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# ORDER–DISORDER TRANSITIONS IN IONIC CRYSTALS CONTAINING REORIENTABLE DIPOLES

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The dielectric properties of a crystal made of several interpenetrating lattices of ions and reorientable permanent point dipoles are investigated. The ions and dipoles are both assumed to be polarizable. A set of functions $n_i$ is introduced to describe the orientational disordering of the permanent dipoles. The electrostatic internal energy is calculated in the mean-field approximation, and from it the free energy is obtained in terms of the $n_i$'s. A transcendental system of equations for the latter is derived, from which the equilibrium configuration as a function of $T$ can be found by numerical computation. The model predicts the possible occurrence of an ordered phase (which may be ferro-, antiferro- or ferri-electric) and a disordered, para-electric phase. The electric susceptibility, specific heat and other quantities of interest are evaluated as functions of $T$. The formalism is applied to several simple tetragonal structures. In each case a ferro- or antiferro- to para-electric transition is found, the Curie temperature is evaluated and some interesting features of the model are discussed.

## 1. Introduction

The first mechanism to be proposed in order to explain a ferro- to para-electric phase transition was the disordering of the dipole moments of the water molecules[1]) (this model was applied to the Rochelle salt). Later on, this mechanism was largely forsaken, as increasing experimental evidence showed that in most ferroelectrics the transition was due either to the relative displacement of differently charged sublattices or to the disordering of protons in the double-well potential of hydrogen bonds.

However, it has been established that the ferroelectric behaviour of $NaNO_2$ is due to the ordering of the dipole moments associated with the nitrite groups (see, for instance, ref. 2), and a recent calculation[3]) has supported the conclusions of earlier authors[4,5]) about the fact that the ferroelectricity of $K_4Fe(CN)_6 \cdot 3H_2O$ is due to co-operative reorientations of the water molecules. In other ferroelectrics too (such as the hydrogen halides) the transition might be discussed in terms of the disordering of permanent dipoles. For this reason we believe that it is worthwhile to investigate from a statistical point

of view the behaviour of a crystal containing one or more sublattices of reorientable dipoles, in order to see under which conditions it may be para-, ferro- or antiferro-electric.

The problem was recently treated by Biemond et al.[6]), by making series expansions in terms of the dipole polarizability. This formalism, however, is not well-suited for investigating solid–solid phase transitions, because the convergence of the series is good only at high temperatures, as stated in ref. 6. In this paper, following Takagi[7]), we will proceed according to a different approach. This author considered a crystal made of two simple cubic interpenetrating lattices, one with ions and the other with reorientable point dipoles. The dipole lattice was split into two tetragonal sublattices because in the limiting case of vanishing ionic charge, at low temperature the antiferroelectric ordering is more stable than the ferroelectric one. Both the ions and the dipoles were considered as polarizable, i.e. were assumed to acquire an induced dipole moment if the local field at their site was different from zero. It was found that such a crystal undergoes a transition from an ordered configuration, which is ferro- or antiferro-electric according to the values of the polarizabilities, to a disordered, paraelectric configuration.

In this paper we consider a crystal made of an arbitrary number of different reorientable dipole sublattices, with arbitrary dipole moments and charges. The crystal symmetry and the relative location of any two sublattices are also arbitrary. All the sublattices are assumed to be rigid. Both the permanent dipoles and the ions are assumed to be isotropically polarizable.

Our model generalizes that of Takagi in several aspects that are relevant from the point of view of ferroelectricity. First of all, any dipole sublattice can have an arbitrary orientation, while in ref. 7 only polarization in the $\pm z$ direction was considered. Secondly, as the physical properties (ferro- or antiferro-electric character of the transition, Curie temperature, etc.) of the system depend, among other things, on the Lorentz factors of the lattice sites, it is important to extend the formalism to non-cubic structures (as will be seen in section 4, for a tetragonal crystal the polarization properties depend, both quantitatively and qualitatively, on the Lorentz factors, i.e. on the ratio $c/a$). Thirdly, by considering an arbitrary number of dipole sublattices we are able to investigate the possible occurrence of ferro-, antiferro-, and also ferri-electric ordering. Finally, the ionic sub-lattices can create a permanent local field at the dipole sites, which plays an important role in the ordering of the dipoles (see, for instance, ref. 3).

In our model of the crystal, at 0 K all the dipoles are oriented and they, as well as the ions, acquire an induced moment in such a way as to minimize the total electrostatic energy. As the temperature is increased the dipoles are

disordered with respect to their equilibrium positions. The average value of the polarization is thereby decreased, so that the local field at each lattice site is modified and the average orientations and induced moments are also affected. For $T \neq 0$ K the new equilibrium position is attained when the free energy is at a minimum. Depending on the type of crystal under consideration, it may occur that at a given temperature the dipoles are totally or partially disordered*, or that a new type of ordering sets in.

In order to find the configuration with the least free energy we introduce a distribution function $n_i(\theta, \phi)$ giving the fraction of the dipoles of the sublattice $i$ which are pointing in the $(\theta, \phi)$ direction; we then find the particular set of functions $n_i(\theta, \phi)$ that minimize $F$ by a variational technique, as in ref. 7.

In section 2 we describe our model and develop its formalism, calculating the free energy $F$ and the net polarization $\boldsymbol{P}$ as functions of the temperature. In section 3 we evaluate some properties of the model, such as the dielectric susceptibility, specific heat and pyroelectric coefficient. In section 4 we apply our results to several tetragonal structures and investigate their dielectric properties.

## 2. General formalism

The ideal crystal we are considering is made of $N$ interpenetrating Bravais lattices. To each point of the lattice $i$ a point charge distribution is attached having an electric charge $q_i$, a permanent dipole moment $\mu_i$ and an isotropical polarizability $\alpha_i (i = 1, \ldots, N)$. All the polarizabilities are assumed to be constant, i.e. the induced moments depend linearly on the local field. In most real cases, for each sublattice either $\mu_i$ or $q_i$ is zero (however, in $NaNO_2$ the nitrite group has $q = -e$ and $\mu \neq 0$). Let there be $N_p$ dipolar sublattices (corresponding to distributions with $\mu_i \neq 0$, $i = 1, \ldots, N_p$) and $N_q$ ionic sublattices (corresponding to distributions with $\mu_i = 0$, $i = N_p + 1, \ldots, N_p + N_q$). Let $v_i$ be the volume of the unit cell $i$.

At $T = 0$ K all the dipoles on each sublattice are fixed, equal in magnitude and parallel to each other. As $T$ increases, thermal agitation introduces a certain degree of disordering in each sublattice, so that at any instant any individual dipole deviates from its average position in a random way. Let us describe the effect of this disorder on the permanent dipoles by a set of functions $n_i(\theta, \phi)$ $(i = 1, \ldots, N_p)$ such that the probability for any permanent dipole moment of the sublattice $i$ of pointing in the solid angle $(\omega, \omega + d\omega)$ is

* It must be noticed that a ferro- to para-electric transition does not imply the disordering of all the dipoles (or of all their components) of the crystal, but only of some of them, having two (or more) equilibrium positions, between which they can be switched by an external field.

$n_i(\omega)\,\mathrm{d}\omega$. The functions $n_i$ must of course satisfy the condition

$$\int n_i(\omega)\,\mathrm{d}\omega = 1, \quad i = 1, \ldots, N_p. \tag{1}$$

The contribution to the $\beta$-component of the dipole moment due to the permanent moment $\mu_i$ is therefore given by

$$p_{i;\beta}^{\mathrm{perm}} = \mu_i \int c_\beta(\omega) n_i(\omega)\,\mathrm{d}\omega, \quad 1, \ldots, N_p, \tag{2}$$

where $c_\beta(\omega)$ is the cosine of the angle between the direction determined by $\omega$ and the $\beta$ axis. Here and in the following, the Latin subindices refer to sublattices and the Greek ones to cartesian components.

The part of the dipole moment induced by the local field $\boldsymbol{F}_i$ is

$$\boldsymbol{p}_i^{\mathrm{ind}} = \epsilon_0 \alpha_i \boldsymbol{F}_i. \tag{3}$$

This equation applies also to the ions, so that it holds for $i = 1, \ldots, N$. The total dipole moment on the sublattice $i$ is of course

$$\boldsymbol{p}_i = \boldsymbol{p}_i^{\mathrm{perm}} + \boldsymbol{p}_i^{\mathrm{ind}}, \tag{4}$$

where $\boldsymbol{p}_i^{\mathrm{perm}} = 0$ if $i > N_p$.

The local field components at the sites of the sublattice $i$ are given by

$$F_{i;\beta} = E_\beta^{\mathrm{ext}} + E_{i;\beta}^q + E_{i;\beta}^p. \tag{5}$$

Here, $\boldsymbol{E}^{\mathrm{ext}}$ is the external field, while $\boldsymbol{E}_i^q$ and $\boldsymbol{E}_i^p$ are the contributions to the field at the sublattice $i$ from the charges and dipole moments present in the crystal:

$$E_{i;\beta}^q = \sum_{j=1}^{N} E_{ij;\beta}^q \tag{6}$$

and

$$E_{i;\beta}^p = \sum_{j=1}^{N} E_{ij;\beta}^p \tag{7}$$

Now, the orientations and magnitudes of the local field at all the sites and of the moments (both the permanent and the induced ones) are inextricably interrelated; in fact, the local field depends on the dipole moments present in the crystal, while the latter depend on the field both via the torque exerted by it on the permanent dipoles and via the polarizabilities. Due to the thermal agitation the instantaneous value of each one of the above magnitudes fluctuates about its average; therefore, an exact calculation of the l.h.s. of (6) and (7) is out of question. Following Takagi[7]), we will calculate them in the mean-field approximation. So, we assume that the fields at all the lattice sites

are equal to their respective average values. This implies that in calculating them we must also take all the permanent and induced dipole moments as equal to their respective average values. The values of $\boldsymbol{E}_i^q$, $\boldsymbol{E}_i^p$, $\boldsymbol{p}_i^{\text{perm}}$, $\boldsymbol{p}_i^{\text{ind}}$ (and consequently $\boldsymbol{F}_i$ and $\boldsymbol{p}_i$) are, in this approximation, constant in time and uniform through the same sublattice.

As is well known, if the interaction decays slowly with the distance, as for the dipole–dipole interaction, the mean-field approximation is a quite adequate way of taking into account the long-range interactions (see for instance ref. 8)*. Short-range interactions, on the other hand, are not taken into account in an exact way, so that the model does not give information about fluctuations or collective modes.

In the above-described approximation the contribution to the field at the sublattice $i$ coming from the dipoles of the sublattice $j$, i.e. the term $E_{ij;\beta}^p$ of eq. (7), can be calculated in terms of the Lorentz factors $f_{ij;\beta\gamma}$:

$$E_{ij;\beta}^p = \frac{1}{\epsilon_0} \sum_{\gamma} f_{ij;\beta\gamma} P_{j;\gamma} \tag{8}$$

($P_{j;\gamma} = p_{j;\gamma}/v_j$ is the $\gamma$ component of the polarization of the sublattice $j$). This equation holds for a short-circuited slab-shaped specimen: for a more general case we must include the depolarization field. About this point see, for instance, ref. 9, where a very convenient method for calculating Lorentz factors is described. Similarly, the contribution to the field at sublattice $i$ coming from the charges of the sublattice $j$, i.e. the term $E_{ij;\beta}^q$ appearing in eq. (6), can be calculated, for instance, as described in ref. 10, where its shape dependence is also discussed. So, from (5) and (8) we have

$$F_{i;\beta} = E_{\beta}^{\text{ext}} + E_{i;\beta}^q + \frac{1}{\epsilon_0} \sum_{j,\gamma} f_{ij;\beta\gamma} P_{j;\gamma}. \tag{9}$$

As we already said, the system is in thermal equilibrium when the distribution functions $n_i(\omega)$ are such that the free energy $F = U - TS$ is at a minimum. In order to find the $n_i$ we need to write $F$ as a functional of them†

The electrostatic energy per unit volume associated with the dipole moments, $U$, can be calculated by adapting to this case the general procedure

* When the range of interaction is long the contribution to the field at a given site coming from the dipoles at a great distance is larger than that from the neighbouring ones; as the former is due to a very great number of dipoles, small local fluctuations have little effect on its value.

† The quantities which are affected by the temperature in our model are $P_{i;\beta}^{\text{perm}}$, $P_{i;\beta}^{\text{ind}}$ and $F_{i;\beta}$. Substituting (3) and (4) into (9) we obtain a system of $3N$ equations with $3N + 3N_p$ unknowns. This system can be written in terms of the $F_{i;\beta}$ or of the $P_{i;\beta}$. We prefer to write it in terms of the $P_{i;\beta}$ as unknowns, with the $3N_p$ components of the $P_{i;\beta}^{\text{perm}}$ as parameters, so that if the latter are given, the values of the $P_{i;\beta}^{\text{ind}}$ (and therefore $F_{i;\beta}$) are uniquely determined. Therefore, we can write the free energy $F$ as a functional of the $3N_p$ distribution functions $n_i$.

described by Böttcher[11]). So, the dipoles $\boldsymbol{p}_i$ are assumed to be assembled by bringing from infinity a very large number of very small dipoles $d\boldsymbol{p}_i = \boldsymbol{p}_i d\lambda$. At a given stage of this ideal procedure a fraction $\lambda$ of the actual value of each moment has been brought to the respective site. Therefore, from (5) and (8) the local field at that stage is given by

$$\boldsymbol{F}_i(\lambda) = \boldsymbol{E}'_i + \lambda \boldsymbol{E}^p_i,$$

where $\boldsymbol{E}'_i = \boldsymbol{E}^{\text{ext}} + \boldsymbol{E}^q_i$. Notice that eq. (3) does not hold during this fictitious process.

According to ref. 11 we have

$$U = -\int_0^1 \sum_i \boldsymbol{F}_i(\lambda) \cdot \boldsymbol{P}_i \, d\lambda$$

$$= -\sum_{i,\beta} E'_{i;\beta} P_{i;\beta} - \frac{1}{2\epsilon_0} \sum_{i,j,\beta,\gamma} f_{ij;\beta\gamma} P_{i;\beta} P_{j;\gamma}. \tag{10}$$

Now we need to substitute the $P_{i;\beta}$ in terms of the $P^{\text{perm}}_{i;\beta}$ components. Using (3), (4) and (9) we can write

$$\sum_{j,\gamma} \left( \delta_{ij}\delta_{\beta\gamma} - \frac{\alpha_i}{v_i} f_{ij;\beta\gamma} \right) P_{j;\gamma} = \frac{\epsilon_0 \alpha_i}{v_i} E'_{i;\beta} + P^{\text{perm}}_{i;\beta}. \tag{11}$$

This can be considered as a linear system of $3N$ equations in the $3N$ $P_{j;\gamma}$ components, which can be solved by inverting the matrix whose elements are*

$$M_{ij;\beta\gamma} = \delta_{ij}\delta_{\beta\gamma} - \frac{\alpha_i}{v_i} f_{ij;\beta\gamma}.$$

Calling Q the inverse matrix of M we have†

$$P_{i;\beta} = \sum_{j,\gamma} Q_{ij;\beta\gamma} \left( \frac{\epsilon_0 \alpha_j}{v_j} E'_{j;\gamma} + P^{\text{perm}}_{j;\gamma} \right). \tag{13}$$

Substituting into (10) we obtain, after some algebraic steps,

$$U = -\epsilon_0 \sum_{i,j,\beta,\gamma} R_{ij;\beta\gamma} E'_{i;\beta} E'_{j;\gamma} - \sum_{i,\beta} G_{i;\beta} P^{\text{perm}}_{i;\beta} - \frac{1}{2\epsilon_0} \sum_{i,j,\beta,\gamma} \sigma_{ij;\beta\gamma} P^{\text{perm}}_{i;\beta} P^{\text{perm}}_{j;\gamma}, \tag{14}$$

* We assume that "no polarization catastrophe" occurs, i.e. that

$$\det M \neq 0. \tag{12}$$

In our model, if a polarization catastrophe occurs, it does so at any temperature, i.e. it is not related to any phase transition.

† Throughout this paper, the index $i$ always runs from 1 to $N$, except in sums of the type $\Sigma_i C_{i;\beta} P^{\text{perm}}_{i;\beta}$, where it can be taken as running from 1 to $N_p$, because $\boldsymbol{P}^{\text{perm}}_i = 0$ if $i > N_p$. For sums of the type $\Sigma_i C'_i n_i$, of course, $i$ must go from 1 to $N_p$ because $n_i$ is defined only for sublattices with $\mu_i \neq 0$.

where

$$R_{ij;\beta\gamma} = \frac{\alpha_j}{v_j} \sum_{k,l,\lambda,\nu} \left( \delta_{ik}\delta_{jl}\delta_{\beta\lambda}\delta_{\gamma\nu} Q_{ij;\beta\gamma} + \tfrac{1}{2}\frac{\alpha_i}{v_i} f_{kl;\lambda\nu} Q_{ki;\lambda\beta} Q_{lj;\nu\gamma} \right),$$

$$G_{i;\beta} = \sum_{\substack{j,k,l \\ \gamma,\lambda,\nu}} \left( \delta_{lk}\delta_{ij}\delta_{\lambda\nu}\delta_{\beta\gamma} Q_{ki;\lambda\beta} + \frac{\alpha_k}{v_k} f_{lj;\nu\gamma} Q_{lk;\nu\lambda} Q_{ji;\gamma\beta} \right) E'_{k;\lambda}$$

and

$$\sigma_{ij;\beta\gamma} = \tfrac{1}{2}(g_{ij;\beta\gamma} + g_{ji;\gamma\beta}),$$

with

$$g_{ij;\beta\gamma} = \sum_{k,l,\lambda,\nu} f_{kl;\lambda\nu} Q_{ki;\lambda\beta} Q_{ij;\nu\gamma}.$$

Notice that

$$\sigma_{ij;\beta\gamma} = \sigma_{ji;\gamma\beta}. \tag{15}$$

The entropy per unit volume is given in terms of the $n_i$ by

$$S = -k \sum_i \frac{1}{v_i} \int n_i(\omega) \ln n_i(\omega)\, \mathrm{d}\omega \tag{16}$$

($k$ = Boltzmann constant).

Using eqs. (2), (14) and (16) the free energy per unit volume is written as a functional of the distribution functions:

$$F\{n_i\} = -\epsilon_0 \sum_{i,j,\beta,\gamma} R_{ij;\beta\gamma} E'_{i;\beta} E'_{j;\gamma} - \sum_{i,\beta} G_{i;\beta} P_{0i} \int c_\beta(\omega) n_i(\omega)\, \mathrm{d}\omega$$

$$- \frac{1}{2\epsilon_0} \sum_{i,j,\beta,\gamma} \sigma_{ij;\beta\gamma} P_{0i} P_{0j} \int\int c_\beta(\omega) n_i(\omega) c_\gamma(\omega') n_j(\omega')\, \mathrm{d}\omega\, \mathrm{d}\omega'$$

$$+ kT \sum_i \frac{1}{v_i} \int n_i(\omega) \ln n_i(\omega)\, \mathrm{d}\omega,$$

where $P_{0i} = \mu_i / v_i$.

Now we must find the minimum of the functional $F\{n_i\}$, subject to the constraint given by the normalization condition (1). The latter can be taken into account by introducing Lagrange multipliers $\lambda_i$, so that we actually have to minimize the functional

$$F' = F + \sum_i \lambda_i \int n_i(\omega)\, \mathrm{d}\omega.$$

The first variation of $F'$ when the distribution functions are varied according

to $n_i(\omega) \to n_i(\omega) + \delta_i(\omega)$ is

$$\delta F' = \sum_i \int \Gamma_i(\omega)\delta_i(\omega)\,\mathrm{d}\omega + \tfrac{1}{2}\sum_{i,j} \int\int [\Gamma_{ij}(\omega, \omega')n_i(\omega)\delta_j(\omega') + \Gamma_{ij}(\omega, \omega')\delta_i(\omega)n_j(\omega')]\,\mathrm{d}\omega\,\mathrm{d}\omega' + kT \sum_i \frac{1}{v_i} \int [1 + \ln n_i(\omega)]\delta_i(\omega)\,\mathrm{d}\omega = 0,$$

where we put

$$\Gamma_i(\omega) = -P_{0i} \sum_\beta G_{i;\beta} c_\beta(\omega) + \lambda_i \tag{17}$$

and

$$\Gamma_{ij}(\omega, \omega') = -P_{0i}P_{0j} \sum_{\beta,\gamma} \sigma_{ij;\beta\gamma} c_\beta(\omega) c_\gamma(\omega'). \tag{18}$$

From (15) we have $\Gamma_{ij}(\omega, \omega') = \Gamma_{ji}(\omega', \omega)$. Therefore

$$\sum_i \int \left\{ \frac{kT}{v_i} [1 + \ln n_i(\omega)] + \Gamma_i(\omega) + \sum_j \int \Gamma_{ij}(\omega, \omega')n_j(\omega')\,\mathrm{d}\omega' \right\} \delta_i(\omega)\,\mathrm{d}\omega = 0.$$

This equality must hold for arbitrary variations $\delta_i(\omega)$, so that

$$\frac{kT}{v_i} [1 + \ln n_i(\omega)] + \Gamma_i(\omega) + \sum_j \int \Gamma_{ij}(\omega, \omega')n_j(\omega')\,\mathrm{d}\omega' = 0. \tag{19}$$

Let us try the solutions

$$n_i(\omega) = A_i \exp\left\{ \sum_\beta c_\beta(\omega) u_{i;\beta} \right\} \tag{20}$$

The normalization constants can be found from (1) by making use of

$$\int_0^\pi \exp(\mathrm{i}z \cos\theta \cos u) J_m(z \sin\theta \sin u) P_n^m(\cos u) \sin u\,\mathrm{d}u = \mathrm{i}^{n-m} \sqrt{\frac{2\pi}{z}}\, P_n^m(\cos\theta) J_{n+1/2}(z) \tag{21}$$

(see ref. 12). They are

$$A_i = \frac{u_i}{4\pi \sinh u_i}, \tag{22}$$

where $u_i = [u_{i;1}^2 + u_{i;2}^2 + u_{i;3}^2]^{1/2}$.

We must now find the $3N_p$ parameters $u_{i;\beta}$. Each integral in (19) can be evaluated by using (21):

$$\int c_\beta(\omega)n_i(\omega)\,\mathrm{d}\omega = \frac{u_{i;\beta} L(u_i)}{u_i} \tag{23}$$

where $L(x) = \coth x - 1/x$ (Langevin function). In the following we set

$$\frac{L(u_i)}{u_i} \equiv \Lambda(u_j) \equiv \Lambda_j. \tag{24}$$

Substituting (17), (18), (20), (23) and (24) into (19) we obtain

$$\frac{kT}{v_i}(1 + \ln A_i) + \lambda_i + \sum_\beta \left\{ \frac{kT}{v_i} u_{i;\beta} - P_{0i} G_{i;\beta} - \sum_j P_{0i} P_{0j} \sum_\gamma \sigma_{ij;\beta\gamma} u_{j;\gamma} \Lambda_j \right\} c_\beta(\omega) = 0. \tag{25}$$

This equation must hold for any direction $\omega$. This is possible only if the bracketed term in (25) vanishes, and the Lagrange parameters are chosen as

$$\lambda_i = -\frac{kT}{v_i}(1 + \ln A_i).$$

In this way we obtain a system of $3N_p$ transcendental equations to be satisfied by the parameters $u_{i;\beta}$ characterizing the $n_i$:

$$u_{i;\beta} = e_{i;\beta} + \sum_{j,\gamma} s_{ij} \sigma_{ij;\beta\gamma} \Lambda_j u_{j;\gamma}, \tag{26}$$

where

$$e_{i;\beta} = \frac{\mu_i}{kT} G_{i;\beta}$$

and

$$s_{ij} = \frac{\mu_i \mu_j}{\epsilon_0 kT} \frac{1}{v_j} = \frac{v_i P_{0i} P_{0j}}{\epsilon_0 kT}.$$

This system is in a suitable form to be solved by numerical iteration.

Once the $u_{i;\beta}$ are known the average value of the permanent moments can be evaluated from (2) and (23):

$$P_{i;\beta}^{\text{perm}} = P_{0i} u_{i;\beta} \Lambda_i. \tag{27}$$

By substituting (27) into (13) we get the total moments $\boldsymbol{P}_i$, so that once we solved the system (26) we have all the basic information needed for knowing the polarization state of the crystal. In the remaining part of this section we are going to discuss how this information can be obtained from the $u_{i;\beta}$.

For each permanent dipole the $u_{i;\beta}$ determine a direction $\omega_{0i} \equiv (\theta_{0i}, \varphi_{0i})$: in fact we can always write

$$\boldsymbol{u}_i \equiv u_i(\sin\theta_{0i} \cos\varphi_{0i} \boldsymbol{i} + \sin\theta_{0i} \sin\varphi_{0i} \boldsymbol{j} + \cos\theta_{0i} \boldsymbol{k}).$$

From (2) and (20) it is seen that $\boldsymbol{p}_i^{\text{perm}}$ is preferentially oriented in the $\omega_{0i}$

direction, its distribution being more peaked when $u_i$ is larger. In the limiting case $T \to 0$, from (26) we have $u_i \to \infty$, and from (20) and (22)

$$\lim_{u_i \to \infty} n_i(\omega) = \delta^2(\omega - \omega_{0i}).$$

Of course, this physically means that at 0 $K$ all the dipole moments are fixed in their equilibrium positions.

Now we are going to discuss the connection between the solutions of (26) and the ferroelectric properties of the crystal.

(a) We first consider the case where the local field at the dipole sites is only due to dipole–dipole interactions, i.e. $E'_{i;\beta} = 0$, so that $G_{i;\beta} = 0$. In such a case eqs. (26) always admit the trivial solution, $u_{i;\beta} = 0$ for all $i$ and $\beta$. This corresponds to total disorder in the orientations of the permanent dipoles. The average values of the latter vanish and the same happens for the induced moments, provided a polarization catastrophe does not occur [see eqs. (3), (9) and (12)]. This case corresponds to a paraelectric phase. It may happen, however, that a certain set of $u_{i;\beta}$ not all equal to zero is also a solution of (26). In such a case the set $-u_{i;\beta}$ is another solution, so that it is possible to switch the system from one configuration to the opposite one by means of an external field. The non-trivial solutions correspond to a ferro-, antiferro- or ferri-electric ordering, according to the relative values and signs of the $u_{i,\beta}$ components. At a given $T$ the system will actually be in the phase with the least free energy. The Curie temperature can be obtained from the condition

$$F_{\mathrm{PE}}(T_c) = F_{\mathrm{NPE}}(T_c) \tag{28}$$

(NPE means "non paraelectric" and refers generically to ferro-, antiferro- and ferri-electric phases). We will see some examples in section 4.

(b) Now we consider a crystal in which $G_{i;\beta} = 0$ for some values of $i$ and $\beta$ (this is the general situation, because we can always choose the coordinate axes in such a way that some of the field components at some site are zero). Again we have a PE solution ($u_{i;\beta} \neq 0$ for the above-mentioned values of $i$ and $\beta$ while $u_{i;\beta} = 0$ for the others) and perhaps a NPE solution too (at least one of the $u_{i;\beta}$, with $i$ and $\beta$ such that $G_{i;\beta} = 0$, is different from zero). Now in the PE phase there may be a permanent total moment per unit cell, which remains unchanged in the NPE phase. Again, the stable solution is the one with the least free energy, and the transition temperature is obtained from (28).

In all the above cases, we expect that at high temperature the PE phase is the stable one. In the particular case of the structures considered in section 4 it is shown that this is indeed so. On the other hand, the non-linearity of eqs. (26) makes it difficult to find a proof for the general case, so that this will not be done in this paper.

We are going to end this section by writing down the expression of the free energy, in terms of the $u$'s, that is required in order to apply condition (28).

$$F = -\sum_{i,\beta}\left[\epsilon_0 \sum_{j,\gamma} R_{ij;\beta\gamma} E'_{i;\beta} E'_{j;\gamma} + \tfrac{1}{2} G_{i;\beta} P_{0i} u_{i;\beta} \Lambda_i\right] + kT \sum_i \frac{1}{v_i}\left[\ln\left(\frac{u_i}{4\pi \sinh u_i}\right) + \tfrac{1}{2} u_i L(u_i)\right]. \tag{29}$$

Here, the expression of the electrostatic energy has been obtained by substituting (26) and (27) into (14), and that of the entropy by substituting (20) and (22) into (16) and making use of (21).

## 3. Calculation of some quantities of interest

In this section we calculate some physical quantities of the crystal. We recall that in our model the only external variables are $T$ and $\boldsymbol{E}^{\text{ext}}$.

The isothermal dielectric susceptibility is, by definition,

$$\chi_{\beta\gamma} = \lim_{\substack{\text{ext} \\ E_\gamma \to 0}} \frac{\partial P_\beta}{\partial(\epsilon_0 E_\gamma^{\text{ext}})}\bigg|_{T=\text{const.}} \quad (\text{with } E_\lambda^{\text{ext}} = 0 \quad \text{for } \lambda \neq \gamma), \tag{30}$$

where $P_\beta = \Sigma_i P_{i;\beta} = \Sigma_i (P_{i;\beta}^{\text{perm}} + P_{i;\beta}^{\text{ind}})$ is the total polarization vector. It can be written in terms of the $u_{i;\beta}$ by using (13) and (27):

$$P_\beta = \sum_{i,j,\gamma} Q_{ij;\beta\gamma}\left(\frac{\epsilon_0 \alpha_j}{v_j} E'_{j,\gamma} + P_{0j} u_{j;\gamma} \Lambda_j\right). \tag{31}$$

This expression depends on $E_\gamma^{\text{ext}}$ directly through $E'_{j;\gamma}$ and indirectly through the $u$'s. The susceptibility could be calculated from it by numerical differentiation, in the limit $E_\gamma^{\text{ext}} \to 0$. However, the following procedure is better in order to obtain a more accurate result. Differentiating (31) we have

$$\chi_{\beta\gamma} = \sum_{i,j} \frac{\alpha_j}{v_j} Q_{ij;\beta\gamma} + \sum_{i,j,\nu,\lambda} P_{0j} Q_{ij;\beta\nu} H_{j;\nu\lambda} \frac{\partial u_{j;\lambda}}{\partial(\epsilon_0 E_\gamma^{\text{ext}})}, \tag{32}$$

where,

$$H_{j;\nu\lambda} = \Lambda_j \delta_{\nu\lambda} + \frac{u_{j;\nu} u_{j;\lambda}}{u_j^2}\left[L'(u_j) - \Lambda_j\right]$$

($L'(x) = \mathrm{d}L(x)/\mathrm{d}x$). Everything in (32) is known except the partial derivatives $\partial u_{j;\lambda}/\partial E_\gamma^{\text{ext}}$. These can be found without any differentiation, by numerically

solving a linear system of $3N_p$ equations obtained by differentiating eq. (26):

$$\sum_{j,\lambda}\left(\delta_{ij}\delta_{\beta\lambda} - s_{ij}\sum_{\nu}\sigma_{ij;\beta\nu}H_{j;\nu\lambda}\right)\frac{\partial u_{j;\lambda}}{\partial(\epsilon_0 E_\gamma^{\text{ext}})}$$

$$= \frac{\mu_i}{\epsilon_0 kT}\sum_{\substack{j,k,l\\ \lambda,\nu}}\left(\delta_{lk}\delta_{ij}\delta_{\gamma\nu}\delta_{\beta\lambda}Q_{ki;\gamma\beta} + \frac{\alpha_k}{v_k}f_{lj;\nu\lambda}Q_{lk;\nu\gamma}Q_{ji;\lambda\beta}\right). \tag{33}$$

The specific heat at constant external field and the pyroelectric coefficient are calculated by similar procedures. The results are

$$C_E = \left.\frac{\partial U}{\partial T}\right|_{E^{\text{ext}}=\text{const.}} = -kT\sum_{i,\beta}\frac{1}{v_i}u_{i;\beta}L'(u_i)\frac{\partial u_{i;\beta}}{\partial T} \tag{34}$$

and

$$\varphi_\beta = \left.\frac{\partial P_\beta}{\partial T}\right|_{E^{\text{ext}}=\text{const.}} = \sum_{i,j,\gamma,\lambda}Q_{ij;\beta\gamma}P_{0j}H_{j;\gamma\lambda}\frac{\partial u_{j;\lambda}}{\partial T}. \tag{35}$$

The partial derivatives $\partial u_{i;\beta}/\partial T$ are obtained from the linear system

$$\sum_{j,\gamma}\left[\delta_{ij}\delta_{\beta\gamma} - s_{ij}\sum_{\lambda}\sigma_{ij;\beta\lambda}H_{j;\lambda\gamma}\right]\frac{\partial u_{j;\gamma}}{\partial T} = -\frac{u_{i;\beta}}{T}. \tag{36}$$

## 4. Examples

Let us apply the above-developed formalism to some simple cases that can be studied without any computational work and yet present several interesting features. For the sake of brevity, most intermediate steps will be skipped and only the most essential features of each case will be discussed.

(a) One dipole sublattice with zero polarizability and electric field. Tetragonal symmetry ($a = b \neq c$).

Having only one sublattice we can drop the Latin indices. The only non-vanishing Lorentz factors are: $f_{xx} = f_{yy} \equiv f_x$ and $f_{zz} \equiv f_z$. System (26) reduces to

$$u_x = sf_x u_x \Lambda(u),$$
$$u_y = sf_x u_y \Lambda(u),$$
$$u_z = sf_z u_z \Lambda(u).$$

We see that a non-trivial solution exists provided one of the following equations holds

$$sf_x\Lambda(u) = 1, \tag{37}$$

$$sf_z\Lambda(u) = 1. \tag{38}$$

Notice that if $\boldsymbol{u}$ is a solution so is $-\boldsymbol{u}$; therefore, both solutions correspond

to the two opposite orientations of a FE ordering. If (38) holds (case a1), then $u_x = u_y = 0$; if (37) holds (case a2), then $u_z = 0$.

(a1) This solution describes a lattice polarized in the $z$ direction ($u = |u_z|$). The parameter $u$ is obtained by solving eq. (38). The transition temperature is obtained by taking $u \to 0$. As $\lim_{u \to 0} \Lambda(u) = \frac{1}{3}$ we have

$$T_{c,z} = \mu^2 f_z / 3\epsilon_0 k v.$$

For $\mu \simeq 2$ Debye and $v \simeq 500\ \mathring{A}^3$ we obtain $T_{c,z} \simeq 200 f_z$ K.

(a2)

$$u_x^2 + u_y^2 = u^2. \tag{39}$$

$u$ is obtained from (37), and any pair $(u_x, u_y)$ satisfying (39) is a solution. As $F$ depends only on $u$ [see eq. (29)] all these solutions are thermodynamically equivalent. So, without loss of generality we can take $u = |u_x|$, $u_y = 0$. This will also be done in the next examples. Now the critical temperature is:

$$T_{c,x} = \mu^2 f_x / 3\epsilon_0 v k. \tag{40}$$

The physical solution is the one with the least value of $F$. From (29)

$$F = \frac{kT}{v} [\ln(u/4\pi \sinh u) + \tfrac{1}{2} u L(u)], \tag{41}$$

where $u$ is given by (37) or by (38) as the case may be. It is easy to show that $\sinh^2 u e^{-uL(u)}/u^2$ is an increasing function of $u$, so that $F(u)$ is smaller when $u$ is larger. From the graphical solution of eqs. (37) or (38) it is seen that at a given temperature the solution with the largest $u$ is the one with the largest Lorentz factor.

We conclude that a tetragonal lattice always tends to polarize in the direction for which the Lorentz factor is larger (from the formulae of ref. 9 we have $f_z > f_x$ for $c < a$ and $f_z < f_x$ for $c > a$). We will see below that in a certain range of values of the ratio $c/a$ this FE ordering is less stable than an AFE ordering.

Notice that whenever $u$ is obtained from an equation such as (37) or (38) (as in all the examples treated in this section), it can be seen using the series expansion of $L(u)$ that when $T$ approaches $T_c$ from below, the polarization tends to zero as $(T_c - T)^{1/2}$. This result agrees with the theory of second-order phase transitions in the mean field approximation[13]).

(b) Same as above, but with $E' \neq 0$; $\alpha = 0$.

Several cases may arise, according to whether $E'_x$, or $E'_z$, or both are different from zero, and to whether $f_x > f_z$ or viceversa. Let us consider the

case $f_x > f_z$, $e_z \neq 0$, $e_x = e_y = 0$. System (26) becomes

$$u_x = sf_x u_x \Lambda(u),$$
$$u_z = e_z + sf_z u_z \Lambda(u).$$

We already saw that for $e_z = 0$ the stable solution is $|u_x| = u \neq 0$, $u_z = 0$, where $u$ obeys eq. (37). If $e_z$ is increased from zero, $u_z$ no longer vanishes, but satisfies

$$u_z = e_z f_x / (f_x - f_z). \tag{42}$$

The sign of $u_z$ is the same as that of $e_z$, so that this polarization in the $z$ direction does not correspond to a FE ordering. On its turn, $u_x$ satisfies the equation

$$sf_x \Lambda(u) = 1, \tag{43}$$

where $u = (u_x^2 + u_z^2)^{1/2}$ and $u_z$ is given by eq. (42). It is easy to see that the value of $u_x$ satisfying eq. (43) is smaller than the one obtained from (37). Therefore, the appearance of an external or ionic field at the dipole sites at 90° to the FE axis introduces a component of $\boldsymbol{P}$ in that direction, thereby lowering the spontaneous polarization. The transition temperature in the present case is

$$T_{c,x} = \frac{\mu^2 f_x}{\epsilon_0 v k} \Lambda\left(\frac{e_z f_x}{f_x - f_z}\right).$$

As $\Lambda(u) < \frac{1}{3}$ for $u > 0$, $T_{c,x}$ is lowered with respect to the case with $e_z = 0$ [see eq. (40)].

(c) One tetragonal lattice divided in two interpenetrating tetragonal sublattices (see fig. 1); $\alpha_1 = \alpha_2 = 0$, $\boldsymbol{E}' = 0$.

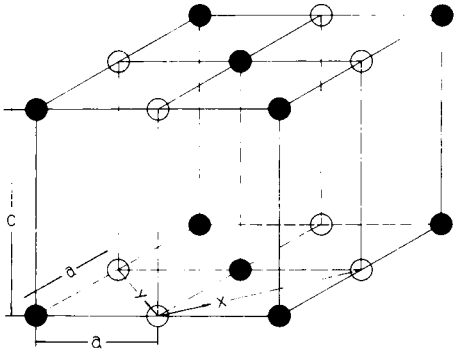


Fig. 1. Tetragonal lattice subdivided into two interpenetrating tetragonal sublattices. Notice that the unit cell volume of each one of the latter is written as $2v$, where $v$ is the unit cell volume of the original tetragonal lattice.

The only non vanishing Lorentz factors are:

$$f_{11;xx} = f_{11;yy} = f_{22;xx} = f_{22;yy} \equiv f_{1x}; \quad f_{11;zz} = f_{22;zz} \equiv f_{1z};$$
$$f_{12;xx} = f_{12;yy} \equiv f_{2x}; \quad f_{12;zz} \equiv f_{2z}.$$

System (26) becomes

$$\begin{aligned}
u_{1;x} &= s[f_{1x}\Lambda_1 u_{1;x} + f_{2x}\Lambda_2 u_{2;x}],\\
u_{2;x} &= s[f_{2x}\Lambda_1 u_{1;x} + f_{1x}\Lambda_2 u_{2;x}],\\
u_{1;y} &= s[f_{1x}\Lambda_1 u_{1;y} + f_{2x}\Lambda_2 u_{2;y}],\\
u_{2;y} &= s[f_{2x}\Lambda_1 u_{1;y} + f_{1x}\Lambda_2 u_{2;y}],\\
u_{1;z} &= s[f_{1z}\Lambda_1 u_{1;z} + f_{2z}\Lambda_2 u_{2;z}],\\
u_{2;z} &= s[f_{2z}\Lambda_1 u_{1;z} + f_{1z}\Lambda_2 u_{2;z}].
\end{aligned} \tag{44}$$

The internal energy depends on $u_1$ and $u_2$ separately:

$$U = -\frac{kT}{4v}[L(u_1) + L(u_2)].$$

As both sublattices are identical, in the equilibrium configuration they should have the same energy. Therefore, $u_1 = u_2 = u$. Furthermore, it can be seen from (44) that $u_{1;\beta} = \pm u_{2;\beta} = u_\beta$. Using this, it can be seen that four possibilities arise, with $u$ satisfying in each case an equation of the form

$$sfL(u) = u.$$

The four cases are the following:

(c1) $u_{1;z} = u_{2;z} \neq 0, \quad u_{1;x} = u_{2;x} = 0, \quad f = f_{1z} + f_{2z} \equiv f_{+z},$

(c2) $u_{1;z} = -u_{2;z} \neq 0, \quad u_{1;x} = u_{2;x} = 0, \quad f = f_{1z} - f_{2z} \equiv f_{-z},$

(c3) $u_{1;x} = u_{2;x} \neq 0, \quad u_{1;z} = u_{2;z} = 0, \quad f = f_{1x} + f_{2x} \equiv f_{+x},$

(c4) $u_{1;x} = -u_{2;x} \neq 0, \quad u_{1;z} = u_{2;z} = 0, \quad f = f_{1x} - f_{2x} \equiv f_{-x}$

(again, $u_y$ can be taken as equal to zero). Here we assumed that all the above defined $f$'s are different from each other. If, on the contrary, we had for instance $f_{+z} = f_{-x}$, a solution with both $u_x$ and $u_z$ different from zero could exist. This case will not be considered here.

The phases corresponding to the above-listed cases are

(c1) FE, $\boldsymbol{P}$ in the $z$ direction,

(c2) AFE, $\boldsymbol{P}_1$ and $\boldsymbol{P}_2$ in the $z$ direction,

(c3) FE, $\boldsymbol{P}$ in the $xy$ plane,

(c4) AFE, $\boldsymbol{P}_1$ and $\boldsymbol{P}_2$ in the $xy$ plane.

TABLE I
Combinations of Lorentz factors for the tetragonal sublattices of fig. 1.

| $c/a$ | $f_{1x}+f_{2x}$ | $f_{1x}-f_{2x}$ | $f_{1z}+f_{2z}$ | $f_{1z}-f_{2z}$ |
|---|---|---|---|---|
| 0.6 | −0.061 | −1.064 | 2.129 | 2.123 |
| 0.8 | 0.416 | −0.611 | 1.168 | 1.222 |
| 1.0 | 0.667 | −0.426 | 0.667 | 0.852 |
| 1.1 | 0.761 | −0.382 | 0.478 | 0.764 |
| 1.2 | 0.846 | −0.357 | 0.309 | 0.714 |
| 1.5 | 1.075 | −0.350 | −0.150 | 0.700 |
| 2.0 | 1.438 | −0.426 | −0.875 | 0.852 |
| 2.5 | 1.797 | −0.527 | −1.594 | 1.054 |

In each case the critical temperature is

$$T_{c,\pm\beta} = \frac{\mu^2}{6\epsilon_0 kv} f_{\pm\beta}$$

and the free energy is formally the same as in (41). As for a single lattice, the most stable phase is the one with the largest value of $f$. We calculated $f_{1x}$, $f_{2x}$, $f_{1z}$ and $f_{2z}$ using the formulae of ref. 9 for different values of $c/a$. The values of the $f_{\pm\beta}$'s are given in table I. We see that for $c/a \leqslant 0.6$ the system is FE, with $\boldsymbol{P}$ in the $z$ direction; for $0.6 \leqslant c/a \leqslant 1.1$ we have AFE ordering in the $z$ direction (for $c = a$ Luttinger and Tisza's result quoted in ref. 7 is recovered); for $1.1 \leqslant c/a$ the system is FE, with $\boldsymbol{P}$ in the $xy$ plane, where all directions are equivalent.

(d) Same as (c), but with $\alpha_1 = \alpha_2 \equiv \alpha \neq 0$.

A system similar to (44) is obtained, with the matrix $\boldsymbol{\sigma}$ replacing $f$. The $\sigma_{ij;\beta\gamma}$ are

$$\sigma_{11;\beta\beta} = \frac{f_{1\beta}[1+\alpha^2 f_{+\beta}f_{-\beta}] - 2\alpha f_{+\beta}f_{-\beta}}{(1-\alpha f_{+\beta})^2(1-\alpha f_{-\beta})^2} \equiv \sigma_{1\beta},$$

$$\sigma_{12;\beta\beta} = \frac{f_{2\beta}(1-\alpha^2 f_{+\beta}f_{-\beta})}{(1-\alpha f_{+\beta})^2(1-\alpha f_{-\beta})^2} \equiv \sigma_{2\beta}, \tag{45}$$

$$\sigma_{ij;\beta\gamma} = 0, \quad \text{if} \quad \beta \neq \gamma$$

[the $f$'s are the same as in the case (c)]. The same arguments as for case (c) can be brought forward, leading to the following conclusion. There are four possible solutions, with $u$ satisfying in each case an equation of the form

$$s\sigma L(u) = u.$$

The four solutions are

$$\begin{aligned}
&(d1)\quad u_{1;z} = u_{2;z} \neq 0, \quad u_{1;x} = u_{2;x} = 0, \quad \sigma = \sigma_{1z} + \sigma_{2z} \equiv \sigma_{+z},\\
&(d2)\quad u_{1;z} = -u_{2;z} \neq 0, \quad u_{1;x} = u_{2;x} = 0, \quad \sigma = \sigma_{1z} - \sigma_{2z} \equiv \sigma_{-z},\\
&(d3)\quad u_{1;x} = u_{2;x} \neq 0, \quad u_{1;z} = u_{2;z} = 0, \quad \sigma = \sigma_{1x} + \sigma_{2x} \equiv \sigma_{+x},\\
&(d4)\quad u_{1;x} = -u_{2;x} \neq 0, \quad u_{1;z} = u_{2;z} = 0, \quad \sigma = \sigma_{1x} - \sigma_{2x} \equiv \sigma_{-x}.
\end{aligned}$$

From (45) it follows

$$\sigma_{\pm\beta} = \frac{f_{\pm\beta}}{\left(1 - \frac{\alpha}{2v} f_{\pm\beta}\right)^2}$$

and the critical temperature is

$$T_{c,\pm\beta} = \frac{\mu^2}{6\epsilon_0 k v} \sigma_{\pm\beta}. \tag{46}$$

The most stable solution corresponds to the largest value of the $\sigma$'s. Let us assume that $f_{+z} > f_{-z} > f_{+x} > f_{-x}$. It can be seen that for $\alpha/2v < (f_{+z} f_{-z})^{-1/2}$, $\sigma_{+z}$ is the largest among the $\sigma$'s so that we obtain the same type of phase as for $\alpha = 0$, but with different $u$'s and a different $T_c$. As $\sigma_{+z} > f_{+z}$, a non-vanishing polarizability gives a larger $u$ and a higher transition temperature, i.e. it increases the stability of the system. For $\alpha/2v = f_{+z}$ a polarization catastrophe occurs. For $(f_{+z} f_{-z})^{-1/2} < \alpha/2v < (f_{+z} f_{+x})^{-1/2}$, $\sigma_{-z}$ is larger than $\sigma_{+z}$; now the polarizability gives rise to a different kind of ordering. For the present example we would have an AFE, instead of a FE ordering. It should be noticed that this possibility is perhaps only of academic interest, because an unusually large value of $\alpha$ is required in order that $\sigma_{-z} > \sigma_{+z}$.

For this model, as for the previous ones, the susceptibility, specific heat and pyroelectric coefficients can be calculated using the formulae of section 3. As an example, let us give the susceptibility in the direction of the polarization. Assuming that the latter lies in the $x$ direction we have

$$\chi_{xx} = \frac{\alpha/v}{1 - \alpha f_{+x}/2v} + \frac{6L'(u) T_{c,+x}/T}{f_{+x}(1 - \alpha f_{+x}/2v)(1 - 3T_{c,+x} L'(u)/T)}. \tag{47}$$

$T_{c,+x}$ is the Curie temperature for the FE transition [eq. (46)]. Eq. (47) holds both for the FE and the AFE cases, the difference lying in the term $L'(u)$. It can be seen that for $a = c$ our result agrees with Takagi's formula (35)[7]).

If the more stable low-temperature phase is the FE one, it can be seen that the susceptibility agrees with the Curie–Weiss law:

$$\chi_{xx} = \frac{2}{f_{+x}(1 - f_{+x}\alpha/2v)} \frac{T_c}{T - T_c} \equiv \frac{C}{T - T_c}, \quad T \geq T_c,$$

$$\chi_{xx} = \frac{1}{f_{+x}(1 - f_{+x}\alpha/2v)} \frac{T_c}{T_c - T} \equiv \frac{C'}{T_c - T}, \quad T \lesssim T_c.$$

The ratio $C/C'$ is equal to 2, a result that is common to the solutions based on a mean-field approximation[13]).

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