as a function of temperature. The solid curve is for the model (2), the dashed curve is for the approach (1), and the dotted curve is calculated for the commensurate phase. The vertical line indicates the location of the lock-in transition. Experimental data are from Ref. 26.

$=0.05$ ($|P_{5k}|/|P_k|=0.0026$). These results are in good agreement with experimental data.[1,2,7]

The temperature dependence of wave number k is presented in Fig. 2. According to recent neutron scattering experiments,[2] the average error per experimental point of the measurements of wave number $k(T)$ is about 10%. Bearing this in mind, we may state that the model (2) reproduces the temperature behavior of the wave number in $Sn_2P_2Se_6$ very well.

In the proximity of the paraelectric-IC phase transition point ($T\approx 218-221$ K), model (2) is close to the one-harmonic approach (1) (the upper part of the dashed curve in Fig. 2). With cooling, the ''nonlinear'' mechanism becomes dominating in the wave number behavior (the lower part of the solid curve in Fig. 2), which leads to qualitative and quantitative fit of experimental data.

The mentioned ''nonlinearity'' in the wave number behavior[12,13] means that the modulation period of the function (2) is $P=4K(\mu)/b$, where $K(\mu)$ is the complete elliptic integral of the first type. Hence the period P and the wave number $k=2\pi/P$ depend not only on the coefficient b, but also on the elliptic modulus μ which controls the power of nonlinearity of the modulation wave (2). The result of such a control is clearly seen in Fig. 2 (just compare the dotted line for b and the solid one for k): in spite of the small nonlinear contribution to the OP structure ($|P_{3k}|/|P_k|$), the consequences of this contribution to the $k(T)$ dependence should be admitted as being essential.

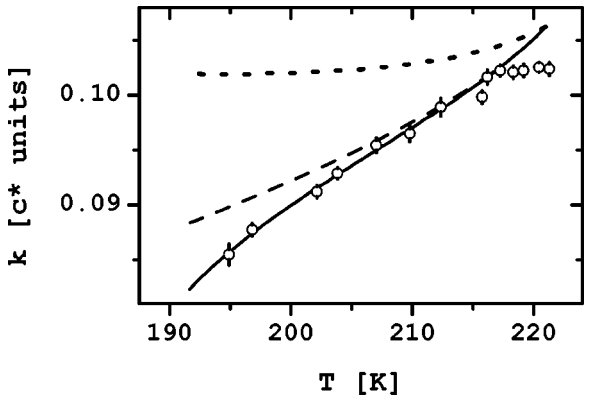

FIG. 2. Temperature dependence of the wave number k of the order parameter $\varphi(x)$ in the IC phase. The solid curve is for the model (2), while the dashed one corresponds to the approach (1). The dotted curve depicts the temperature behavior of the coefficient b in the expression (2). $\mathbf{c}^*$ is the reciprocal lattice vector along the modulation direction, $c^*=2\pi\times 0.1469\times 10^{10}\ \mathrm{m}^{-1}$ (Ref. 2). Experimental data are from Ref. 7.

It is remarkable that the curvature of the wave number k in model (2) changes its sign within the range of the IC phase stability. Usually, the experimental temperature dependence of the wave number is assumed to be purely convex. The one-harmonic approximation (1) gives a wrong curvature for the $k(T)$ function.[8,10,25] Note that an analogous result is also obtained for sodium nitrite $NaNO_2$ for which the TP has the same form as for $Sn_2P_2Se_6$.[11]

In the model (2) (as well as in the one-harmonic approximation), there exist such sets of material parameters which provide convex behavior of the wave number. However, the values of the anomalous heat capacity at $T=T_I$ calculated for these sets appear to be far away from the experimentally observed ones. We still do not know of any investigations in which important characteristics such as wave number and anomalous heat capacity are simultaneously correctly described in the framework of a model having only one additional fitting parameter as compared to the one-harmonic approximation.

The nonlinear contribution also improves the description of the $\Delta C_p(T)$ behavior, particularly at the low-temperature boundary of the IC phase (Fig. 3). Unfortunately, the tendency of ΔC_p to increase with cooling is reproduced only partially, and the absolute values of ΔC_p in the vicinity of lock-in transition point T_L are still smaller than the experimental ones.[26] However, an appropriate behavior is observed somewhat lower than T_L (solid line in Fig. 3). A possible mechanism which can ''shift'' the theoretical region where ΔC_p increases inside the region of the IC phase and, hence,

provides a more correct description of the experimental data is the temperature dependence of material parameter δ.[27,28] Remember that in the model given by Eqs. (2) and (3) the parameter δ does not depend on the temperature.

V. CONCLUSIONS

In the present paper we have made the first step in applying the phenomenological model described by Eqs. (2) and (3) (Ref. 12) to explain some interesting experimental data for ferroelectric $Sn_2P_2Se_6$ in the IC phase.

While implementing the genetic algorithm we have proposed a simple way to avoid the ''hamming cliffs'' effect, simulated the dynamic degeneracy of the binary code to reduce the number of function evaluations, and devised an error correction algorithm which makes the multilevel genetic optimization possible. The developed GA technique was originally suited for parallel computation, but it has appeared so powerful that it can be successfully used on a single sequential processor as well.

We have found a set of material parameters which allows the order parameter $\varphi(x)$, the wave number $k(T)$, and the anomalous heat capacity $\Delta C_p(T_I)$ to be well reproduced.

Our analysis shows that for $Sn_2P_2Se_6$ (and plausibly for $NaNO_2$, whose TP has the same structure) the role of nonlinear effects is more important than it is usually thought. The TP for these systems contains a φ^6 invariant, making them strongly nonlinear. As a consequence, the temperature dependence of the wave number in the IC phase cannot be correctly described simultaneously with the anomalous heat capacity without taking into account nonlinear properties of the IC order parameter. At the same time the contribution of higher harmonics to the modulation wave $\varphi(x)$ is relatively small.

Surely, to make the role of nonlinear phenomena in the $Sn_2P_2Se_6$ thermodynamics more illuminated one should take into consideration all experimentally measured points of ΔC_p and investigate the behavior of other important characteristics, such as the susceptibility. However, the susceptibility properties are not discussed in this paper because the present model should be modified for their correct description. Generally speaking, such a modification requires one to find nonlinear OP configurations corresponding to the equilibrium state in the presence of an external electric field. But this study is beyond the scope of the current paper.

ACKNOWLEDGMENT

The authors are deeply indebted to Y. M. Vysochanskii for stimulating discussions and the opportunity to read some of his results before publication.

*Electronic address: ipct@pem.kharkov.ua

[1] Yu. M. Vysochanskii and V. Yu. Slivka, Usp. Fiz. Nauk **162**, 139 (1992) [Sov. Phys. Usp. **35**, 123 (1992)].
[2] S. W. H. Eijt, R. Currat, J. E. Lorenzo, P. Saint-Grégoire, S. Katano, T. Janssen, B. Hennion, and Yu. M. Vysochanskii, J. Phys.: Condens. Matter **10**, 4811 (1998).
[3] R. M. Hornreich, M. Luban, and S. Shtrikman, Phys. Rev. Lett. **35**, 1678 (1975).
[4] A. D. Bruce, R. A. Cowley, and A. F. Murrey, J. Phys. C **11**, 3591 (1978).
[5] Y. Ishibashi and H. Shiba, J. Phys. Soc. Jpn. **45**, 409 (1978).
[6] Y. Ishibashi, W. Buchheit, and J. Peterson, Solid State Commun. **38**, 1277 (1981).
[7] T. K. Barsamian, S. S. Khasanov, and V. Sh. Shekhtman, Ferroelectrics **138**, 63 (1993).
[8] Yu. M. Vysochanskii, M. M. Major, V. M. Rizak, V. Yu. Slivka, and M. M. Khoma, Zh. Eksp. Teor. Fiz. **95**, 1355 (1989) [Sov. Phys. JETP **68**, 782 (1989)].
[9] Yu. M. Vysochanskii, M. M. Khoma, and A. A. Molnar, Ferroelectrics **191**, 231 (1997).
[10] M. M. Khoma, A. A. Molnar, and Yu. M. Vysochanskii, J. Phys. Stud. **2**, 524 (1998).
[11] K. Ema, K. Hamano, and A. P. Levanyuk, J. Phys. Soc. Jpn. **59**, 1438 (1990).
[12] S. V. Berezovsky, V. F. Klepikov, V. Yu. Korda, and N. A. Shlyakhov, Int. J. Mod. Phys. B **12**, 433 (1998).
[13] S. V. Berezovsky, V. F. Klepikov, and Yu. V. Sereda, J. Phys. Stud. **2**, 518 (1998).
[14] S. V. Berezovsky, cond-mat/9909079 (unpublished).
[15] J. H. Holland, *Adaptation in Natural and Artificial Systems* (The University of Michigan Press, Ann Arbor, 1975).
[16] D. E. Goldberg, *Genetic Algorithms in Search, Optimization and Machine Learning* (Addison-Wesley, Reading, MA, 1989).
[17] Z. Michalewicz, *Genetic Algorithms+Data Structures=Evolution Programs* (Springer-Verlag, Berlin, 1994).
[18] J. R. Morris, D. M. Deaven, and K. M. Ho, Phys. Rev. B **53**, R1740 (1996).
[19] K. Michaelian, Rev. Mex. Fis. **42**, 203 (1996).
[20] C. Winkler and H. M. Hofmann, Phys. Rev. C **55**, 684 (1997).
[21] J. C. Tolédano and P. Tolédano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987).
[22] S. V. Berezovsky and V. F. Klepikov, J. Phys.: Condens. Matter **12**, 311 (2000).
[23] N. N. Schraudolph and R. K. Belew, Mach. Learn. **12**, 9 (1992).
[24] M. Yčas, *The Biological Code* (North-Holland, Amsterdam, 1969).
[25] Yu. M. Vysochanskii, M. M. Maior, V. M. Rizak, S. I. Perechenskii, V. Yu. Slivka, and M. M. Khoma, Izv. Akad. Nauk SSSR, Ser. Fiz. **54**, 677 (1990).
[26] K. Moriya, H. Kuniyoshi, K. Tashita, Y. Ozaki, S. Yano, and T. Matsuo, J. Phys. Soc. Jpn. **67**, 3505 (1998).
[27] D. G. Sannikov and G. Schaack, J. Phys.: Condens. Matter **10**, 1803 (1998).
[28] J. Hlinka, M. Iwata, and Y. Ishibashi, J. Phys. Soc. Jpn. **68**, 126 (1999).