

**Zeitschrift:** Helvetica Physica Acta

**Band:** 59 (1986)

**Heft:** 5

**Artikel:** Microscopic investigations of the ferroelectric phase transitions in BaTiO<sub>3</sub> by paramagnetic resonance

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**DOI:** <https://doi.org/10.5169/seals-115770>

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## MICROSCOPIC INVESTIGATIONS OF THE FERROELECTRIC PHASE TRANSITIONS IN BaTiO<sub>3</sub> 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<sub>3</sub>. Then, recent pressure and temperature-dependent EPR experiments on Fe<sup>3+</sup> are summarized which prove microscopically the existence of substantial order-disorder behavior in BaTiO<sub>3</sub>. The most recent Mn<sup>4+</sup> experiments are then presented which show that the Ti<sup>4+</sup> 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 SrTiO<sub>3</sub>, 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

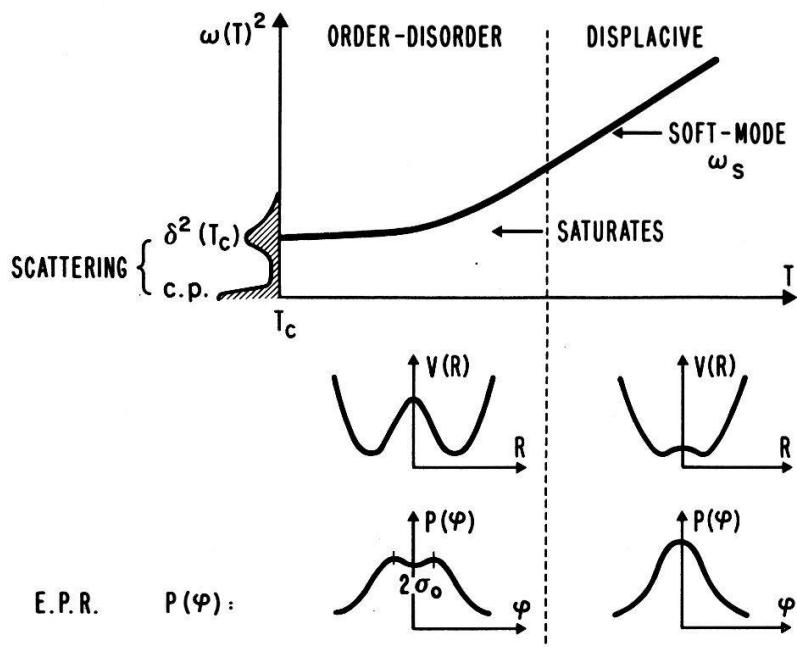


Fig. 1. Schematic representation of displacive to order-disorder crossover behavior in a structural phase transition, with soft mode  $\omega_s$  saturation, averaged local potential  $V(R)$  renormalization, and single-to-double peaked order-parameter  $\varphi$  distribution  $P(\varphi)$ .

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  $\varphi$ ,  $P(\varphi)$ . 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  $\text{ABO}_3$  ferroelectrics quite probably have  $\epsilon = 1$  like the short-range system  $\text{SrTiO}_3$ . Thus, in 1983, the experimental situation was addressed whether or not displacive to order-disorder crossover is observable. The situation in these  $\text{ABO}_3$  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  $\text{PbTiO}_3$ , the first-order transition occurs before correlated fluctuations set in, but they are noticeable in  $\text{BaTiO}_3$  and even more so in  $\text{KNbO}_3$  [6].

In the next two sections, we concentrate on recent microscopic insight obtained by EPR in  $\text{BaTiO}_3$ . 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 SrTiO<sub>3</sub> and BaTiO<sub>3</sub> have to be different. In SrTiO<sub>3</sub>, the ferroelectric (not structural) mode is *underdamped* but heavily *overdamped* in BaTiO<sub>3</sub> [6,9]. Therefore, one expects the Ti ion to move in quite a more harmonic potential in SrTiO<sub>3</sub> ( $V_m < kT$ ) than in BaTiO<sub>3</sub> ( $V_m > kT$ ). This is probably in part due to the larger size of the Ba<sup>2+</sup> ion as compared to that of the Sr<sup>2+</sup>. The question, therefore, arises whether one can probe  $V(R)$  microscopically. The next two sections summarize recent EPR results on Fe<sup>3+</sup> and Mn<sup>4+</sup> to this end.

## 2. Probing order-disorder versus displacive behavior in BaTiO<sub>3</sub> by Fe<sup>3+</sup> 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

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

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  $\Gamma_8$  quartet and a  $\Gamma_6$  doublet by  $3a$  which can be determined by EPR.

The dependence of  $a$  for  $Fe^{3+}$  in various cubic oxides as a function of lattice spacing  $2d$  was found to follow an empirical curve  $a = a_0/d^n$  with  $n \approx 7$  except for  $SrTiO_3$ ,  $BaTiO_3$  and  $KNbO_3$ . Whereas for  $SrTiO_3$  the EPR parameter  $a$  is only slightly lower than the empirical curve, in the latter two crystals  $a$  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  $a$  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  $a$  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  $a$  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  $a(d)$  dependence in the following way. We first compute, from  $a(d)$ , 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  $a$  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  $\text{BaTiO}_3$ ,  $V_m(\text{BaTiO}_3) = 1.3 V_m(\text{IO})$ , a 30% enhanced anharmonicity  $\propto 1/B$ . The same enhanced anharmonicity also has to be present in  $\text{KNbO}_3$ .

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  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ ; 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  $\text{Fe}^{3+}$  in  $\text{SrTiO}_3$  [24], and more recently for  $\text{KTaO}_3$  [25]. In the latter publication, Rytz *et al.* compared the values obtained for  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  in  $\text{MgO}$  as well as  $\text{Fe}^{3+}$  in  $\text{SrTiO}_3$  and  $\text{KTaO}_3$ . 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  $\text{MgO}$ ,  $\text{SrTiO}_3$ , or  $\text{KTaO}_3$ , being underdamped, indicate quite harmonic potentials. The explicit temperature effect is negative in  $\text{KTaO}_3$  and  $\text{SrTiO}_3$ , whereas it is positive for  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  in  $\text{MgO}$ . 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 <sub>3</sub> :Fe <sup>3+</sup>	305	-16.9	-10.4	-3.4	-6.5	-2.13
SrTiO <sub>3</sub> :Fe <sup>3+</sup>	198	-11	-7.5	-3.8	-3.5	-1.75
MgO:Fe <sup>3+</sup>	205	-4	-7.0	-3.4	+3.0	+1.46
MgO:Mn <sup>2+</sup>	19.01	-0.51	-0.70	-3.7	+0.19	+1.00
BaTiO <sub>3</sub> :Fe <sup>3+</sup>	97	-4.1	-10.7	-11.0	+6.6	+6.6

attributed to the temperature dependence of the soft mode present in SrTiO<sub>3</sub> and KTaO<sub>3</sub>, but absent in MgO [25].

The bottom row in Table I shows the recent values for BaTiO<sub>3</sub> 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 BaTiO<sub>3</sub> 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 KTaO<sub>3</sub> and SrTiO<sub>3</sub>, 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 Fe<sup>3+</sup> in BaTiO<sub>3</sub>, clearly point to a strong anharmonic local potential.

### 3. Local position and dynamics of Ti<sup>4+</sup> probed by Mn<sup>4+</sup> EPR

In the previous section, we postponed mentioning why the Fe<sup>3+</sup> remains centered in the octahedral cage. Understanding this effect has led to a new paramagnetic probe which follows the cooperative motion of the Ti<sup>4+</sup>, namely, the Mn<sup>4+</sup> ion. The

reason why the Fe<sup>3+</sup> remains centered is two-fold. Fe<sup>3+</sup> is nominally one unit negatively charged with respect to the Ti<sup>4+</sup> it replaces, and therefore repels the negative nearest-neighbor O<sup>2-</sup> ions as follows from a recent theory of Sangster [28]. Furthermore, the 3d shell of Fe<sup>3+</sup> (3d<sup>5</sup>) is half-filled with configuration (t<sub>2g</sub>)<sup>3</sup>(e<sub>g</sub>)<sup>2</sup>. The e<sub>g</sub> orbitals are antibonding and add repulsive forces between the Fe<sup>3+</sup> and O<sup>2-</sup>, whereas the t<sub>2g</sub> are nonbonding. Cr<sup>3+</sup> with configuration (t<sub>2g</sub>)<sup>3</sup> is still centered because of its negative effective charge but less than Fe<sup>3+</sup>, owing to the two missing e<sub>g</sub> electrons [20].

The Cr<sup>3+</sup> has three d-electrons. The half-filled t<sub>2g</sub> 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<sub>3</sub>. 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<sup>P</sup>(T) is proportional to the square of the polarization P(T), and D<sup>T</sup> is linear in T above 100 K and quite large. The existence of D<sup>P</sup> shows that the Cr<sup>3+</sup> 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<sup>3+</sup> [20]. The existence of D<sup>T</sup>, not observed for Fe<sup>3+</sup>, points to large thermal fluctuations of the Cr<sup>3+</sup> owing to the absence of repelling e<sub>g</sub> electrons. Saturation of D<sup>T</sup>(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<sup>3+</sup>. The Debye energy for Fe<sup>3+</sup> is by comparison  $\theta_D = 450$  K, close to the one of BaTiO<sub>3</sub> [29].

The  $\text{Mn}^{4+}$ ,  $(t_{2g})^3$ , is isoelectronic to  $\text{Cr}^{3+}$ . Its charge is the same as the substitutional  $\text{Ti}^{4+}$  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  $\text{Cr}^{3+}$  despite the superposition model parameters of the  $\text{Mn}^{4+}$  being closely the same [26]. An analysis in terms of the superposition model for the  $\text{Mn}^{4+}$  gave:

$\text{Ti}^{4+}$ 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  $\text{Mn}^{4+}$  has closely the same coordinates as  $\text{Ti}^{4+}$  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  $\text{Ti}^{4+}$  ions to lie off-center along  $\langle 111 \rangle$  directions [30].

From the above, it follows that the  $\text{Mn}^{4+}$  with nearly the same atomic mass as  $\text{Ti}^{4+}$  follows its cooperative motion and allows the probing of its dynamics. No EPR spectrum of  $\text{Mn}^{4+}$  has so far been observed in the orthorhombic, tetragonal or cubic phases of  $\text{BaTiO}_3$  along  $\langle 111 \rangle$  directions of the magnetic field applied. This is only possible when the  $\text{Mn}^{4+}$  spectra are motionally smeared out. For this to be the case, a component of the movement of the  $\text{Mn}^{4+}$  and, therefore,  $\text{Ti}^{4+}$  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  $\nu$ , a dynamically averaged  $\text{Mn}^{4+}$  should be visible. A local mode of the  $\text{Mn}^{4+}$  can be excluded with certainty because in the non-ferroelectric  $\text{SrTiO}_3$ , the  $\text{Mn}^{4+}$  spectrum is visible between 4 and 300 K [31].

The EPR of  $\text{Mn}^{4+}$  being a reliable probe of the  $\text{Ti}^{4+}$  position and motion resolves an important aspect of the statics and dynamics of the ferroelectric phase transition in  $\text{BaTiO}_3$ . 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  $1 \text{ cm}^{-1}$ , 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 Mn<sup>4+</sup> EPR investigations [26].

The author thanks K. W. Blazey for improvements in the manuscript.

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