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STATIC AND DYNAMIC ASPECTS OF PERTURBED ANGULAR CORRELATION MEASUREMENTS IN PEROVSKITE CRYSTALS

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The static and dynamic aspects of the Electric Field Gradient (EFG) in ionic perovskite (anti-) ferroelectric crystals have been studied with particular emphasis on the Perturbed Angular Correlation method. We analyze the effect of the lattice fluctuations on the temperature behavior of the EFG. The proper averaging procedure of the perturbation function is outlined. This results in a simple relationship between the electric (sub-) lattice susceptibility and the measured EFG, predicting a critical behavior of EFG on approaching T_c. In addition to this dynamical effect we show that well below T_c, the temperature dependence of EFG is dominated by P_s^2, the square of the spontaneous polarization of the (sub-) lattice. These predictions are shown to be in qualitative agreement with published experimental data.

THE INTERACTION between the Electric Nuclear Quadrupole Moment of a nucleus with the Electric Field Gradient, V_{zz}, at the nuclear site is a valuable tool for the investigation of the local structure and its changes in a solid [1]. The EFG being determined by the distribution of the charges serves as a microscopic probe sensitive to any changes or rearrangements of the charge distribution occurring in the vicinity of the probe nucleus. Specifically, in an ionic crystal the changes in EFG reflect the deviations of the ionic sites from a higher to a lower symmetry configuration during a structural phase transition.

Theoretical calculations of the local EFG are usually performed by a lattice sum calculation taking into account the Sternheimer antishielding correction [2]. However, calculations of this type are of a static nature, being based on the assumption of a static ionic lattice.

In this work we show that the lattice sum calculation can be generalized and extended to describe also the dynamical nature of the lattice, namely to incorporate in the calculation the time-dependent fluctuations of the ionic coordinates. Our interest in this work is the description of V_{zz} in perovskite-type (anti-) ferroelectric ionic crystals. Above T_c these crystals possess a cubic symmetry. Below T_c they undergo a structural phase transition resulting in a slight deformation of the cubic symmetry.

In the following we develop a relationship between the fluctuation of the EFG and the macroscopic dynamical properties of the lattice. The shift of the ions from their corresponding cubic sites generates an electric dipole moment of the unit cell. This moment can be expressed as $q\zeta$ where q is the effective ionic charge and ζ is the separation between the positive and negative charge centres, in the deformed cubic unit cell. The size of the dipole, ζ, is proportional to the ionic displacements.

The time dependence of ζ can be expressed in the following way:

$$\zeta(t, T) = z_0(T) + \Delta z(t, T); \tag{1}$$

$z_0(T)$ is the average charge separation at temperature T, $\Delta z(t, T)$ expresses the time dependent fluctuations about z_0. Both the amplitude and frequency of Δz depend on the temperature T.

The instantaneous local EFG can be expanded in powers of ζ:

$$V_{zz}^{\mathrm{loc}} = V_{zz}(\zeta = 0) + \left(\frac{\mathrm{d}V_{zz}}{\mathrm{d}\zeta}\right)_0 \zeta + \frac{1}{2}\left(\frac{\mathrm{d}^2 V_{zz}}{\mathrm{d}\zeta^2}\right)_0 \zeta^2 + \ldots . \tag{2}$$

According to the definition of ζ, the constant term in this expansion corresponds to an instantaneous cubic symmetry configuration, thus being equal to zero. Furthermore, it can be shown [3] that for cubic symmetry V_{zz} is symmetric in ζ and thus $(\mathrm{d}V_{zz}/\mathrm{d}\zeta)_0$ vanishes also. Thus equation (2) can be written as:

$$V_{zz}^{\mathrm{loc}} \propto \zeta^2 = z_0^2 + 2z_0\Delta z + (\Delta z)^2 . \tag{3}$$

The connection between the instantaneous local V_{zz} [equation (3)] and the averaged measured EFG values depends on the experimental technique used. Thus it is important to specify, at this stage, the experimental method applied to measure V_{zz}. We concentrate in this work on the Differential Perturbed Angular

Correlation [4] technique, though most of the conclusions are of more general character and apply to other techniques (NQR, Mössbauer, etc.) as well. In the above technique the probe nucleus is radioactive and emits two successive γ-ray photons in cascade. The angular correlation between these two photons is measured as a function of the lifetime of the intermediate level. The ordinary angular correlation function is modified, due to the *static* electric quadrupole interaction, by a time dependent factor:

$$G_{22}(t) = \sum_{n=0} \sigma_{2n} \cos(\omega_n t). \tag{4}$$

The frequencies ω_n correspond to the quadrupole splitting of the level and for a cylindrically symmetric structure they are proportional to V_{zz}. The time-dependent factor $G_{22}(t)$ arises due to the quadrupole interaction induced precession of the nuclear spin in the intermediate nuclear state in a static V_{zz}.

When the quadrupole interaction is time-dependent, the situation is more complicated. In such case it is important to distinguish between two types of time dependence: stochastic and regular-periodic. The case of stochastic fluctuations has been extensively treated in literature [4–6] and is known to lead to an exponentially damped G_{22} due to a partial loss of spin "memory" On the other hand, in the case of regular-periodic fluctuations, the spin "memory" is retained and thus G_{22} possesses a definite periodic character as will be demonstrated.

In the following we divide our discussion into two frequency regimes.

(a) *Fast regime*, $\Omega_q \gg 2\pi/\tau$, where τ is the mean lifetime of the intermediate nuclear level and Ω_q is the frequency of a lattice mode with a wave vector $\mathbf{q}$. In this case the lattice fluctuation period $2\pi/\Omega q$ is much smaller than the time of measurement (which is of the order of τ). The rapid motion of the ions (both periodic as well as random) relative to the probe is reflected by the correspondingly rapid changes of V_{zz}. During the time of interaction, the nucleus experiences an effective, time averaged interaction proportional to $\bar{V}_{zz}$ (where the bar indicates time averaging).

In the cubic phase (above T_c) of a perovskite crystal, the first two terms in equation (3) vanish and thus the measured precession frequency $\omega_Q \propto \bar{V}_{zz}$ is also proportional to $\overline{(\Delta z)^2}$ [7]. However, according to the Fluctuation Dissipation Theorem [8–10] the mean square of the fluctuations is proportional to the susceptibility summed over all $\mathbf{q}$ vectors [11, 12] hence

$$V_{zz} \propto \overline{(\Delta z)^2} \propto T \sum_q \chi_q.$$

The significance of this result rests in the fact that it predicts a non-vanishing V_{zz} (and correspondingly – a non-vanishing ω_Q) even at temperatures well above T_c (which corresponds to the fast regime) in the cubic phase. This result is in contrast to the prediction of vanishing V_{zz} according to the rigid lattice sum calculation.

Extending our discussion to the temperature region below T_c (in the antiferro- or ferroelectric phase) it becomes evident that the z_0 term in equation (3) is related to the dipole moment of the (sub-) unit cell and thus proportional to the spontaneous polarization of the (sub-) lattice. Each probe experiences a locally time-averaged interaction, which upon applying the Fluctuation Dissipation Theorem, as well as recognizing that $\overline{\Delta z} = 0$ locally, leads to:

$$\bar{V}_{zz} = aP_s^2 + bT \sum_q \chi_q \tag{5}$$

where the averaging is performed both locally in time as well as experimentally over a large number of sites. Hence, the experimentally observed ω_Q reflects two kinds of temperature dependent features of the lattice. Far below T_c, ω_Q follows the temperature dependence of the square of the spontaneous polarization P_s^2 (in the case of an antiferroelectric crystal P_s corresponds to the spontaneous sublattice polarization). The second term in equation (5) predicts a critical behaviour of ω_Q in the close proximity of the transition temperature. This is due to the dominant contribution of χ_{q_0}, the (sub-) lattice susceptibility, which is connected with the soft mode [13] frequency Ω_{q_0} by the relation $\chi_{q_0} \propto \Omega_{q_0}^{-2}$ where $\Omega_{q_0}^2 \propto T - T_c$. In a ferroelectric transition the dominant susceptibility χ_{q_0} is connected with the wave vector $\mathbf{q_0} = 0$ while for an antiferroelectric crystal $\mathbf{q_0}$ corresponds to the Brillouin zone boundary wave vector and χ_{q_0} is the sub-lattice susceptibility.

(b) *Slow regime*, $\Omega_q \ll 2\pi/\tau$. In this case each nucleus senses an essentially constant perturbation. However, as there is no correlation between the phase of the fluctuating mode and the instant of the emission of the photon, the strength of the interaction at each site is different. Thus the experiment performs effectively a random sampling of the phases of the fluctuating modes. Although this situation is obviously different from that in the fast regime, we will be able to show that the measured G_{22} should possess a periodic character also in the slow regime. Moreover, we will show that in this case as well the observed perturbation frequency ω_Q above T_c is simply related to the (sub-) lattice susceptibility χ_{q_0}.

The experimentally observed perturbation function is given [4, 14] by the average of equation (4) over the frequency distribution function $f(\omega)$:

$$G_{22}^{\exp} = \int G_{22}(\omega t) f(\omega)\, d\omega. \tag{6}$$

Thus, in order to predict the behaviour of $G_{22}^{\exp}$ in the slow regime, it becomes essential to calculate the distribution function $f(\omega_Q)$ from which the distribution $f(\omega)$ can be obtained in a straightforward way.

We expect the slow regime to exist only very close to the transition temperature, due to the softening of the polarizing mode. Thus, assuming that the dominant fluctuations are due to a single (soft) mode, V_{zz} can be written as:

$$V_{zz}^{\text{loc}} \propto (\Delta z)^2 = A^2 \cos^2 \phi \tag{7}$$

where ϕ is the essentially constant random phase of the fluctuation during the time of interaction. Assuming a uniform distribution of ϕ over the range $0 \leqslant \phi \leqslant \pi/2$ (justified by the assumption of uniform distribution of the sampling-time instants), one can easily [15] obtain the distribution for V_{zz} above T_c and also the corresponding distribution for the precession frequency ω_Q:

$$f(\omega_Q) = \pi^{-1}[\omega_Q(\omega_Q^{\max} - \omega_Q)]^{-1/2}. \tag{8}$$

The form of this distribution function indicates that there will be two principal contributions to the observed perturbation frequency: one of low frequency (near $\omega_Q = 0$) and one of high frequency (near $\omega_Q = \omega_Q^{\max}$). Following the common procedure, namely expressing the experimentally measured perturbation factor $G_{22}^{\exp}$ as the average of G_{22} over the distribution of frequencies [equation (6)], expressions of the following type are obtained:

$$\int_0^{\omega_Q^{\max}} f(\omega_Q) \cos \omega_Q t\, d\omega_Q = J_0(\tfrac{1}{2}\omega_Q^{\max} t) \cos(\tfrac{1}{2}\omega_Q^{\max} t) \tag{9}$$

where J_0 is the zeroth order Bessel function and $\omega_Q^{\max}$ is proportional to the square of the fluctuation amplitude.

It can be shown that the periodicity of the last expression (not too close to $t = 0$, because of the particular behaviour of J_0 in that region) is very close to that of $\cos^2(\frac{1}{2}\omega_Q^{\max} t)$. Thus, approximately:

$$G_{22}^{\exp} \propto 1 + \cos \omega_Q^{\max} t \tag{10}$$

which is an extreme form of the perturbation function as already indicated above by equation (8). Equation (9) also indicates that close to the transition temperature, where the amplitude of the polarization fluctuations varies rapidly with temperature, a temperature dependent modulation should be observed in the perturbation factor. The frequency of this modulation should closely follow the critical temperature dependence of the mean square of the fluctuation amplitude, to which it is proportional. Thus, according to the fluctuation Dissipation Theorem, this frequency $\omega_Q^{\max}$ is again proportional to the susceptibility at a given temperature as explained previously.

In the argument that follows we show that *if* there exists in the polar phase ($T < T_c$) a significant contribution to V_{zz} from the slow motion of the lattice, no conclusive results can be obtained, due to the limitation of the experiment (limited statistics, narrow time-range, etc.). Reasoning, identical to that presented above for the cubic phase, leads to a distribution function for the ω_Q, having the form:

$$f(\omega_Q) = \frac{1}{\pi}\{\omega_Q[\omega_m - (\omega_Q + \omega_0 - 2\sqrt{\omega_Q \omega_0})]\}^{-1/2} \tag{11}$$

where ω_0 is the perturbation frequency due to the static displacement in the absence of fluctuations, and ω_m is the maximum frequency due to the fluctuations. Thus the experimentally observed perturbation factor $G_{22}^{\exp}(t)$ is obtained by averaging equation (4) over the frequency distribution, with the weighting function in equation (11). Hence $G_{22}^{\exp}$ will be a sum of expressions of the form:

$$\int f(\omega_Q) \cos \omega_Q t\, d\omega_Q = \frac{2}{\pi} \int_0^{\pi/2} \cos[(\sqrt{\omega_0} + \sqrt{\omega_m} \cos \phi)^2 t]\, d\phi. \tag{12}$$

Due to the complex structure of the above expression, it would be futile to attempt to derive a physically meaningful parameter from the experimental data in the slow regime below T_c.

As a result of the analysis of both slow and fast regimes, the following conclusions can be drawn. Above T_c, in both regimes, the frequency ω_Q turns out to be simply related to the (sub-) lattice susceptibility. This relationship should be manifested by a non-vanishing frequency ω_Q well above T_c, and by a critical behaviour of ω_Q on approaching T_c from above. Below T_c, in most of the temperature range, the interaction frequency ω_Q follows the temperature dependence of the square of the spontaneous (sub-) lattice polarization; close enough to T_c (still in the fast regime) it behaves critically due to the (sub-) lattice susceptibility.

Finally, we wish to refer to some previously reported experimental results which, as we show, can be interpreted as supporting our model. Bhide and Multani [16] found, by Mössbauer effect experiment in $BaTiO_3$, that V_{zz} in the tetragonal phase is closely proportional to P_s^2. The deviation from the relation

$V_{zz} \propto P_s^2$ which was found by Bhide and Hedge [17] in $PbTiO_3$ can be attributed to the relatively high covalency of this crystal. This was also pointed out by Schaefer *et al.* [18]. There are also numerous DPAC experiments [18–21] which report a non-vanishing EFG in the cubic phase of perovskite type crystals. This anomaly is commonly attributed to the presence of defects and impurities. However, according to the model presented here, the relationship $V_{zz} \propto T\chi_{Q_0}$ implies a non-vanishing V_{zz} even in the cubic phase of a perfect crystal. Indication of this type of behaviour can be found in NMR-experiments on the order–disorder type ferroelectric KDP crystals which show that for $T > T_c$ the EFG is proportional to $(T - \gamma T_c)^{-1}$ [10]. This observation agrees qualitatively with our predictions [12].

Preliminary experimental results [22] on $PbHfO_3$ in close proximity of T_c exhibit definitely the $(T - T_c)^{-1}$ behaviour of V_{zz}, substantiating our theoretical predictions. The complete report on the experimental data on $PbHfO_3$ will be published in the near future.

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