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MICROSCOPIC INVESTIGATIONS OF THE FERROELECTRIC PHASE TRANSITIONS IN BaTiO$_3$ 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 BaTiO$_3$. Then, recent pressure and temperature-dependent EPR experiments on Fe^{3+} are summarized which prove microscopically the existence of substantial order-disorder behavior in BaTiO$_3$. The most recent Mn^{4+} experiments are then presented which show that the Ti^{4+} is located off-center along equivalent $\langle 111 \rangle$ directions, and reorients in the high-temperature phases with $\nu \geq 1 \times 10^{10}$ 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 SrTiO$_3$, by EPR [1] was soon followed by the detection of a central peak (c. p.) at frequency $\nu \simeq 0$, distinct from the underdamped 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

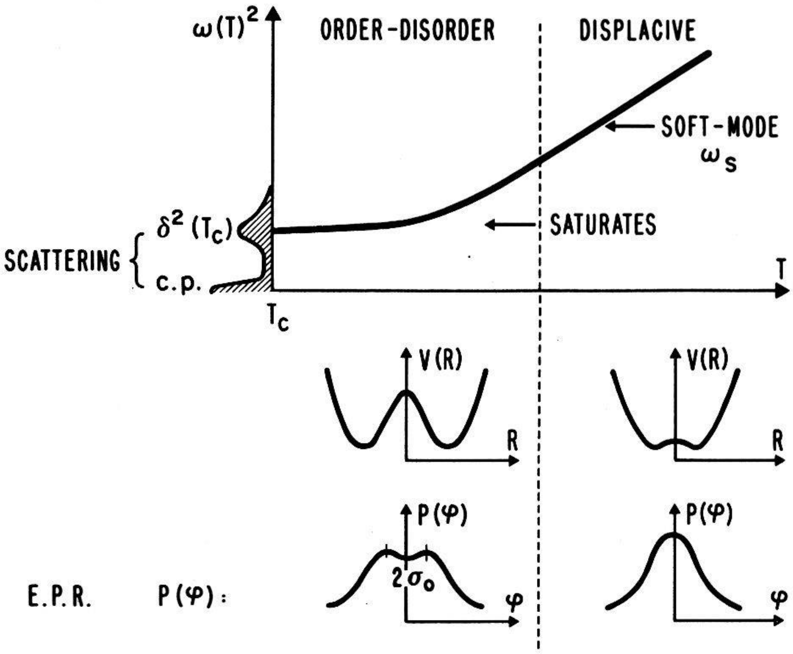

Fig. 1. Schematic representation of displacive to order-disorder crossover behavior in a structural phase transition, with soft mode ω_s saturation, averaged local potential V(R) renormalization, and single-to-double peaked order-parameter φ distribution $P(\varphi)$.

order-disorder crossover upon cooling towards T_c. In the order-disorder regime, the local potential $V(\vec{R})$, 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 $\varepsilon = d_c - d$, 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 $\varepsilon = 1$ 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 $R = |R|$ dependence of $V(\vec{R})$ in single mode [18] or statistical mechanics [4,5] theory as

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

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

$$\begin{aligned} V_m &<< kT_c: \quad \text{displacive, or} \\ V_m &>> kT_c: \quad \text{order-disorder.} \end{aligned} \tag{2}$$

From the above, it is important to obtain information on $V(\vec{R})$. For example, the cubic potentials of the Ti ion in $SrTiO_3$ and $BaTiO_3$ have to be different. In $SrTiO_3$, the ferroelectric (not structural) mode is *underdamped* but heavily *overdamped* in $BaTiO_3$ [6,9]. Therefore, one expects the Ti ion to move in quite a more harmonic potential in $SrTiO_3$ ($V_m < kT$) than in $BaTiO_3$ ($V_m > kT$). This is probably in part due to the larger size of the Ba^{2+} ion as compared to that of the Sr^{2+}. The question, therefore, arises whether one can probe $V(\vec{R})$ microscopically. The next two sections summarize recent EPR results on Fe^{3+} and Mn^{4+} to this end.

2. Probing order-disorder versus displacive behavior in $BaTiO_3$ by Fe^{3+} EPR

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

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

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

$$\mathscr{H} = \frac{a}{6}\left(S_x^4 + S_y^4 + S_z^4 - C\right). \tag{4}$$

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 $n \simeq 7$ 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 $\underline{a}$ reduced by a factor of 2.5. From the exponential law of $\underline{a}$ on d, we get $d_{eff}/d = (2.5)^{1/7} \doteq 1.14$, 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

$R_m(BaTiO_3)/R(I\,O) = d_{eff}/d$, where I O 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 $BaTiO_3$, $V_m\,(BaTiO_3) = 1.3\,V_m\,(I\,O)$, 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 $\underline{a}(p,T)$ [22] whose total differential is given by

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

$(\partial\underline{a}/\partial p)_T$ and $(\partial\underline{a}/\partial T)_p$ 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

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

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. $(\partial\underline{a}/\partial p)_T$ and $(\partial\underline{a}/\partial T)_p$ 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 $\underline{a}(p,T)$ were noticed, see Table I. The explicit volume effect relative to $\underline{a}$ 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 a according to Eq. (6) for $S = 5/2$ ions in cubic oxides, after Refs. [25] and [26].

	a	$\left.\frac{\partial a}{\partial T}\right\rvert_p$	$-\left.\frac{3\alpha}{\beta}\frac{\partial a}{\partial p}\right\rvert_T$	$-\left.\frac{3\alpha}{a\beta}\frac{\partial a}{\partial p}\right\rvert_T$	$+\left.\frac{\partial a}{\partial T}\right\rvert_V$	$+\left.\frac{1}{a}\frac{\partial a}{\partial T}\right\rvert_V$
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 $SrTiO_3$ and $KTaO_3$, but absent in MgO [25].

The bottom row in Table I shows the recent values for $BaTiO_3$ obtained from the pressure and temperature dependences of 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 $BaTiO_3$ arrived at earlier in this section. From this, one expects microscopically a relaxator behavior in agreement with the *large positive relative explicit temperature effect* $(1/a)(\partial a/\partial T)_V$ in contrast to the negative ones in $KTaO_3$ and $SrTiO_3$, where a is dominated by the soft-mode behavior. The magnitudes of a, $(\partial a/\partial T)_V$ and $(\partial a/\partial p)_T$, i.e., three different quantities of Fe^{3+} in $BaTiO_3$, clearly point to a strong anharmonic local potential.

3. Local position and dynamics of Ti^{4+} probed by Mn^{4+} EPR

In the previous section, we postponed mentioning why the Fe^{3+} remains centered in the octahedral cage. Understanding this effect has led to a new paramagnetic probe which follows the cooperative motion of the Ti^{4+}, namely, the Mn^{4+} ion. The reason why the Fe^{3+} remains centered is two-fold. Fe^{3+} is nominally one unit negatively charged with respect to the Ti^{4+} it replaces, and therefore repels the negative nearest-neighbor O^{2-} ions as follows from a recent theory of Sangster [28]. Furthermore, the 3d shell of Fe^{3+} ($3d^5$) is half-filled with configuration $(t_{2g})^3,(e_g)^2$. The e_g orbitals are antibonding and add repulsive forces between the Fe^{3+} and O^{2-}, whereas the t_{2g} are nonbonding. Cr^{3+} with configuration $(t_{2g})^3$ is still centered because of its negative effective charge but less than Fe^{3+}, owing to the two missing e_g electrons [20].

The Cr^{3+} 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 $BaTiO_3$. The appropriate Hamiltonian is now reduced,

$$\mathscr{H} = D\left(S_z^2 - (1/3)S(S+1)\right) + E\left(S_x^2 - S_y^2\right). \tag{7}$$

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

$$D(T) = D^P(T) + D^T(T). \tag{8}$$

$D^P(T)$ 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 Cr^{3+} 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 Fe^{3+} [20]. The existence of D^T, not observed for Fe^{3+}, points to large thermal fluctuations of the Cr^{3+} 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 Cr^{3+}. The Debye energy for Fe^{3+} is by comparison $\theta_D = 450$ K, close to the one of $BaTiO_3$ [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 ⟨111⟩ 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:
$D =$	$+0.44 \pm 0.23\ \mathrm{cm}^{-1}$	$+0.0350 \pm 0.0088\ \mathrm{cm}^{-1}$

as compared to the one observed of

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

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 $\simeq 0.14$ Å along the ⟨111⟩ directions. We recall here that nearly two decades ago, Bersuker predicted from vibronic theory the Ti^{4+} ions to lie off-center along ⟨111⟩ 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 ⟨111⟩ 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 $\nu = \frac{1}{h} g\mu_B(H_h - H_l) \sim 0.9 \times 10^{10}\ \mathrm{sec}^{-1}$, 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 ⟨111⟩ directions in *all* phases: at rest in the low-temperature phase, motionally averaging between two equivalent ⟨111⟩ directions in the orthorhombic, four in the tetragonal, and all eight ⟨111⟩ 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 ⟨100⟩ 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 Mn^{4+} EPR investigations [26].

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