Comparison between two simple numerical models for the magnetoelectric interaction in multiferroics

Cesar J. Calderon Filho and Gaston E. Barberis
Instituto de Física "Gleb Wataghin", UNICAMP,
13083-970, Campinas, São Paulo, Brazil.
(ΩDated: January 20, 2013)

We developed numerical calculations to simulate the magnetoelectric coupling in multiferroic compounds, using the Monte Carlo technique. Two simple models were used to simulate the compounds. In the first one, the magnetic ions are represented by a spin 1/2 2D Ising lattice of ions, and the electric lattice by classical moments, coupled one to one with the magnetic moments. The coupling between both lattices allows to the leading lattice, that is, the magnetic one, to change the orientation of the electrical dipoles in one direction perpendicular to the magnetic dipoles. This direction was chosen to accomplish the symmetry requirements of the magnetoelectric effect. In the second case, the magnetic lattice is also a 2D Ising lattice, but the electric momenta are in a lattice that also behaves as an Ising lattice, perpendicular to the magnetic moments. In this case, the one-to-one coupling of the electric and magnetic momenta is represented by a two-valued energy parameter, allowing the possibility of independent transition temperatures for both lattices. Both models contain three independent parameters. We studied the physical properties obtained with both models, as functions of the ratio of the three parameters. The results in both cases allowed us to compare changes in the physics of the models, and with the physics of compounds measured experimentally.

PACS numbers: 75.10.-b, 75.10.Hk

I. INTRODUCTION.

Recently, there has been a revived interest in the research of multiferroics due to several new discoveries, and the possibility to use them technologically.\(^1\) The electric and magnetic transitions are not necessarily correlated, but when it occurs - and the so called magnetoelectric effect appears - the materials suggest possible use as memories, etc. Besides the technical applications, several families of those compounds present very rich physics. Just as an example, one of this compounds, LiNiPO\(_4\), shows a phase transition where the electric lattice is not only first order, but in a very short range of temperature several incommensurable transitions appear.\(^2\) Even in front of those interesting phenomena, we found very few theoretical papers on this subject, and most of them using very elaborated theoretical methods.\(^3\)

With the motivation presented above, we developed two simple numerical models, based on the Monte Carlo method, and the Metropolis minimization of total energy.

We present here two simple and understandable models for the magnetoelectricity. The electromagnetic Hamiltonian is solved for very simple cases, and the solutions present similitude with the reported experiments. The first model study the phase transitions at the same temperature, independently of the temperature value. The second model, a little more elaborated, allows the ferroelectric and ferromagnetic transitions to occur at different temperatures, and we studied the behavior of the model as function of this temperature difference. We compare the results between the models and with experimental cases.

II. THE MODELS.

The physics behind the magnetoelectric effect consists, as seen in a bird’s eye view, in the creation or orientation of electric dipoles by the magnetic moments or vice-versa. In the first case, the magnetic dipoles, which are permanent, when change their orientation, modify the lattice in such a way that the negative electric charges displace relatively to the positive. This is accomplished via spin-orbit coupling of the spins, changing the total energy as the orbit lattice Hamiltonian explains. Simplifying the model, the spin-orbit-lattice energy is calculated as a spin-lattice Hamiltonian. We simplified the calculation even more, representing the magnetic lattice as a 2D Ising lattice in all the cases. This corresponds with many real compounds, as the olivines mentioned above, where the structure of the real lattice presents separated planes of magnetic ions.\(^4\)–\(^6\)

We assume that the magnetoelectric system is a set of magnetic dipoles, coupled via the exchange interaction, in a lattice with a distribution of electric charges, susceptible to change when the magnetic dipoles change their orientations. The change in orientation of the magnetic dipoles modify their environment, via spin-orbit interaction, creating local strains, and creating or orienting a set of electric dipoles in the lattice. We assume that our crystal suffers the strain in such a way that electric dipoles are oriented to a particular direction when the magnetic dipoles relax.

The model Hamiltonian used in the models follows:

\[
H = H_M + H_E + H_{ME} 
\]  

(1)

where \(H_M\) is the magnetic energy, \(H_E\) the electric energy.
and $H_{ME}$ the magnetoelectric coupling.

A. The first model

The first approach for a solution of eq. (1) is obtained replacing the first term in the sum of the right side by a square sublattice of Ising magnetic moments, and the electric moments in the second and third terms by random oriented classical electrical dipoles, located in a separated square sublattice. The Ising spins are coupled to their nearest neighbors only, and with periodic boundary conditions. The interaction Hamiltonian allows only nearest neighbors magnetoelectric interaction. Symmetry requires that the magnetic point group of the magnetic moment is one of the 58 Shubnikov groups that allow magnetoelectricity. This forces our magnetic moments to have only one electric dipole as a nearest neighbor. The electromagnetic coupling is divided in two parts: the local interaction between the spin and the electric dipole, and the lattice total electromagnetic energy, that takes into account the interaction between the electric dipoles and their electric neighbors. As most of the electric parameters are measured perpendicularly to the magnetization, we chose the $\hat{z}$ direction for the magnetic moments, and the $\hat{x}$ axis for the electric dipoles.

The numerical solution of the problem was done using the importance sample Monte Carlo method, looking for the minimum in energy for our system.

Thus,

$$H = -J \sum_{<i,j>} \sigma_i \sigma_j - h \sum_{i} \sigma_i - \beta \sum_{\{i,j\}} P_{ix} P_{jx} + \gamma \sum_{i} P_{ix}$$

(2)

is the approximated Hamiltonian, where $J$ is the exchange coupling of the Ising magnetic spins $\sigma$, and $P$ the electric dipoles. The symbol $<i,j>$ indicates sums over the nearest neighbors only. The first and second terms constitute the magnetic energy, where we included the possibility of an applied or external magnetic field $h$. The third term represent the electric energy, proportional to the orientation of the neighboring electric momenta. As the system to be ferroelectric, the direction of the polarized dipoles the $\hat{x}$ axis of the crystal, we considered only the energy coupling in that direction, which is represented by $\{i,j\}$, indicating sum over the two first neighbors located in the $\hat{x}$ axis.

The interaction term, which represents a spin - lattice Hamiltonian, was separated into two parts. One of them is the local interaction between the spin and the $\hat{x}$ projection of the electric dipole, which makes that every transition of the spin changes simultaneously the dipole; the second, represented the last term in eq. (2) is the contribution of the lattice as a whole to the total energy. As the local interaction is the same for every pair spin-dipole, we did not include it in the Hamiltonian. However, the meaning of this local part of the energy is important, as we will see below.

1. Ferromagnetic case.

Our first calculation was performed in a $100 \times 100$ 2D lattice of Ising ferromagnetic spins coupled to $100 \times 100$ electric dipoles, located in another square lattice, parallel to the magnetic one, and slightly shifted from it. The electric dipoles were oriented at random, together with magnetic lattice, to begin with infinite temperature. The temperature was then fixed to a value, and a Monte Carlo program, where the transitions are allowed following the Metropolis technique, is iterated the time necessary to obtain thermal equilibrium of the system. Then, the results are used as the initial condition for the following temperature. The calculation was performed reducing the temperature in each step.

The complete calculation was performed after a study of convergence in our model. As first step, we unconsidered the electric and interaction energies when we looked for the minimum. This means that the model is just a 2D Ising system, moving electric dipoles together, and as expected, the magnetization follows the Ising model. The exact calculation published by Onsager allows a very good comparison, and the electric dipoles also feel a transition at the same temperature. This calculation decided the size of the set of moments, which we selected as $100 \times 100$ on this basis.

The following step was to study the convergence when the parameters $\beta$ and $\gamma$ in the model are different from zero. It is well known that the Ising model converges slowly near by the transition temperature, due to fluctuations, and the equal value for the energy when the system is oriented in any of the both possible directions. This is easily solved with the addition of the small external field $h$; however, we observed that for particular values of $\gamma$, the convergency is the slowest. This can be explained by the fact that $\gamma$ appears in the Hamiltonian as an external field, in some manner. We can use the local coupling of the spin-dipole pair to write

$$P_{ix} = P_{ix} |\sigma_i| = |\sigma_i| P_{ix}$$

(3)

for the modulus of $\sigma_i$ is always the unity; that can be used to write the second and last terms in the Hamiltonian as

$$\gamma \sum_{i} P_{ix} - h \sum_{i} \sigma_i = - \sum_{i} (h - \gamma P_{ix}) |\sigma_i|$$

(4)

which shows that the value of $\gamma |P_{ix}|$ appears as an extra magnetic field. The mean value of $|P_{ix}|$ annulate the external field when $\gamma/J \approx 0.02$ for an applied field $h/J = 0.01$, and the convergency is the slowest for this
value of $\gamma$. Taking this into account, we found that it was necessary 5000 iterations per spin to obtain thermal equilibrium and other 5000 to get the mean values of the energy and magnetization; this numbers were used in every case.

Eq. (4) may also be used to analyze the meaning of the $\beta$ parameter. The first and third terms in eq.(2) can be written

$$H_1 = -J \sum_{<i,j>} \sigma_i \sigma_j - \beta \sum_{\{i,j\}} P_{ix} P_{jx}$$

$$= -J \sum_{<i,j>} \sigma_i \sigma_j - \beta \sum_{\{i,j\}} |P_{ix}| |\sigma_i| |P_{jx}| |\sigma_j|$$

$$=- \sum_{\{i,j\}} (J + \beta |P_{ix}||P_{jx}|) \sigma_i \sigma_j - J \sum_{<i,j> \neq \{i,j\}} \sigma_i \sigma_j$$

So it can be seen that the $\beta$ parameter makes the exchange anisotropic, modifying its value in the $\vec{x}$ direction, leaving the coupling in the $\vec{y}$ direction unaltered.

We performed the calculation as function of the temperature for different values of the $\beta$ parameter for $\gamma = 0$; then repeated the calculation for $\beta = 0$ to study the dependence of the results from $\gamma$, and finally we made a complete study of the form and transition temperature of the system as a function of both parameters. As $J$ determines the transition temperature for the Ising model, we used it as unit of energy for the whole system.

To make the results clear, we made calculations as function of the temperature for different values of $\beta$, when $\gamma$ is zero-meaning that the electric interaction is bigger than the magnetoelectric one. After that, we calculated the minimum as function of $\gamma$, when $\beta$ is zero. The complete calculation, with both parameters different from zero gives a clear vision of the total behavior of our model. The results for the ferromagnetic case are shown in Figs. 1, 2, and 3. The first and second figures show the change in the shape of the transition caused by the $\beta$ and $\gamma$ parameters. The effect of the $\beta$ parameter is principally to shift the transition, as seen in Fig. 2. The $\gamma$ value can be positive and negative, and the effect is to broaden the transition, and invert the magnetization-polarization when the sign of it is changed. Fig. 3 shows the complete dependence of the transition temperature depending of both parameters.

Figs. 1, 2 and 3 show the results for the ferromagnetic case. Fig. 1 shows the effect of the $\gamma$ parameter: as the transition is determined by $J$, the effect of $\gamma$ is to broaden the transition. Fig. 2 shows the effect of $\beta$, which is to shift the transition without great modifications in the shape of it. Fig. 3 resumes the complete model, showing the effect of both parameters together. The induced electric polarization appears at the same temperature as the magnetic transition in all the cases, as it is defined by the model. As the model only allows, both $P/P_0$ and $M/M_0$ curves coincide.

FIG. 1: (color online) Normalized magnetization (and electric polarization) as function of the temperature when $\beta = 0$ in the first model.

FIG. 2: (color online) The same temperature dependencies as in Fig. 1, when $\gamma = 0$, in the first model.

2. Antiferromagnetic case

The antiferromagnetic case was treated similarly. It requires a negative value of $J$, but several changes in the other terms of the Hamiltonian are necessary. The magnetization of both sublattices will be coupled to the electric lattice opposed, in order to obtain the required ferroelectricity. The magnetic field is set to zero, because only can be directed parallel to one of the magnetic sublattices. The convergence is slowest for zero field, which we used to obtain the values for convergence. Our results in this case are very similar to those above, and we lack here of space to show them completely. Fig. 4 presents the transition temperature dependence for this case, which can be compared with the ferromagnet. The complete results will be publish elsewhere, together with a more sophisticated model for the spin-lattice coupling.
FIG. 3: (color online) The general results for the first model. The transition temperature is the same for both the electric and the magnetic transitions (see text).

FIG. 4: (color online) The general results for the first model in the antiferromagnetic case. The transition temperature is the same for both the electric and the magnetic transitions (see text).

FIG. 5: (color online) Normalized magnetization and electric polarization as functions of T for $\beta/J = 1$ in the second model.

B. The second model

As seen above, the first model does not contain the capacity to allow different temperatures for the electric and the magnetic transitions, giving us only the changes generated in the shape of the transitions by the magneto-electric coupling. We decided to develop a second model, where the transition temperatures are independent. To maintain the simplicity of the model, and the number of independent parameters reduced to three, we included an energy $\Delta = \varepsilon_2 - \varepsilon_1$ for the pair of magnetic-electric moments. When the spin is up, and the electric dipole points the left, or when the spin points down, and the electric dipole to the right, they will have an energy $\Delta$ higher than in the other two cases. If we make $\Delta \to \infty$ we recover the first model again, for the system will be in the lower state all time.

We changed some other things in the new model. In-
FIG. 6: (color online) Calculated magnetization and polarization per spin/dipole, for the second model when $\beta/J = 2$ as functions of $T$. It can be seen that $M/M_0$ is strongly distorted, while $P/P_0$ is not.

Instead of the classical electric dipoles oriented at random at $T \to \infty$, we substituted the electric lattice by an Ising lattice, oriented in the $\hat{x}$ direction, that is, as formerly, the electric dipoles form the ferroelectric part of the lattice when they are oriented in the positive $\hat{x}$ direction. We excluded the local interaction between the pairs, considering that the electric interaction is only in the $\hat{x}$ direction, let’s say, the tails of the interaction after first neighbors cutted off. The result is that we substitute the magnetoelectric interaction for this two-level system.

We used again the exchange coupling parameter $J$ as energy unit; as can be seen, this model has two independent transition temperatures for the magnetic and electric lattices, as $J$ and $\beta$ are independent in this model.

To use the Monte Carlo method again, we need to preserve the mathematical requirements for it, then our model needs to behave as a Markovian one. To accom-

FIG. 7: (color online) Results for $\beta/J = 0.5$ in the second model. In this case, the magnetic function is not distorted, but the polarization is.

Hence, the complete Hamiltonian is, in this case

$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i - \beta \sum_{\langle i,j \rangle} P_{ix} P_{jx} + \sum_i \epsilon_i \quad (6)$$

where the symbols are the same as before, and the $\epsilon_i$ the energy of the pair magnetic-electric momenta as defined above. We used again the exchange coupling parameter $J$ as energy unit; as can be seen, this model has two independent transition temperatures for the magnetic and electric lattices, as $J$ and $\beta$ are independent in this model.
FIG. 8: (color online) Results of the second model when $\Delta/J = 0.5$ and changing the $\beta$ parameter for $\beta/J \leq 1$. The shape of the polarization curves are distorted and shifts as the electric transition temperature is increased.

FIG. 9: (color online) Calculated polarization and magnetization for $\Delta/J = 0.5$, for values of the $\beta$ parameter when $\beta/J \geq 1$.

To accomplish this requirement, the minimum of energy is calculated through the following steps:

a - As in the first model, the initial state of the system is at $T \to \infty$. Then the value of the temperature is inserted in the calculation.

b - One number $A$ is then chosen at random between zero and one. If this number is zero, we invert the corresponding spin; instead, for $A = 1$, the inversion is performed on the electric dipole.

c - One of the pair of moments is chosen at random. If $A = 0$, we calculate the energy difference if the spin is inverted. From eq. (6), this energy difference will be

$$\Delta E_1 = 2\sigma_i(JS_S + h) + \sigma_iP_{ix}\Delta$$  \hspace{1cm} (7)

where $\sigma_i$ is the chosen spin, $S_S$ the sum of the first spins which are nearest neighbors to it, and $P_{ix}$ the component of the electric dipole of the pair. If $\Delta E_1$ is negative, the spin is inverted. If $\Delta E_1$ is positive, we use the Metropolis comparison: if a new random number $0 \leq r \leq 1$, when compared with the energy population is less than that (that is $r \leq \exp(-\Delta E_1/k_B T)$) the spin is inverted too. If not, the spin is left unaltered.

d - If $A = 1$ the electric dipole is inverted; the energy
difference in this case is
\[ \Delta E_2 = 2P_{ix}\beta S_D + \sigma_i P_{ix}\Delta \] 
(8)

Here the value of \( S_D \) is the sum over electric dipoles which are nearest neighbors to the one chosen. The other symbols have the meaning above. Again, if \( \Delta E_2 \) is negative, the dipole is inverted, and if positive, the random number \( r \) is calculated and used to compare with the populations in order to decide the inversion of the dipole.

e - The procedure from b) to d) is repeated as many times as necessary to obtain convergence to thermal equilibrium as defined for the first model. Then the temperature is reduced further and the calculation repeated to equilibrium.

The model respects the symmetry requirements for magnetoelectricity. The system does not contain temporal nor spacial inversion, so this exigency is accomplished too.

1. Convergence.

Differently from the first case, this second one does not contain a strong local coupling for the pair, and even the local change is not always decided by the spin system. It was necessary, then, to realize an independent study for every pair of the parameters, \( \Delta \) and \( \beta \). We do not believe that the insertion of the whole convergence study could be interesting for the reader, so we just mention that the number of Monte Carlo steps per spin for convergence varies from 5 to 50 thousand steps, the small value for \( \Delta/J = 0, \beta/J = 1 \) and the maximum for \( \Delta/J = 1, \beta/J = 2 \).

2. Results

We performed complete calculations for several cases, described below

1 - Thermal dependence of polarization and magnetization when \( \beta/J = 1 \) (that is, the transitions occur at the same temperature) and \( \Delta \) varies.

2 - The same study, for \( \beta/J > 1 \).

3 - The same again, when \( \beta/J < 1 \).

4 - The thermal dependence, as function of \( \beta \), for \( \Delta/J = 0.5 \).

Now we will describe the results for every case from 1 to 4.

1 - As the electric dipoles are not strongly coupled to his magnetic neighbor, and they can assume both orientations, the shapes of the transitions are different, as can be seen in Fig. (5). As there is not an applied electric field, the relative orientation of the polarization and the magnetization could be at random, as can be seen in the figure. The transition temperature increases with the value of \( \Delta \), meaning that the coupling helps to maintain the system ordered.

2 - Fig. (6) shows the results for \( \beta/J = 2 \). As can be seen, the transitions differ strongly in shape, and the curve of magnetization is shifted to accompany the polarization transition, as \( \Delta \) increases. This coincides with the idea that the second model limits with the first, when \( \Delta \to \infty \). Anyway, we were not able to calculate this case for high values of \( \Delta \), for the time of convergence increases too much.

3 - The case where the electric transition occurs at lower temperature than the magnetic one is presented in Fig. (7). Here, the magnetic transition is not deformed, and the electric one is distorted, with the tendency to accompany the magnetization for \( \Delta \to \infty \). Again, we were limited to values of \( \Delta \) allowed by the time of convergence of the calculation.

4 - The calculation was performed for \( \Delta/J = 0.5 \) for different values of the transition temperatures (\( J \leq \beta \)).
The results are shown graphically in Figs. (8) and (9). We separated the results when the electric transition is at lower temperature than the magnetic (Fig. (8)), and the opposite, when $\beta \geq J$ (Fig. (9)). It can be observed in both cases that the transition occurring at higher temperature remains almost undistorted, and the one whose transition temperature is smaller, distorted and shifts. Fig. (10) shows the transition temperatures, electric and magnetic, when $\Delta / J = 0.5$ as functions of $\beta$. Of course, both curves equal when $\beta / J = 1$.

The magnetic transition tends to saturate for small or great values of $\beta$, while the electric transitions behave almost linearly.

III. CONCLUSIONS AND PERSPECTIVES.

Magnetoelectricity and magnetoferroics are studied experimentally using the phenomenological free energy obtained just from symmetry and the (possible) interaction between magnetic and electric fields, as follows:

$$F(\vec{E}, \vec{H}) = F_0 - P_i^S E_i - M_i^S H_i - \frac{1}{2}\epsilon_{ijkl} E_i E_j - \frac{1}{2}\mu_0 \mu_{ijkl} H_i H_j - \alpha_{ij} E_i H_j - \ldots$$

and we have:

$$P_i = -\frac{\partial F}{\partial E_i} = P_i^S + \epsilon_0 \epsilon_{ij} E_j + \alpha_{ij} H_j + \ldots$$

$$M_i = -\frac{\partial F}{\partial H_i} = M_i^S + \mu_0 \mu_{ij} H_j + \alpha_{ji} E_j - \ldots$$

where it can be seen that the experimental measurement of the magnetoelectric tensor, $\alpha_{ij}$, is performed looking for the difference of the observed magnetization (polarization) with and without an external magnetic (electric) field. To calculate that parameter, we followed the same procedure, calculating for every temperature the magnetic polarization with and without an applied field, that is

$$\alpha_{ij}(T) \simeq \frac{P_i - P_i^S}{H_j}$$

as the experiments are made.

Fig. (11) presents the results for both models, when the transition temperatures are the same ($J = \beta$) in the second model. The magnetoelectric coefficients go to zero at $T = 0$, which is expected in a system that saturates magnetically and electrically too. Our models do not include the possibility to change the energy saturated at 0 K, but the experiments (see ref. 3) show a remanent value of the parameter. Our model does not include any effect in other than the $\hat{x}$ axis, thus, we only obtained the $\alpha_{xz}$ magnetoelectric coefficient within both models.

The transition in ref. 3 is first order, that is, the coefficient does not exist for temperatures above the magnetic transition, contrary to our models, where both transitions are second order, and as that, the curves in Fig. (11) extend to high temperatures.

Resuming, our calculation arrives to many similitudes and differences with experiment. We believe that this can be the simpler way to simulate real systems, and developing more elaborated spin-lattice terms in the Hamiltonians will help to interpret the experimental results in an easy way.

1. M. Fiebig, J. Phys. D: Appl. Phys. 38, R123 (2005).
2. D. Vaknin, J.L. Zarestky, J-P. Rivera and H. Schmid, Phys. Rev. Lett. 92, 207201 (2004).
3. As an example see J.M. Kosterlitz, D.R. Nelson and M.E. Fischer, Phys. Rev. B 13, 412 (1976).
4. D. Vaknin, J.L. Zarestky, J.E. Ostensen, B.C. Chakoumakos, A. Goñi, P.J. Pagliuso, T. Rojo and G.E. Barbara, Phys. Rev. B 60, 1100 (1999).
5. D. Vaknin, J.L. Zarestky, L.L. Miller, J-P. Rivera and H. Schmid, Phys Rev. B 65, 224414 (2002).
6. J. Li, W. Tian, Y. Chen, J.L. Zarestky, J.W. Lynn and D. Vaknin, Phys. Rev. B 79, 144410 (2009).
7. T.H. O’Dell The Electrodynamics of Magneto-Electric Media (Amsterdam: North-Holland) (1970).
8. N. Hur, S. Park, P.A. Sharma, S. Guha and S.-W. Cheong, Phys. Rev. Lett., 107207 (2004).
9. M.E.J. Newman and G.T. Barkema Monte Carlo Methods in Statistical Physics (Oxford: Claredon Press) (2001).