Ferrroelectric Phase Transitions and the Ising Model

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The Ising model has been an important theoretical tool in the understanding of phase transitions in ferroelectric materials. We first review how it relates to the underlying physics of order-disorder phase transitions in these systems, as well as mean-field results for the spontaneous polarization and the dielectric constant near the critical temperature. For hydrogen-bonded ferroelectrics, a term of interaction with an external transverse field is necessary to account for proton tunneling between the two minima of a double-well potential. Finally, we discuss both experimental and theoretical results for the problems of proton-lattice interactions, central peak dynamics, dynamical behavior of pseudo-one-dimensional ferroelectrics and pressure effects on hydrogen bonded ferroelectrics.

I Introduction

We begin with the Hamiltonian of a crystal used in the study of ferroelectric phase transitions [1]. A ferroelectric phase transition is classified as a displacive-type or order-disorder type transition. For a displacive phase transition some requirements are imposed on the Hamiltonian parameters so that a transition takes place on the crystal. For an order-disorder transition a disordered lattice becomes ordered with lowering of the temperature. Quantum effects may also become important in this case.

In order to obtain the Hamiltonian we take a single-ion model. Consider a diatomic crystal consisting of atoms A and B and assume that in a phase transition A atoms move while B atoms remain fixed. The forces acting on atom A are due to the neighboring B atoms and also from next-neighbor A atoms. Let $u(\vec{R})$ be the displacement along an axis, say the z-axis, of an atom A in the unit cell whose center is located at $\vec{R}$. The Hamiltonian is

$$H=\sum_{\vec{R}}(\frac{1}{2}au(\vec{R})^2+\frac{1}{4}bu(\vec{R})^4)+\frac{1}{2}c\sum_{\vec{R},\vec{R}'}(u(\vec{R})-u(\vec{R}'))^2 \tag{1}$$

where $a<0$, $b>0$ and c is the stiffness coefficient for the forces (strings) linking the particles. The first term in Eq. (1) describes the interaction between A and B atoms while the second term describes the interaction between atoms A. Let us explain how the two types of phase transitions are described by this Hamiltonian.

(a) *Displacive phase transitions ($|a|\ll c$).* For $T>T_c$, the mean positions of atoms A are in the centers of the cells and, therefore, $u(\vec{R})=0$, except for $\vec{R_0}$, which is the coordinate of the cell center. The potential acting on an A atom is

$$U=\frac{1}{2}(a+6c)u(\vec{R_0})^2+\frac{1}{4}bu(\vec{R_0})^4 \tag{2}$$

The coefficient of the first term is positive and the individual A atom moves in an effective potential with a single minimum (Fig. 1).

(b) *Order-disorder phase transitions ($|a|\gg c$).* In Eq. (2), if $|a|\gg c$ the first term is negative, while the second is positive. An individual atom moves in a symmetric phase in a double well potential (Fig. 2). Each atom occupies one of the two equilibrium positions corresponding to the energy minima,

$$u_{1,-1}=\pm\sqrt{\frac{|a|}{b}}=\pm u(\vec{R_0}). \tag{3}$$

The displacement of an A atom from the center of the unit cell is a quantity which can have only two values,

$$u(\vec{R})=uS(\vec{R_0}), \tag{4}$$

where $S(\vec{R})=\pm1$. Inserting Eq. (4) into Eq. (1) and considering that $S(\vec{R})^2=1$, we find that

$$H=\frac{1}{2}\sum_{\vec{R},\vec{R}'}JS(\vec{R})S(\vec{R}') \tag{5}$$

where $J=2cu_0^2$ and terms not containing $S(\vec{R})$ have been omitted. This is the Ising Hamiltonian, used to describe order-disorder phase transitions.

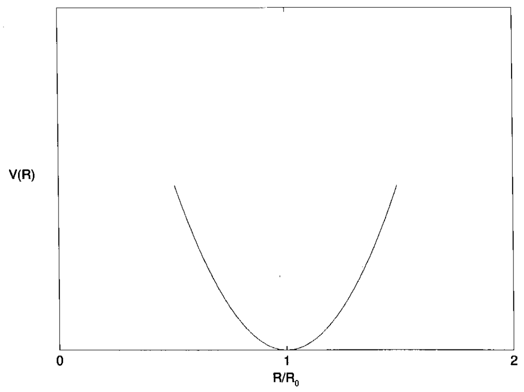

Figure 1. Effective potential with a single minimum, occurring in displacive phase transitions.

II Order-disorder ferroelectrics

In these ferroelectrics, the particles perform oscillations relative to their equilibrium positions, and can also move from one equilibrium position to the other, under the action of randon thermal forces. Therefore, they move a distance of $2u(\vec{R_0})$ and a charged particle performing such a motion, from position 1 to -1, or from -1 to 1, can be regarded as a reversible electric dipole. The dipole moment is $p = \pm eu(\vec{R_0})$. So, in the disordered phase the crystal is a system of randomly aligned dipoles. The particles occupy either equilibrium position with the same probability. In a phase transition the probabilities of the two equilibrium positions are unequal. In the ordered phase each particle occupies one of the positions for a longer period of time than in the other. As we mentioned earlier the Ising Hamiltonian describes this mechanism.

In order to get some basic information on order-disorder ferroelectrics we use the results of the mean field approximation, which are more accurate the larger the radius of interaction of the particles. The main results are the following:

(i) The temperature dependence of the spontaneous polarization is given by

$$P^2 = -(\frac{3p^2}{v^2})\frac{(T-T_c)}{T_c}, \tag{6}$$

where p is the dipole moment, v is the volume of the unit cell, $T_c = J_0/k_B$ is the Curie transition temperature, and $J_0 = \sum_{\vec{R'}} J(\vec{R}, \vec{R'})$ is a constant representing the interaction of the particle at $\vec{R}$ with all the other particles in the range of interaction of radius $\vec{R_0}$.

(ii) The dielectric constant along the direction of the polarization is

$$\varepsilon = 1 + \frac{4\pi p^2}{J_0 v}\frac{T_c}{T - T_c}. \tag{7}$$

The Curie-Weiss law is thus obtained, with the Curie constant $C = 4\pi p^2 T_c / J_0 v$. The type of interaction in the system has to be given so that the value of J_0 can be obtained before quantitative calculations are performed.

(iii) The electric field (mean value) acting on each particle is

$$E = E_0 + \frac{J_0 v}{p^2} P, \tag{8}$$

where E_0 is the macroscopic field. For crystals belonging to the order-disorder type, the relation $C/T_c = 4\pi/\beta = 3$ is approximately fulfilled, where $\beta = J_0 v/p^2$ is known as the Lorentz factor. The following are examples of order-disorder crystals: (a) TGS, $T_c = 322\,\mathrm{K}$ and $C = 3200\,\mathrm{K}$; (b) $NaNO_2$, $T_c = 433\,\mathrm{K}$ and $C = 5000\,\mathrm{K}$; (c) KH_2PO_4, $T_c = 123\,\mathrm{K}$ and $C = 3600\,\mathrm{K}$. On the other hand, in the case of crystals of the displacive type that relation is not fulfilled even approximately, as in $BaTiO_3$, where $T_c = 400\,\mathrm{K}$ and $C = 170000\,\mathrm{K}$.

(iv) Another test to characterize an order-disorder transition is the change of the entropy from $T = 0\,\mathrm{K}$ to $T = T_c$. In that case one obtains $\Delta S = R \ln 2$ per mole. In orders of magnitude the value $\Delta S/R \sim 1$ is an indication of an order-disorder type crystal. In fact, for TGS, $\Delta S/R = 1.1$, while $NaNO_2$ and KH_2PO_4 have the same numerical value, namely 0.7.

III Tunneling effects in ferroelectrics

An order-disorder phase transition occurs when the disorder effects ($k_B T$) are comparable with the ordered effects (J_0). However, if the masses of the particles responsible for the dynamics are small, such as hydrogen, then quantum-mechanical tunneling of the particles through the barrier (see Fig. 2) will add to the disorder mechanism. We will now sketch the deduction of the Hamiltonian which describes quantum-mechanical order-disorder phase transitions. The Hamiltonian will turn out to be the transverse Ising model [2].

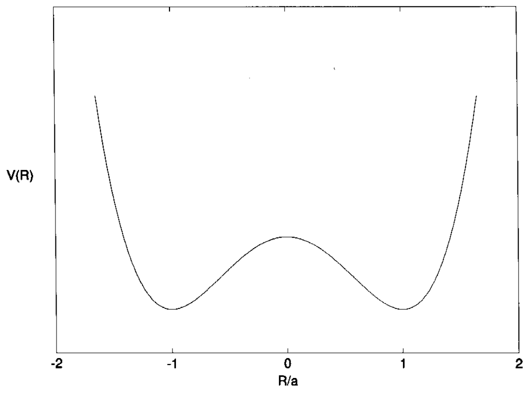

Figure 2. Effective double-well potential, where an atom lies at one of the equilibrium positions with minimum energy.

The state of each particle in a double-well potential can be represented by the wave function,

$$\varphi = c_1\varphi_1 + c_2\varphi_2, \tag{9}$$

where φ_1 and φ_2 are the wavefunctions describing the states of the particle on the left and right sides of the potential, with the normalization condition $c_1^2 + c_2^2 = 1$. Note that excited states are not considered here. Upon considering the effects of tunneling across the double-well internal barrier, the ground state energy ε_0 will split into two levels, with energies $\varepsilon_1 = \varepsilon_0 - \Omega$ and $\varepsilon_2 = \varepsilon_0 + \Omega$, corresponding to symmetric (ψ_1) and anti-symmetric (ψ_2) combinations. Hence the wavefunction describing the system is

$$\psi = a_1\psi_1 + a_2\psi_2, \tag{10}$$

where

$$a_1 = \frac{1}{\sqrt{2}}(c_1 - c_2) \qquad \text{and} \qquad a_2 = \frac{1}{\sqrt{2}}(c_1 + c_2). \tag{11}$$

The Hamiltonian of the many-particle system is given by

$$H = \sum_{\vec{R}} H_0(\vec{R}) + \frac{1}{2}\sum_{\vec{R},\vec{R}'} V(\vec{r} - \vec{r'}), \tag{12}$$

where $\vec{r'} = \vec{R} + u(\vec{R})$ and

$$H_0 = \begin{pmatrix} \Omega & 0 \\ 0 & -\Omega \end{pmatrix} = \Omega S^z(\vec{R}). \tag{13}$$

Notice that the energies have been shifted by ε_0. Here $S^z(\vec{R})$ are the spin-1/2 Pauli matrices, and $V(\vec{r} - \vec{r'})$ is the interaction operator. The latter can be expanded in terms of the displacements of the particles $u(\vec{R}) = u$, for $u \ll \vec{R}$, as follows,

$$V(\vec{r} - \vec{r'}) = V(\vec{R} - \vec{R}') + (\vec{u}(\vec{R}) - u(\vec{R}')V'(\vec{R} - \vec{R}') + \frac{1}{2}(u(\vec{R}) - u(\vec{R}'))^2 V''(\vec{R} - \vec{R}') + \ldots \tag{14}$$

The matrix representation of the particle displacement is,

$$u(\vec{R}) = \begin{pmatrix} u_{11} & u_{12} \\ u_{21} & u_{22} \end{pmatrix}, \tag{15}$$

where

$$u_{ij} = \int \psi_i u \psi_j^* dv. \tag{16}$$

By taking into account the symmetries of the displacements (u is an odd function of the coordinates), of the potential (even function of the coordinates) and of the functions ψ_1 and ψ_2 (even and odd, respectively), we obtain after a straightforward calculation the Hamiltonian in terms of spin-1/2 Pauli operators, $S^x(\vec{R})$ and $S^z(\vec{R})$,

$$H = V_0 + \Omega' \sum_{\vec{R}} S^z(\vec{R}) - \frac{1}{2}\sum J(\vec{R} - \vec{R}')S^x(\vec{R})S^x(\vec{R}'), \tag{17}$$

where $V_0 = \sum_{\vec{R},\vec{R}'} V(\vec{R} - \vec{R}')$, $\Omega' = \Omega + \frac{1}{4}\sum_{\vec{R}'} V''(\vec{R} - \vec{R}')(u_{11}^2 - u_{22}^2)$ and $J(\vec{R} - \vec{R}') = 2V''(\vec{R} - \vec{R}')u_{12}^2$. In the representation of the functions φ_1 and φ_2, we obtain,

$$H = -\Omega \sum_{\vec{R}} S^x(\vec{R}) - \frac{1}{2}\sum_{\vec{R},\vec{R}'} J(\vec{R} - \vec{R}')S^z(\vec{R})S^z(\vec{R}'), \tag{18}$$

which is the transverse Ising model Hamiltonian.

The polarization is proportional to $< S^z >$ and, in the mean field approximation, it can be obained by solving the transcendental equation,

$$\frac{\sqrt{(\Omega^2 + J_0^2 < S^z >^2)}}{J_0} = \tanh(\frac{\sqrt{(\Omega^2 + J_0^2 < S^z >^2)}}{k_B T}). \tag{19}$$

The transition temperature obtained within the mean field approximation is

$$T_c = \frac{2J_0}{k_B} / \frac{\Omega/J_0}{\ln\frac{1+\Omega/J_0}{1-\Omega/J_0}}. \tag{20}$$

With the increase of tunneling (as we are setting $\hbar = 1$, the tunneling frequency is 2Ω) the transition temperature drops and $T_c \to 0$ as $\Omega \to J_0$. Therefore, tunneling works as a disorder mechanism.

IV Discussion of experimental and theoretical results

We shall present now some experimental results that have been explained by the use of the models discussed previously. They are the result of investigations done in the Physics Department of the Federal University of Minas Gerais, Brazil. More recent experimental and theoretical results can be found elsewhere [3].

(a) Proton-Lattice Interactions.

The addition of a $B_{ij}S_i^x S_j^x$–type coupling between the tunneling motion of one proton and that of another to the Ising model in a transverse-field Hamiltonian, or the addition of the probably larger $S_i^z F_i^x Q_i$–type pseudospin phonon coupling (describing the modulation of the distance between the two equilibrium sites in a *O-H-O* bond by nonpolar phonons), results in a temperature-dependent renormalization of the proton tunneling integral [4]. This is important close to T_c, where the soft-mode frequency vanishes, $\omega_{crit} \to 0$. This may lead to large isotope shifts in T_c on deuteration even for small values of the tunneling integral and may explain some phenomena observed in $PbHPO_4$ [5,6] and squaric acid [7] as well as the dependence of the effective proton-lattice interaction constant on hydrostatic pressure in KH_2PO_4-type systems. This last effect may be also due to the presence of a $S_i^x D_i^x Q_i^2$ term in addition to the Kobayashi term $S_i^z F_i^z Q_i$ when coupling with polar optic phonons is taken into account [4]. When the lattice motion is so anharmonic that the lattice ions move in a double-well potential and the proton-lattice coupling are so strong that the protons can tunnel in only one out of the two possible lattice configurations, two Curie temperatures may appear [4].

(b) Dynamic Central Peak.

Measurements of the temperature and frequency dependence of the proton and deuteron spin-lattice relaxation, T_1, show the presence of a dynamic central peak in paraelectric KH_2PO_4, which exhibits a dramatic narrowing on deuteration. The results of an NMR study of the frequency and temperature dependence of the proton and deuteron T_1 in paraelectric KH_2PO_4 and deuterated KD_2PO_4, represented the first direct observation of the narrowing of a dynamic central peak on deuteration [8]. The central peak in deuterated KD_2PO_4 is more than two orders of magnitude narrower than the dynamic central peak in paraelectric KH_2PO_4. A continued-fraction calculation of the order-parameter fluctuation spectrum of KH_2PO_4 as a function of deuterium content qualitatively reproduces the observed central-peak narrowing on deuteration. The two studies together represent strong evidence that small dynamic intrinsic clusters occur in KDP-type crystals in addition to large static defect-induced clusters observed in light-scattering experiments. The study showed as well that naturally abundant deuterium cannot be the cause of the observed static (light-scattering) and dynamic (T_1 NMR) central peaks in KH_2PO_4.

(c) Dynamics of Pseudo-One-Dimensional Crystals.

Cesium dihydrogen phosphate CsH_2PO_4 is a hydrogen bonded ferroelectric crystal which undergoes an order-disorder phase transition at $T_c = 152$K. The shift of the phase transition temperature $T_c = 267$K in the isomorph deuterated compound CsD_2PO_4 indicates that the motion of the proton in the hydrogen bonds has an important role for the ferroelectricity in these materials. Results of X-ray diffraction [9] and neutron scattering experiments [10] showed that the hydrogen bonds in CsH_2PO_4 run along chains. It has been also shown [11] that the intrachain interactions due to the hydrogen bonds are much stronger than the interchain ones, a fact which characterizes the quasi-one-dimensional behavior of these crystals. Therefore, in order to study their properties theoretically it is desirable to take into account the strong intrachain interactions as exactly as possible while the interchain interactions can be treated within a mean field approximation. The dynamics of the strongly-anisotropic Ising model in a transverse field was used with the purpose of explaining the dielectric critical slowing down observed experimentally in the quasi-one-dimensional hydrogen-bonded ferroelectric crystal CsH_2PO_4. Good agreement with the experimental data on the temperature dependence of the dielectric constant and relaxation time has been obtained [12].

(d) Pressure Effects.

Experimental studies [13,14] indicate that the transition temperature of both $C_sH_2PO_4$ and $C_sD_2PO_4$ decreases as the pressure is increased. For $C_sD_2PO_4$ the critical temperature of the paraelectric-ferroelectric transition decreases at a rate $dT_c^d/dp = -8.5\,^oC/\text{Kbar}$, and for pressures larger than about 5.0–6.0 kbar the system orders antiferroelectrically. The Néel temperature of the paraelectric-antiferroelectric transition also decreases with pressure at a rate $dT_n^d/dp = -2.5\,^oC/\text{Kbar}$. The ferroelectric-antiferroelectric transition line in the T-p phase diagram was observed to be associated with a slope of about $35\,^oC/\text{kbar}$. The triple point was located at $P_c^d = 5.2\,\text{kbar}$ and $T_c^d = -55.2\,^oC$. A compressible pseudo-spin Ising model Hamiltonian is used to calculate the pressure-temperature phase diagram of quasi-one-dimensional hydrogen-bonded ferroelectric crystals such as CsD_2PO_4 [15]. Strong effective interactions, which are treated exactly along chains, and weak volume dependent interactions, which are treated in the mean field approximation, between chains, were assumed. In agreement with the experimental findings, the phase diagram exhibits a triple point and transition lines between ferroelectric, antiferroelectric and paraelectric phases. However, the results suggested that the Ising model may be too simple to account for the detailed form of the phase diagram of CsD_2PO_4.

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