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MICROSCOPIC INVESTIGATIONS OF THE FERROELECTRIC PHASE TRANSITIONS IN BaTiO₃ BY PARAMAGNETIC RESONANCE

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Abstract: The crossover from displacive to order-disorder behavior in structural phase transitions upon approaching T_c is recalled, followed by a discussion of its implications for those in the ferroelectric BaTiO₃. Then, recent pressure and temperature-dependent EPR experiments on Fe³⁺ are summarized which prove microscopically the existence of substantial order-disorder behavior in BaTiO₃. The most recent Mn⁴⁺ experiments are then presented which show that the Ti⁴⁺ is located off-center along equivalent $\langle 111 \rangle$ directions, and reorients in the high-temperature phases with $\nu \geq 1 \times 10^{10} \text{ sec}^{-1}$ reconciling x-ray "static" observations and dynamic scattering results.

1. Introduction

Structural-phase transitions (SPT's) of the displacive variety can be nicely probed microscopically by Electron Paramagnetic Resonance (EPR). The observation of static critical behavior, near the SPT in SrTiO₃, by EPR [1] was soon followed by the detection of a central peak (c. p.) at frequency $\nu \simeq 0$, distinct from the under-damped soft mode [2]. The extensive experimental and theoretical efforts promoted by these observations have been critically reviewed by the author concerning their intrinsic and extrinsic origin [3]. The understanding of the intrinsic part reached from computer simulations [4] is depicted in Fig. 1. Upon approaching T_c , short-range order exists owing to correlated order-parameter fluctuations which yield a saturating soft mode. This is an intrinsic property of the c. p. phenomenon. On the other hand, pinning of the correlated regions by lattice defects and strains can yield a very narrow or even vanishing c. p. width. The short-range order implies a displacive to

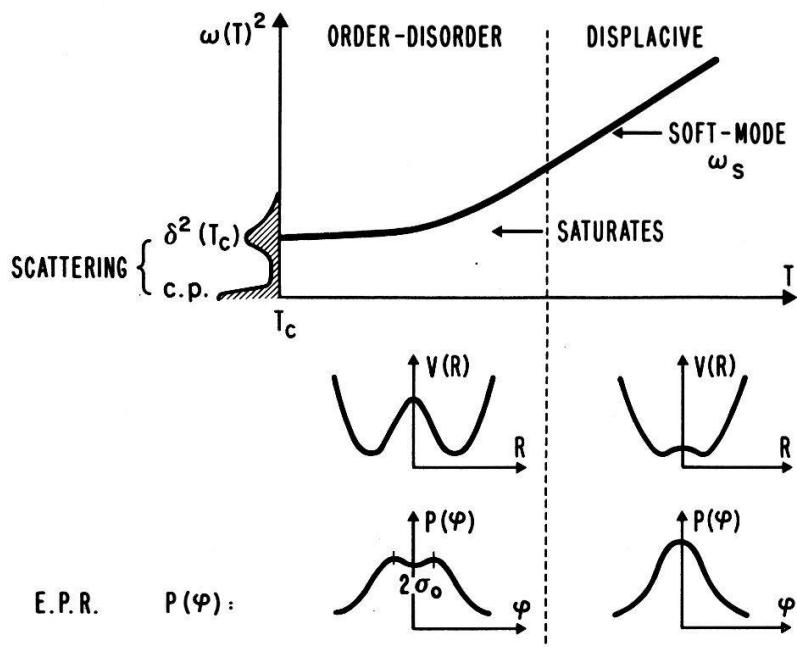


Fig. 1. Schematic representation of displacive to order-disorder crossover behavior in a structural phase transition, with soft mode ω_s saturation, averaged local potential $V(R)$ renormalization, and single-to-double peaked order-parameter φ distribution $P(\varphi)$.

order-disorder crossover upon cooling towards T_c . In the order-disorder regime, the local potential $V(R)$, averaged over the correlated region, is more anharmonic. EPR proved the existence of short-range order clusters with an Ising component $\pm\sigma_0$ in the distribution of the order parameter φ , $P(\varphi)$. This short-range order accounted quantitatively for the non-vanishing soft mode [3,5].

The behavior depicted in Fig. 1 is more pronounced the lower the effective lattice dimensionality d , and the shorter the range of forces for a given symmetry. The two latter properties determine the upper critical dimensionality d_c of a system, above which classical behavior occurs. Therefore, the larger the Wilson parameter $\epsilon = d_c - d$, the more one expects the cluster formation and c. p. phenomenon to be observable. This was expanded in two NATO Lectures in 1981 and their update in 1983 [6]. In the former, it was pointed out that cubic ABO_3 ferroelectrics quite probably have $\epsilon = 1$ like the short-range system SrTiO_3 . Thus, in 1983, the experimental situation was addressed whether or not displacive to order-disorder crossover is observable. The situation in these ABO_3 ferroelectrics is difficult because they exhibit overdamped soft modes and are first order, that is, they may not have a

stable fixed point. Therefore, it is not easy to assess whether a c. p. phenomenon is present and whether one is in the critical region at all. The view then was that at ambient pressure in PbTiO_3 , the first-order transition occurs before correlated fluctuations set in, but they are noticeable in BaTiO_3 and even more so in KNbO_3 [6].

In the next two sections, we concentrate on recent microscopic insight obtained by EPR in BaTiO_3 . This crystal is the first oxide ferroelectric ever discovered. The debate as to whether its transition is more displacive or order-disorder-like still continues [7]. Neutron and Raman-scattering experiments [8] clearly revealed a transverse optical soft mode indicative of displacive behavior [8,9]. However, the latter is highly overdamped near the cubic-tetragonal phase transition [6-9]. Infrared reflectivity experiments including data in the tetragonal and orthorhombic phases can be interpreted by strong relaxation excitations and a fading of the real part of the soft mode [10,11]. Near-relaxation behavior is revealed in the GHz region by transmission experiments using backward-wave oscillators [12], allowing a reinterpretation of hyper Raman data [13] as resulting from relaxator dynamics. All these new data indicate that, on cooling, one has to deal with a crossover phenomenon from displacive to order-disorder behavior [5,10]. In the latter, large pre-transitional correlated clusters or rather chains exist as revealed by the important and undisputed x-ray streaks in the cubic and ferroelectric phases [14,15]. These intrinsic pre-transitional correlations have been proposed [6] as being the cause of the anomalous temperature dependence of the index of refraction $n(T)$ in the cubic phase near T_c [16]. The anomalous part, $\Delta n(T)$, has been pointed out in an important paper to result from pre-transitional fluctuations of the polarization $\langle \delta P^2 \rangle$ [17].

Whether a structural or ferroelectric transition is more displacive or order-disorder like, i.e., whether an underdamped soft mode exists or relaxator dynamics are observed, depends on the local potential $V(\vec{R})$ of the ion or molecular unit in question. The displacive regime is characterized by a more harmonic $V(\vec{R})$ than the order-disorder one. In the most simple case, this can be approximated with the radial $R = |\vec{R}|$ dependence of $V(\vec{R})$ in single mode [18] or statistical mechanics [4,5] theory as

$$V(R) = -AR^2 + BR^4, \quad (1)$$

with the constants A and B positive. Such a potential has minima at $R_m = \pm\sqrt{A/2B}$ with energy $V_m = (A/2)R_m^2$ (Fig. 1). The distinction between the limiting cases of displacive versus order-disorder behavior at the transition temperature T_c is determined by whether

$$\begin{aligned} V_m \ll kT_c &: \text{displacive, or} \\ V_m \gg kT_c &: \text{order-disorder.} \end{aligned} \quad (2)$$

From the above, it is important to obtain information on $V(R)$. For example, the cubic potentials of the Ti ion in SrTiO₃ and BaTiO₃ have to be different. In SrTiO₃, the ferroelectric (not structural) mode is *underdamped* but heavily *overdamped* in BaTiO₃ [6,9]. Therefore, one expects the Ti ion to move in quite a more harmonic potential in SrTiO₃ ($V_m < kT$) than in BaTiO₃ ($V_m > kT$). This is probably in part due to the larger size of the Ba²⁺ ion as compared to that of the Sr²⁺. The question, therefore, arises whether one can probe $V(R)$ microscopically. The next two sections summarize recent EPR results on Fe³⁺ and Mn⁴⁺ to this end.

2. Probing order-disorder versus displacive behavior in BaTiO₃ by Fe³⁺ EPR

In a cubic environment, $V(R)$ can be written to lowest order by

$$V(\vec{R}) = \left(x^4 + y^4 + z^4 - \frac{3}{5} R^4 \right). \quad (3)$$

A paramagnetic singlet orbital ground state with spin $S \geq 2$ is split by (3) via spin-orbit and spin-spin interaction. The splitting is described empirically by a spin Hamiltonian of the form

$$\mathcal{H} = \frac{\underline{a}}{6} (S_x^4 + S_y^4 + S_z^4 - C). \quad (4)$$

For a Mn^{2+} or Fe^{3+} ion with half-filled 3d shell $3d^5$, $S = 5/2$, the $^6S_{5/2}$ ground state is split into a Γ_8 quartet and a Γ_6 doublet by $3\underline{a}$ which can be determined by EPR.

The dependence of \underline{a} for Fe^{3+} in various cubic oxides as a function of lattice spacing $2d$ was found to follow an empirical curve $\underline{a} = a_0/d^n$ with $n \approx 7$ except for $SrTiO_3$, $BaTiO_3$ and $KNbO_3$. Whereas for $SrTiO_3$ the EPR parameter \underline{a} is only slightly lower than the empirical curve, in the latter two crystals \underline{a} is a factor of 2.5 smaller. Although this fact was pointed out a decade ago by Müller [19], it has not caught the attention of the ferroelectric community. Furthermore, the low \underline{a} parameter correlates, as then recognized, with the strongly overdamped and anisotropic soft modes in $BaTiO_3$ and $KNbO_3$ and the consecutive tetragonal, orthorhombic and rhombohedral phases not observed in other perovskites. One of the reasons for the little interest was the unclear theoretical relation of \underline{a} to $V(\vec{R})$ for Fe^{3+} and the position of this ion in the octahedral cell was not well understood, either.

The understanding of the position of Fe^{3+} in its octahedral cage was considerably improved with an analysis of Siegel and Müller [20]. Using the superposition model to analyze some 20-year old EPR fine structure splitting measured in the three ferroelectric phases of $BaTiO_3$ [21], it was shown that the Fe^{3+} remains *centered* in the octahedron. Thus, it is also clear why parameter \underline{a} varies by no more than 10% in all phases of $BaTiO_3$ [21]. The reason why the Fe^{3+} is centered while the Ti^{4+} is not will be addressed in Section 3.

To obtain information on $V(\vec{R})$, we can, with restrictions, take advantage of the empirical $\underline{a}(d)$ dependence in the following way. We first compute, from $\underline{a}(d)$, how much larger d_{eff} in $BaTiO_3$ has to be than its actual lattice constant d to observe a reduced by a factor of 2.5. From the exponential law of \underline{a} on d , we get $d_{eff}/d = (2.5)^{1/7} \approx 1.14$, i.e., the probing Fe^{3+} sees the oxygens in $BaTiO_3$ at a 14% *larger distance* than what it should be for an inert oxide. Now, we assume the minimum R_m of $V(|\vec{R}|)$ of (1) also at a distance larger by the same proportion

$R_m(\text{BaTiO}_3)/R(\text{IO}) = d_{\text{eff}}/d$, where IO stands for inert cubic oxide. Of course, $R_m \neq d$, but to lowest order their variation is proportional. With this, we calculate for $V_m = (A/2) R_m^2$ in BaTiO_3 , $V_m(\text{BaTiO}_3) = 1.3 V_m(\text{IO})$, a 30% enhanced anharmonicity $\propto 1/B$. The same enhanced anharmonicity also has to be present in KNbO_3 .

The question arises at this point whether additional experiments can confirm the conclusion reached above. This has indeed been the case most recently by measurements of the pressure p and temperature T dependences of the cubic crystalline splitting parameter $a(p,T)$ [22] whose total differential is given by

$$da = \left(\frac{\partial a}{\partial p} \right)_T dp + \left(\frac{\partial a}{\partial T} \right)_p dT. \quad (5)$$

$(\partial a/\partial p)_T$ and $(\partial a/\partial T)_p$ were first measured for Fe^{3+} and Mn^{2+} ; then, using the differentiated form of the equation of state $V = V(p,T)$ where V is the volume, Walsh, Jeneer and Bloembergen [23] obtained the relation

$$(\partial a/\partial T)_p = - (3\alpha/\beta)(\partial a/\partial p)_T + (\partial a/\partial T)_V, \quad (6)$$

where $\alpha = (1/d)(\partial d/\partial p)$ is the coefficient of linear thermal-expansion, and $\beta = - (3/d)(\partial d/\partial p)_T$ the volume compressibility. The first term on the right side is the explicit volume effect, and the second the explicit temperature effect. $(\partial a/\partial p)_T$ and $(\partial a/\partial T)_p$ have also been measured earlier for Fe^{3+} in SrTiO_3 [24], and more recently for KTaO_3 [25]. In the latter publication, Rytz *et al.* compared the values obtained for Fe^{3+} and Mn^{2+} in MgO as well as Fe^{3+} in SrTiO_3 and KTaO_3 . Two very interesting properties of $a(p,T)$ were noticed, see Table I. The explicit volume effect relative to a was within 6% the same for all four measurements. The optic modes of either MgO , SrTiO_3 , or KTaO_3 , being underdamped, indicate quite harmonic potentials. The explicit temperature effect is negative in KTaO_3 and SrTiO_3 , whereas it is positive for Mn^{2+} and Fe^{3+} in MgO . The negative contribution was

Table I. Numerical values of explicit volume and temperature effects of \underline{a} according to Eq. (6) for $S = 5/2$ ions in cubic oxides, after Refs. [25] and [26].

| | \underline{a} | $\frac{\partial \underline{a}}{\partial T} \Big _p$ | $-\frac{3\alpha}{\beta} \frac{\partial \underline{a}}{\partial p} \Big _T$ | $-\frac{3\alpha}{a\beta} \frac{\partial \underline{a}}{\partial p} \Big _T$ | $+\frac{\partial \underline{a}}{\partial T} \Big _V$ | $+\frac{1}{a} \frac{\partial \underline{a}}{\partial T} \Big _V$ |
|--------------------------------------|---|---|--|---|--|--|
| Definitions | Cubic crystalline field splitting parameter | Temp. dependence | Explicit volume effect | Ratio explicit vol. effect/ cubic splitting parameter | Explicit temp. effect | Ratio explicit temp. effect/ cubic splitting parameter |
| Units | 10^{-4} cm $^{-1}$ | 10^{-6} cm $^{-1}$ K $^{-1}$ | 10^{-6} cm $^{-1}$ K $^{-1}$ | 10^{-4} K $^{-1}$ | 10^{-6} cm $^{-1}$ K $^{-1}$ | 10^{-4} K $^{-1}$ |
| KTaO ₃ :Fe ³⁺ | 305 | -16.9 | -10.4 | -3.4 | -6.5 | -2.13 |
| SrTiO ₃ :Fe ³⁺ | 198 | -11 | -7.5 | -3.8 | -3.5 | -1.75 |
| MgO:Fe ³⁺ | 205 | -4 | -7.0 | -3.4 | +3.0 | +1.46 |
| MgO:Mn ²⁺ | 19.01 | -0.51 | -0.70 | -3.7 | +0.19 | +1.00 |
| BaTiO ₃ :Fe ³⁺ | 97 | -4.1 | -10.7 | -11.0 | +6.6 | +6.6 |

attributed to the temperature dependence of the soft mode present in SrTiO₃ and KTaO₃, but absent in MgO [25].

The bottom row in Table I shows the recent values for BaTiO₃ obtained from the pressure and temperature dependences of \underline{a} in the cubic phase [27]. They show the following remarkable results: the explicit *relative volume effect is larger by a factor 3* than in the other oxides, and reflects the enhanced anharmonicity in BaTiO₃ arrived at earlier in this section. From this, one expects microscopically a relaxator behavior in agreement with the *large positive relative explicit temperature effect* $(1/a)(\partial \underline{a}/\partial T)_V$ in contrast to the negative ones in KTaO₃ and SrTiO₃, where \underline{a} is dominated by the soft-mode behavior. The magnitudes of \underline{a} , $(\partial \underline{a}/\partial T)_V$ and $(\partial \underline{a}/\partial p)_T$, i.e., three different quantities of Fe³⁺ in BaTiO₃, clearly point to a strong anharmonic local potential.

3. Local position and dynamics of Ti⁴⁺ probed by Mn⁴⁺ EPR

In the previous section, we postponed mentioning why the Fe³⁺ remains centered in the octahedral cage. Understanding this effect has led to a new paramagnetic probe which follows the cooperative motion of the Ti⁴⁺, namely, the Mn⁴⁺ ion. The

reason why the Fe³⁺ remains centered is two-fold. Fe³⁺ is nominally one unit negatively charged with respect to the Ti⁴⁺ it replaces, and therefore repels the negative nearest-neighbor O²⁻ ions as follows from a recent theory of Sangster [28]. Furthermore, the 3d shell of Fe³⁺ (3d⁵) is half-filled with configuration (t_{2g})³(e_g)². The e_g orbitals are antibonding and add repulsive forces between the Fe³⁺ and O²⁻, whereas the t_{2g} are nonbonding. Cr³⁺ with configuration (t_{2g})³ is still centered because of its negative effective charge but less than Fe³⁺, owing to the two missing e_g electrons [20].

The Cr³⁺ has three d-electrons. The half-filled t_{2g} shell carries no orbital angular momentum, and the magnetic state is described by S = 3/2. Such a spin state is not split by the cubic term (4), and consequently only second-order ligand-field splittings are observed in the lower than cubic-symmetry ferroelectric phases of BaTiO₃. The appropriate Hamiltonian is now reduced,

$$\mathcal{H} = D(S_z^2 - (1/3)S(S+1)) + E(S_x^2 - S_y^2). \quad (7)$$

EPR spectra in the three ferroelectric phases have recently been reported [28]. The axial ligand parameter D(T) consists of two terms

$$D(T) = D^P(T) + D^T(T). \quad (8)$$

D^P(T) is proportional to the square of the polarization P(T), and D^T is linear in T above 100 K and quite large. The existence of D^P shows that the Cr³⁺ remains centered in the octahedral cell. The D(T) and E(T) parameters have been successfully analyzed by the superposition model [8] as those observed for Fe³⁺ [20]. The existence of D^T, not observed for Fe³⁺, points to large thermal fluctuations of the Cr³⁺ owing to the absence of repelling e_g electrons. Saturation of D^T(T) for low T (below 100 K) is accounted for by a Debye model with energy $\theta_D = 237$ K, proving independently a flat ionic potential for the Cr³⁺. The Debye energy for Fe³⁺ is by comparison $\theta_D = 450$ K, close to the one of BaTiO₃ [29].

The Mn^{4+} , $(t_{2g})^3$, is isoelectronic to Cr^{3+} . Its charge is the same as the substitutional Ti^{4+} ion. Thus, the Sangster effect is absent. Axial EPR spectra have been observed in the rhombohedral phase with ligand-field axes z parallel to the $\langle 111 \rangle$ domain axes [26]. The ligand-field splitting D is some 100 times larger than that of the isoelectronic Cr^{3+} despite the superposition model parameters of the Mn^{4+} being closely the same [26]. An analysis in terms of the superposition model for the Mn^{4+} gave:

| | |
|--------------------------------------|--------------------------------------|
| Ti^{4+} coordinate: | Centered in octahedron: |
| $D = +0.44 \pm 0.23 \text{ cm}^{-1}$ | $+0.0350 \pm 0.0088 \text{ cm}^{-1}$ |

as compared to the one observed of

$$D = +0.65 \pm 0.01 \text{ cm}^{-1}.$$

Comparing the model and experimental values of D , it is clear that the Mn^{4+} has closely the same coordinates as Ti^{4+} in the rhombohedral phase, i.e., displaced from the octahedral center by $\approx 0.14 \text{ \AA}$ along the $\langle 111 \rangle$ directions. We recall here that nearly two decades ago, Bersuker predicted from vibronic theory the Ti^{4+} ions to lie off-center along $\langle 111 \rangle$ directions [30].

From the above, it follows that the Mn^{4+} with nearly the same atomic mass as Ti^{4+} follows its cooperative motion and allows the probing of its dynamics. No EPR spectrum of Mn^{4+} has so far been observed in the orthorhombic, tetragonal or cubic phases of BaTiO_3 along $\langle 111 \rangle$ directions of the magnetic field applied. This is only possible when the Mn^{4+} spectra are motionally smeared out. For this to be the case, a component of the movement of the Mn^{4+} and, therefore, Ti^{4+} is present with a frequency of $\nu = \frac{1}{h} g\mu_B (H_h - H_l) \sim 0.9 \times 10^{10} \text{ sec}^{-1}$, where H_h and H_l are the high and low resonance magnetic fields for $\vec{H} \parallel [111]$ in the rhombohedral phase. If the motion were faster than ν , a dynamically averaged Mn^{4+} should be visible. A local mode of the Mn^{4+} can be excluded with certainty because in the non-ferroelectric SrTiO_3 , the Mn^{4+} spectrum is visible between 4 and 300 K [31].

The EPR of Mn^{4+} being a reliable probe of the Ti^{4+} position and motion resolves an important aspect of the statics and dynamics of the ferroelectric phase transition in BaTiO_3 . In their important x-ray work, Comes, Lambert and Guinier

[14] had concluded that the Ti ion sits off-center along equivalent $\langle 111 \rangle$ directions in *all* phases: at rest in the low-temperature phase, motionally averaging between two equivalent $\langle 111 \rangle$ directions in the orthorhombic, four in the tetragonal, and all eight $\langle 111 \rangle$ in the cubic phase. Because this motion is slow, of the order of 1 cm^{-1} , it escaped observation by neutron, Raman or equivalent scattering experiments but appears static to x-rays [14,15]. From the x-ray streaks, the French group concluded that chains with correlations along $\langle 100 \rangle$ equivalent directions of particular [111] displaced Ti ions exist. Owing to these rather long correlated chains, the re-orientation has to be slow as deduced from the new Mn⁴⁺ EPR investigations [26].

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