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Displacive-order-disorder crossover at the ferroelectric-paraelectric phase transitions of BaTiO_3 and LiTaO_3

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Résumé. — On compare les données reçues de mesures précises de réflectivité infrarouge et de constantes diélectriques $\epsilon_0(T)$ dans certains ferroélectriques ABO_3 . Dans BaTiO_3 , le mode ferroélectrique se sature au-dessus de la transition cubique tétragonale tandis que $\epsilon_0(T)$ tend à diverger. Ceci s'interprète en terme de changement de régime dominant, passant de displacif à ordre-désordre à l'approche de T_c , en accord avec la dimensionalité critique dans les systèmes cubiques dipolaires $d_c = 4 > d = 3$. Dans le composé uniaxe LiTaO_3 où $d = d_c = 3$, le phénomène est en effet moins marqué.

Abstract. — A detailed comparison between accurate infrared reflectivity data and dielectric constant $\epsilon_0(T)$ measurements has been carried out in ABO_3 ferroelectrics. In BaTiO_3 , the ferroelectric mode saturates above the cubic-tetragonal transition, whereas $\epsilon_0(T)$ tends to diverge. This supports an intrinsic crossover from displacive to order-disorder behaviour on approaching T_c because the critical dimensionality in these cubic dipolar systems is $d_c = 4 > d = 3$. In the uniaxial LiTaO_3 with $d = d_c = 3$, the crossover is less pronounced.

From computer simulations [1, 2], as well as analytic theory [3], a new view regarding the behaviour of displacive continuous structural phase transitions (SPT) near T_c has emerged : the crossover from a regime in which the collective behaviour has classical displacive soft-mode behaviour to a regime whose features are better described in the language traditionally reserved for order-disorder systems [4]. The present work indicates this to occur in the important class of ferroelectric perovskite systems, and thus points towards a resolution of the long-standing controversy between the soft-mode *versus* order-disorder description in BaTiO_3 and KNbO_3 as well as in LiTaO_3 . The soft-mode behaviour was supported by early infrared reflectivity measurements [5] and later inelastic neutron-scattering data [6]. The order-disorder picture stemmed from the observation of strong diffusive X-ray scattering [7], as well as Raman activity *above* the tetra-

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gonal-cubic transition [8] and more recent Raman investigations in the tetragonal phase [9]. The situation turned out to be similarly controversial in LiTaO_3 [10].

The displacive to order-disorder regime is due to intrinsic anharmonic behaviour from *correlated* fluctuations near wave vector $\mathbf{q} = 0$ (in space and time). One expects from renormalization-group (R.G.) theory that correlated fluctuations near T_c are more pronounced the larger $\varepsilon = d_c - d$ is, d_c being the critical dimensionality of a system [11]. The antiferrodistortive SPT in SrTiO_3 has $d_c = 4$, $d = 3$, i.e., $\varepsilon = 1$, and experimental results established quantitatively precursor order [12]. In KH_2PO_4 , $d_c = 2.5$ due to soft-mode/acoustic-mode coupling. With $d = 3$, $\varepsilon = -0.5$ one expects Gaussian mean-field behaviour. It has been shown [13] that in KH_2PO_4 , the statics and dynamics follow quantitatively mean-field behaviour. Courtens was the first to suggest [13a] the possible importance of the critical dimensionality d_c in the question of the occurrence of intrinsic central peaks.

Uniaxial ferroelectrics like TGS with their long-range dipolar interactions have a critical dimensionality $d_c = 3$. In this case critical behaviour is given by logarithmic corrections to classical Landau results [14]. Thus, fluctuation effects are already present but not dominating. Isotropic dipolar systems with dipolar and short-range interactions have been investigated using R.G. theory [15]. The static critical behaviour calculated is nearly indistinguishable from that in cubic short-range systems [11, 15] and $d_c = 4$. In real cubic oxide ferroelectrics, cubic anisotropic interactions are also present. Their fixed-point behaviour depends on the cubic anisotropy of the soft-modes. The fixed-point behaviour is either isotropic dipolar, not stable (BaTiO_3 ?) or cubic dipolar [16]. Kind and Müller [17] measured the exponent of the dielectric susceptibility ε_0 above the second-order phase transition in a cubic $\text{KTa}_{0.9}\text{Nb}_{0.1}\text{O}_3$ crystal to be $\gamma = 1.7$ [17], well outside the mean-field behaviour of $\gamma = 1$ [11]. Thus, one might expect that for cubic ferroelectrics like BaTiO_3 and KNbO_3 , a crossover from displacive to order-disorder behaviour may exist on approaching T_c^+ . Infrared reflectivity measurements [18] show this occurs as described below.

The new soft-mode data have been obtained using a Fourier-transform *scanning* interferometer, Bruker IFS113. These modern i.r. spectrometers are extremely well-suited to measure infrared active modes accurately in the frequency range from 10 to 4 000 cm^{-1} and up to high temperatures (1 300 K). The infrared reflectivity data were analysed on the basis of a factorized form of the dielectric function [18]. Typical experimental data and an example of data fits are shown in figure 1a. Simulations of infrared reflectivity, restricted for simplicity to the soft-mode alone and inserted in figures 1b and c, show that changes of TO soft-mode frequency (Fig. 1b) and linewidth (Fig. 1c) typical of oxidic perovskites give rise to *quite significant* changes of reflectivity profiles. In fact, infrared reflectivity yields information on the *real part* of the dielectric function in addition to the imaginary part. Only the latter is accessible by scattering (Raman or neutrons). Soft-mode frequency parameters, in particular, may be accurately deduced from low-frequency reflectivity which appears *slightly* dependent on damping as shown in the left-hand insert of figure 1a *even when the soft mode is overdamped*. Results at room temperature agree with those of [5]. Both data sets disagree with Ballantyne's spectrum [19] at room temperature. Results at other temperatures were previously compared [18] to other spectral data in detail and found to be in agreement with most of the data. In particular, extrapolating neutron data of [6] to $\mathbf{q} = 0$ appears compatible with present soft-mode frequencies.

Results for the soft-mode in BaTiO_3 in the cubic paraelectric and tetragonal ferroelectric phases are given in figure 2a. The curves show a clear-cut soft-mode behaviour over a wide range of temperatures, whose extrapolation intersects the temperature axis near T_c . *However, on approaching T_c , Ω_{TO} starts to level some 120 K above the phase transition to a value of 60 cm^{-1} .* Recent hyper-Raman measurements also confirm the saturation over that temperature range [20]. At T_c an A_1 -type component is abruptly shifted to $\approx 280 \text{ cm}^{-1}$, consistent with the first-order transition, while an E-component continues to soften to the next tetragonal-to-orthorhombic transition. Thus, the E-mode shows no significant discontinuity. Similar behaviour has been observed in the

Fig. 1. — (a) Typical reflectivity profiles in BaTiO₃ at several temperatures. Best fit (heavy full curve) to experimental data (○) at 1 350 K, for example. See text for inserts (b) and (c).

Fig. 2. — Temperature dependence of the three ferroelectric soft-mode components of BaTiO₃ (a), and the ratio of the « static » over the dielectric constant calculated from lattice modes (b) via $\epsilon_{\text{lat}} = \epsilon_{\infty} \prod_j \Omega_{j\text{LO}}^2 / \Omega_{j\text{TO}}^2$. Note that the Ω_j 's are moduli of complex poles (or zeroes). Insert shows passage from underdamped to overdamped soft-mode behaviour.

isomorphous phase of KNbO_3 [21]. Furthermore, in both crystals the soft-mode damping is heavy, over ten times that of the next modes, and persists into the lower tetragonal phase (see figure 2 insert).

The ratio of the dielectric constants $\epsilon_{\text{cap}}/\epsilon_{\text{lat}}$, with ϵ_{cap} measured in the MHz range, *above* piezo-electric resonances, and ϵ_{lat} calculated from the lattice modes shows the following (Fig. 2b) : the soft-mode roughly explains ϵ_{cap} at sufficiently high temperatures (Fig. 1a) but this becomes less and less true on approaching T_c from above [22]. Thus, a dynamical disorder affects the displacive behaviour and an *additional relaxation* can be related to disorder [7]. Therefore, we arrive at the conclusion that a displacive-to-order-disorder crossover occurs as has been shown to be present in the antiferrodistortive SPT of SrTiO_3 [12]. The latter transition is second-order, and deviations from mean-field behaviour appear 10 % in $t = (T - T_c)/T_c$ below $T_c = T_0$ for the rotational order parameter, and above T_c for the soft-mode as measured by inelastic neutrons [23]. In the present case of BaTiO_3 , the deviation in the soft-mode Ω_{TO} appears 25 % above the T_0 , where the mean-field extrapolated Ω_{TO} vanishes. This is thus comparable to the magnitude found for the short-range SrTiO_3 system. In our opinion, these new findings settle the controversy whether the cubic-to-tetragonal transitions in BaTiO_3 and KNbO_3 are displacive or order-disorder.

It should be noted that in figure 2, the high-temperature ratio $\epsilon_{\text{cap}}/\epsilon_{\text{lat}}$ has its low-temperature counterpart *reflected* about T_c , as is expected from scaling for a continuous transition, figure 2a, *but the soft mode has none*, figure 2b, i.e., the A_1 component has jumped to 280 cm^{-1} and therefore *cannot be responsible* for the ϵ_{cap} enhancement towards T_c in any way [22] ! Thus close to T_c an additional time-dependent dynamic motion distinct from the soft-mode behaviour has to be present. In fact, a relaxation of the dielectric constant, along the FE axis has been observed recently near 3-4 GHz at room temperature [24], the high-frequency value being in agreement with

Fig. 3. — Temperature dependence of the soft-mode frequency of LiTaO_3 (lower part), and comparison of ϵ_{lat} with the « static » dielectric constant (upper part-note logarithmic scale).

ϵ_{lat} while no marked relaxation of $\epsilon_{\perp}$ was found perpendicular to the FE axis above piezoelectric resonances, consistent with the results of figure 2. Thus, the vibrational motion of the mobile ion with respect to its neighbours is very anharmonic and should exhibit a central-peak response near T_c , in addition to the saturating soft-mode at $\sim 60 \text{ cm}^{-1}$. It has to be a relaxational motion, which might be slowed-down further by coupling to slowly relaxing impurities. The computer simulations of Schneider and Stoll [25] show that the dynamics are slowed-down by a constant factor but are otherwise unaltered in their critical behaviour. Most recent index of refraction measurements for $T > T_c$ in flux and melt-grown BaTiO_3 crystals have been interpreted in terms of intrinsic dynamic islands of polarization [26].

The uniaxial ferroelectric LiTaO_3 has also been investigated with the same method. Ω_{soft} again does not freeze-out, and $\epsilon_{\text{cap}}/\epsilon_{\text{lat}}$ increases on approaching T_c but the range in temperature is more restricted to the immediate vicinity of the transition (Fig. 3). Thus, the behaviour is all in all more « classical ». This is, however, expected in view of the fact that for this uniaxial crystal $d = d_c = 3$, i.e., the dimensionality is marginal, and correlated fluctuations for $\mathbf{q} = 0$ are present but dominate over a narrower T/T_c temperature range than in BaTiO_3 .

In summary, the soft-mode behaviour in ABO_3 ferroelectrics, especially the cubic ones, saturates well above the ferroelectric transition. A comparison with the measured dielectric constants indicates a crossover from displacive to order-disorder behaviour on approaching T_c . This is in agreement with expectations of precursor order from the renormalization-group point of view. The present findings give indirect evidence that cubic ferroelectrics do not behave classically as has always been assumed except for one experiment [17] on a second-order cubic-to-tetragonal ferroelectric transition.

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