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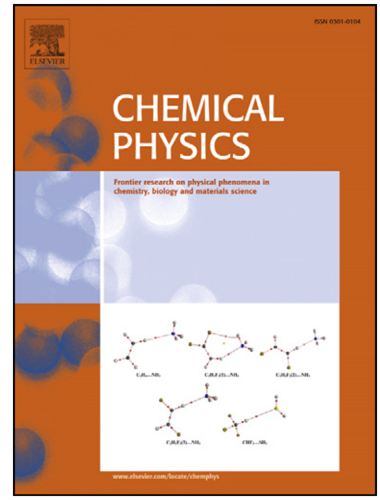

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Quantum Fluctuations in Insulating Ferroelectrics

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Abstract

It has been proposed that in a ferroelectric insulator, an applied magnetic field may couple the transverse phonon modes and produce left and right circularly polarized phonon modes which are no longer degenerate. We quantize the theory and examine the effects of quantal fluctuations. In particular, we show that the zero point fluctuations result in a large diamagnetic contribution to the magnetic susceptibility.

1 Introduction

Motivated by the discovery of a monotonic increase in the specific heat with applied magnetic field[1] in insulating ferroelectric Tri-Glycine Sulphate[2] (TGS), Dzyaloshinkii and Mills pointed out[3] that the degeneracy of the (dipole) phonon modes in a ferroelectric material may be lifted when a magnetic field is applied. The field-dependence of the free-energy that ensues is qualitatively consistent with the experimental results. The splitting originates from a phenomenological interaction term which is related to the standard paramagnetic interaction,

$$\hat{H}_{int} \;=\; -\,\frac{q}{2\;m\;c}\left(\;\overrightarrow{p}\;.\;\overrightarrow{A}\;+\;\overrightarrow{A}\;.\;\overrightarrow{p}\;\right) \tag{1}$$

where the paramagnetic current

$$\overrightarrow{j} \;=\; \frac{q}{m}\;\overrightarrow{p} \tag{2}$$

is replaced by the displacement current in accordance with Maxwell's equations. The analysis was based on a classical field theory where the Lagrangian density had a form similar to that given below

$$\mathcal{L} \;=\; \frac{1}{2}\left[\left(\frac{\partial\overrightarrow{\phi}}{\partial t}\right)^2 - c^2\left(\overrightarrow{\nabla}\;\overrightarrow{\phi}\right)^2 - \left(\frac{m\;c^2}{\hbar}\right)^2\overrightarrow{\phi}\;.\;\overrightarrow{\phi}\;\right] + \frac{\alpha}{2}\;\overrightarrow{B}\;.\;\left(\;\overrightarrow{\phi}\wedge\frac{\partial\overrightarrow{\phi}}{\partial t}\right) \tag{3}$$

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where the last term represents the phenomenological coupling term. The magnetic field is assumed to be applied in the direction parallel to the static polarization. The value of $\alpha\hbar/2$ is unknown but, when non-zero, plays the role of a magnetic moment. The gradient term has the form of a double scalar product, which is explicitly given by

$$\left(\overrightarrow{\nabla} \ \overrightarrow{\phi} \right)^2 = \sum_{\gamma=1}^{3} \overrightarrow{\nabla} \ \phi^\gamma \ . \ \overrightarrow{\nabla} \ \phi^\gamma \tag{4}$$

where the sum over the index γ runs over all the components of the real vector field. In this note, we shall re-derive the results of Dzyaloshinskii and Mills[3] by quantizing the classical field theory and we shall examine the polarization of the normal modes. Furthermore, we shall see that, within this model, the magnetic susceptibility is dominated by the field-dependence of the zero-point fluctuations.

2 The Quantized Excitation Spectrum

The process of Canonical Quantization[4] proceeds by re-writing the Lagrangian in terms of the Fourier transformed coordinate defined via

$$\overrightarrow{\phi}_{\underline{k}} = \frac{1}{\sqrt{V}} \int d^3\underline{r} \ \exp\left[- \ i \ \underline{k} \ . \ \underline{r} \right] \overrightarrow{\phi}(\underline{r}) \tag{5}$$

The Lagrangian is expressed as the sum of the Fourier components

$$\begin{aligned} L \ = \ & \sum_{\underline{k}} \frac{1}{2} \left[\left(\frac{\partial \overrightarrow{\phi}_{\underline{k}}}{\partial t} \right) . \left(\frac{\partial \overrightarrow{\phi}_{-\underline{k}}}{\partial t} \right) - \left(c^2 \ \underline{k}^2 \ + \ \left(\frac{m \ c^2}{\hbar} \right)^2 \right) \overrightarrow{\phi}_{\underline{k}} \ . \ \overrightarrow{\phi}_{-\underline{k}} \right] \\ & + \sum_{\underline{k}} \frac{\alpha}{2} \ \overrightarrow{B} \ . \ \left(\overrightarrow{\phi}_{\underline{k}} \ \wedge \ \frac{\partial \overrightarrow{\phi}_{-\underline{k}}}{\partial t} \right) \end{aligned} \tag{6}$$

where it should be noted that, since the field is real

$$\overrightarrow{\phi}^\dagger_{\underline{k}} = \overrightarrow{\phi}_{-\underline{k}} \tag{7}$$

Next the volume of k-space is partitioned into two disjoint regions, one region contains a set of $\underline{k}$ points which does not contain any pair of points which are related by inversion symmetry and the second region contains the inversion symmetry partners of the points in the first region. On treating the Fourier components $\overrightarrow{\phi}_{\underline{k}}$ and $\overrightarrow{\phi}^\dagger_{\underline{k}}$ as independent variables, one finds that the Lagrangian has the form

$$L = \sum_{\underline{k}}{}' \left[\left(\frac{\partial \overrightarrow{\phi}_{\underline{k}}}{\partial t} \right) . \left(\frac{\partial \overrightarrow{\phi}^\dagger_{\underline{k}}}{\partial t} \right) - \left(c^2 \ \underline{k}^2 \ + \ \left(\frac{m \ c^2}{\hbar} \right)^2 \right) \overrightarrow{\phi}_{\underline{k}} \ . \ \overrightarrow{\phi}^\dagger_{\underline{k}} \right]$$

$$+ \sum_{\underline{k}}{}' \frac{\alpha}{2} \vec{B} \, . \left[\vec{\phi}_{\underline{k}} \wedge \left(\frac{\partial \vec{\phi}^{\dagger}_{\underline{k}}}{\partial t} \right) + \vec{\phi}^{\dagger}_{\underline{k}} \wedge \left(\frac{\partial \vec{\phi}_{\underline{k}}}{\partial t} \right) \right] \tag{8}$$

where the summation is now restricted to half the volume of k-space. The canonically conjugate momenta are defined by

$$\begin{aligned} \vec{\Pi}_{\underline{k}} &= \left(\frac{\partial L}{\partial (\frac{\partial \vec{\phi}_{\underline{k}}}{\partial t})} \right) \\ &= \left(\frac{\partial \vec{\phi}^{\dagger}_{\underline{k}}}{\partial t} \right) + \frac{\alpha}{2} \vec{B} \wedge \vec{\phi}^{\dagger}_{\underline{k}} \end{aligned} \tag{9}$$

and similarly

$$\vec{\Pi}^{\dagger}_{\underline{k}} = \left(\frac{\partial \vec{\phi}_{\underline{k}}}{\partial t} \right) + \frac{\alpha}{2} \vec{B} \wedge \vec{\phi}_{\underline{k}} \tag{10}$$

The Hamiltonian is evaluated as the Legendre Transform of the Lagrangian

$$H = \sum_{\underline{k}}{}' \left[\vec{\Pi}_{\underline{k}} \left(\frac{\partial \vec{\phi}_{\underline{k}}}{\partial t} \right) + \vec{\Pi}^{\dagger}_{\underline{k}} \left(\frac{\partial \vec{\phi}^{\dagger}_{\underline{k}}}{\partial t} \right) \right] - L \tag{11}$$

which leads to the expression

$$\begin{aligned} H &= \sum_{\underline{k}}{}' \left[\vec{\Pi}_{\underline{k}} \vec{\Pi}^{\dagger}_{\underline{k}} - \frac{\alpha}{2} \vec{B} \, . \left(\vec{\phi}_{\underline{k}} \wedge \vec{\Pi}_{\underline{k}} + \vec{\phi}^{\dagger}_{\underline{k}} \wedge \vec{\Pi}^{\dagger}_{\underline{k}} \right) \right] \\ &+ \sum_{\underline{k}}{}' \left[\left(\frac{m c^2}{\hbar} \right)^2 + c^2 \underline{k}^2 + \left(\frac{\alpha}{2} \right)^2 \vec{B}^2 \right] \vec{\phi}_{\underline{k}} \, . \vec{\phi}^{\dagger}_{\underline{k}} \\ &- \sum_{\underline{k}}{}' \left(\frac{\alpha}{2} \right)^2 \left(\vec{B} \, . \vec{\phi}_{\underline{k}} \right) \left(\vec{B} \, . \vec{\phi}^{\dagger}_{\underline{k}} \right) \end{aligned} \tag{12}$$

It is seen that the components of the fields parallel to the applied magnetic field $\vec{B}$ are decoupled and unaffected by the field. Following Dirac[4], the Hamiltonian is quantized by replacing the canonically conjugate coordinate and momenta fields with operators, and their Poisson Brackets are replaced by the commutation relations

$$\begin{aligned} \left[\hat{\Pi}^{\alpha}_{\underline{k}} , \hat{\phi}^{\beta}_{\underline{k}'} \right] &= - i \hbar \, \delta_{\underline{k},\underline{k}'} \, \delta_{\alpha,\beta} \\ \left[\hat{\Pi}^{\alpha}_{\underline{k}} , \hat{\Pi}^{\beta}_{\underline{k}'} \right] &= 0 \\ \left[\hat{\phi}^{\alpha}_{\underline{k}} , \hat{\phi}^{\beta}_{\underline{k}'} \right] &= 0 \end{aligned} \tag{13}$$

The above canonical commutation relations are satisfied if the operators are expressed in terms of bosonic creation and annihilation operators as

$$\begin{aligned} \hat{\Pi}^{\beta}_{\underline{k}} &= i \sqrt{\frac{\hbar \ \Omega_{\beta,\underline{k}}}{2}} \left(a^{\dagger}_{\beta,-\underline{k}} \ - \ a_{\beta,\underline{k}} \right) \\ \hat{\phi}^{\beta}_{\underline{k}} &= \sqrt{\frac{\hbar}{2 \ \Omega_{\beta,\underline{k}}}} \left(a^{\dagger}_{\beta,\underline{k}} \ + \ a_{\beta,-\underline{k}} \right) \end{aligned} \tag{14}$$

where the frequencies $\Omega_{\beta,\underline{k}}$ are to be determined. Substitution of the above two expressions into the Hamiltonian along with the choices of

$$\begin{aligned} \hbar^2 \ \Omega^2_{z,\underline{k}} &= c^2 \ \hbar^2 \ \underline{k}^2 \ + \ m^2 \ c^4 \\ \hbar^2 \ \Omega^2_{x,\underline{k}} &= \hbar^2 \ \Omega^2_{y,\underline{k}} \ = \ c^2 \ \hbar^2 \ \underline{k}^2 \ + \ m^2 \ c^4 \ + \ \left(\frac{\alpha \ \hbar}{2} \right)^2 \ \overrightarrow{B} \ . \ \overrightarrow{B} \end{aligned} \tag{15}$$

yields the form

$$\begin{aligned} \hat{H} \ &= \ \sum_{\underline{k}} \frac{\hbar \ \Omega_{z,\underline{k}}}{2} \left(a^{\dagger}_{z,\underline{k}} \ a_{z,\underline{k}} \ + \ a_{z,\underline{k}} \ a^{\dagger}_{z,\underline{k}} \right) \\ &+ \sum_{x,y;\underline{k}} \frac{\hbar \ \Omega_{x,\underline{k}}}{2} \left(a^{\dagger}_{x,y:\underline{k}} \ a_{x,y:\underline{k}} \ + \ a_{x,y:\underline{k}} \ a^{\dagger}_{x,y:\underline{k}} \right) \\ &- i \sum_{\underline{k}} \frac{\alpha \ \hbar \ B}{2} \left(a^{\dagger}_{y,\underline{k}} \ a_{x,\underline{k}} \ - \ a^{\dagger}_{x,\underline{k}} \ a_{y,\underline{k}} \right) \end{aligned} \tag{16}$$

which is Hermitean and conserves the number of elementary excitations. In the above expression, the range of the summation has been restored to run throughout all of k-space. It is seen that the modes longitudinal w.r.t. B are plane-polarized, but the modes transverse wr.t. B are mixed due to the presence of the last term. It should also be noted that, since the creation and annihilation operators for different polarizations commute, the last term has no effect on the zero-point energy. The Hamiltonian can be diagonalized by performing a unitary transformation

$$\hat{\tilde{H}} \ = \ \hat{U}^{\dagger} \ \hat{H} \ \hat{U} \tag{17}$$

where

$$\hat{U} \ = \ \exp\left[\ - \ i \ \sum_{k} \ \Theta_{\underline{k}} \left(a^{\dagger}_{x,\underline{k}} \ a_{y,\underline{k}} \ + \ a^{\dagger}_{y,\underline{k}} \ a_{x,\underline{k}} \right) \right] \tag{18}$$

and $\Theta_{\underline{k}}$ is a yet to be determined real function. The effect of the transformation on the boson creation operators is given by

$$\begin{aligned} \hat{U}^{\dagger} \ a^{\dagger}_{x,\underline{k}} \ \hat{U} &= \cos\Theta_k \ a^{\dagger}_{x,\underline{k}} \ + \ i \ \sin\Theta_k \ a^{\dagger}_{y,\underline{k}} \\ \hat{U}^{\dagger} \ a^{\dagger}_{y,\underline{k}} \ \hat{U} &= i \ \sin\Theta_k \ a^{\dagger}_{x,\underline{k}} \ + \ \cos\Theta_k \ a^{\dagger}_{y,\underline{k}} \end{aligned} \tag{19}$$

and the transformed annihilation operators are given by the Hermitean conjugate expressions. Substituting the expressions for the transformed operators into the Hamiltonian yields terms diagonal and off-diagonal in the polarization indices. The off-diagonal terms are required to vanish, which occurs when $\Theta_k = \frac{\pi}{4}$. This choice yields the simple result

$$\begin{aligned} \hat{\tilde{H}} &= \sum_{\underline{k}} \left(\frac{\hbar\,\Omega_{z,\underline{k}}}{2} + \hbar\,\Omega_{x,\underline{k}} \right) \\ &+ \sum_{\underline{k}} \hbar\,\Omega_{z,\underline{k}}\, a^{\dagger}_{z,\underline{k}}\, a_{z,\underline{k}} \\ &+ \sum_{\underline{k}} \hbar \left(\Omega_{x,\underline{k}} + \frac{\alpha\, B}{2} \right) a^{\dagger}_{x,\underline{k}}\, a_{x,\underline{k}} \\ &+ \sum_{\underline{k}} \hbar \left(\Omega_{x,\underline{k}} - \frac{\alpha\, B}{2} \right) a^{\dagger}_{y,\underline{k}}\, a_{y,\underline{k}} \end{aligned} \tag{20}$$

which is in complete agreement with the findings of Dzyaloshinskii and Mills[3]. The phenomenological interaction has caused the degeneracy of the transverse modes to be lifted by the applied field, and the terms linear in B exactly cancel in the sum of the zero-point energies.

The above analysis shows that, in the transformed system, the boson creation and annihilation operators create and destroy elementary excitations of the system. The excitations in the untransformed system are given by the inverse transformation

$$\begin{aligned} \alpha^{\dagger}_{-,\underline{k}} = \hat{U}\, a^{\dagger}_{x,\underline{k}}\, \hat{U}^{\dagger} &= \frac{1}{\sqrt{2}} \left(a^{\dagger}_{x,\underline{k}} - i\, a^{\dagger}_{y,\underline{k}} \right) \\ \alpha^{\dagger}_{+,\underline{k}} = \hat{U}\, a^{\dagger}_{y,\underline{k}}\, \hat{U}^{\dagger} &= \frac{1}{\sqrt{2}} \left(a^{\dagger}_{y,\underline{k}} - i\, a^{\dagger}_{x,\underline{k}} \right) \end{aligned} \tag{21}$$

Since the polarization is represented by a vector field, the modes are expected to carry one unit of intrinsic angular momentum[5]. On recalling that the form of the infinitesimal generator for rotations of the vector field about the z-axis is given in the Cartesian coordinate representation by

$$S^{(z)} = \hbar \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{22}$$

one finds that the quantized operator corresponding to the z-component of the intrinsic angular momentum is given by

$$\hat{S}^{(z)} = i\,\hbar \sum_{k} \left(a^{\dagger}_{y,\underline{k}}\, a_{x,\underline{k}} - a^{\dagger}_{x,\underline{k}}\, a_{y,\underline{k}} \right) \tag{23}$$

Therefore, the commutation relations between $\hat{S}^{(z)}$ and $\alpha^{\dagger}_{\pm,\underline{k}}$ are found as

$$[\ \hat{S}^{(z)}\ ,\ \alpha^{\dagger}_{\pm,\underline{k}}\ ]\ =\ \pm\ \hbar\ \alpha^{\dagger}_{\pm,\underline{k}} \tag{24}$$

Hence, the excitations correspond to left and right circularly polarized phonons with $S^{(z)} = \pm\ \hbar$. Although non-planar polarized phonon modes are expected whenever the crystal has no inversion symmetry, the "creation" of circularly polarized phonon modes (w.r.t. B) by an applied magnetic field is highly unusual.

3 Results and Discussion

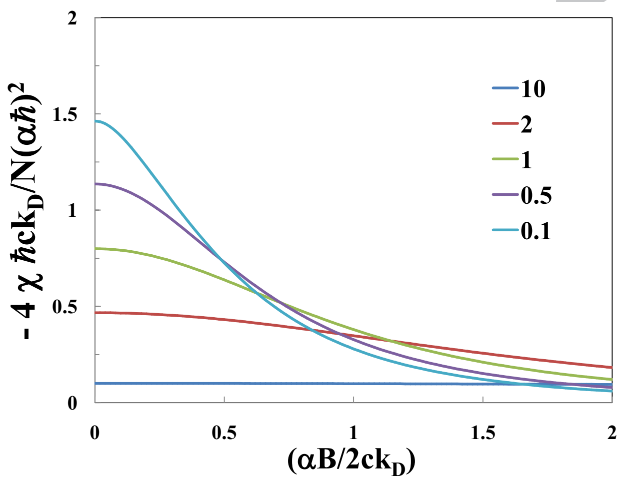

Figure 1: The field-dependence of the anomalous diamagnetic susceptibility (in dimensionless units), for various values of $mc/\hbar k_D$.

Dzyaloshinskii and Mills made several predictions for the thermodynamic behavior, based on the temperature dependence of the free-energy. Since the optic modes are expected to exhibit softening and broadening, their thermodynamic predictions are not easy to verify. By contrast, the zero-point fluctuations are expected to yield a large diamagnetic contribution to the magnetic susceptibility. Although the zero-point energy is formally divergent in the continuum model, much the same way as in an electromagnetic cavity[6], the zero-point energy will remain finite when the periodicity of the solid is re-introduced. The zero-temperature limit of the diamagnetic susceptibility is given by the expression

$$\chi\ =\ -\left(\frac{\alpha\,\hbar}{2}\right)^{2}\sum_{\underline{k}}\frac{\left(m^2\,c^4\ +\ \hbar^2\,c^2\,\underline{k}^2\right)}{\left[\,m^2\,c^4\ +\ \hbar^2\,c^2\,\underline{k}^2\ +\ \left(\frac{\alpha\,\hbar\,B}{2}\right)^2\,\right]^{\frac{3}{2}}} \tag{25}$$

which estimated as being of the order of

$$\chi \ \sim \ - \left(\frac{\alpha \ \hbar}{2}\right)^2 \ \frac{N}{m \ c^2} \tag{26}$$

for small fields, where $m \ c^2$ is the energy of the soft optic phonon and N is the number of atoms in the solid. For systems where the optic phonon modes show significant softening[7, 8], the susceptibility is not expected to diverge but instead is expected to be limited by the value of

$$\chi \ \sim \ - \left(\frac{\alpha \ \hbar}{2}\right)^2 \ \frac{3 \ N}{2 \ \hbar \ c \ k_D} \tag{27}$$

where k_D is a wave vector with a size characteristic of the radius of a spherical approximation to the Brillouin zone. Diamagnetic susceptibilities in insulating materials might be due to other mechanisms. Nevertheless, it might be expected that the field-dependence could be used to identify anomalous contributions due to our mechanism, if the moments are not too small ($\alpha\hbar/2 \sim \mu_B$). This could be expected since the diamagnetism of electronic origin should only show significant variation when the field strength is of the order of the relevant electronic energy scale, whereas the anomalous contribution is expected to show a variation which occurs at the much lower scale ($\sim$ 9.4 meV for TGS[9]) set by the phonon energies. The field-dependence of χ is sketched in figure(1). However, the most direct verification of the the theory would be the observation the frequency and field-dependence of the absorption of light consistent with the selection rules for absorption of circularly polarized light.

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