

on Ferroelectricity, October, 1968 (to be published),
Abstract No. 440.

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CHARACTERISTIC STRUCTURAL PHASE TRANSITION IN PEROVSKITE-TYPE COMPOUNDS

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(Received 1 July 1968)

The tetragonal rotation of TiO_6 octahedra in SrTiO_3 and the trigonal rotation of AlO_6 octahedra in LaAlO_3 were measured by paramagnetic resonance below their respective phase transitions. The normalized rotation angles α vary quantitatively in the same way as a function of reduced temperature. Thus α is the order parameter in such transitions, which are characteristic for perovskite compounds.

Since the discovery of the phase transition from cubic to nonpolar tetragonal in SrTiO_3 near 100°K ,^{1,2} interest in the origin of this transition has not ceased. It was noted at the time² that such a transition may be typical for oxides crystallizing in the perovskite structure. Other possibilities have been proposed by Cowley³ and Horner.⁴ Both authors related the transition—in different ways—to the existence of the soft TO Cochran-Landauer mode at $k=0$ present in this material.³ In an effort to elucidate this phase transition we made a careful structural comparison with the one occurring in LaAlO_3 , an oxide material, whose electric and magnetic properties are similar to normal oxides like Al_2O_3 or MgO . Thus the transition in LaAlO_3 would be characteristic for materials crystallizing with the ABO_3 perovskite structure. In addition, transitions due to magnetic or electric interactions may be present as well (PrAlO_3) and can even dominate (BaTiO_3).

Geller and Bala⁵ made an x-ray analysis of LaAlO_3 and found it to be trigonal at 300°K , becoming cubic at $\sim 720^\circ\text{K}$. EPR powder measurements on Gd^{3+} revealed no other phase transition down to 4.2°K .⁶ Similar measurements on single crystals confirmed this result, but it remained open at what temperature the cubic-to-trigonal transition occurred, and whether it was of first or second order.⁷ We completed such an EPR study recently with a monodomain LaAlO_3 crystal (containing 0.02% Fe^{3+} ions substitutional for Al^{3+}) in the entire range from 4.2 to 900°K .⁸ From the axial constant $D(T)$ reproduced in Fig.

1(a), it is clear that the phase transition occurs at $T_a = 800 \pm 10^\circ\text{K}$, and is of second order.

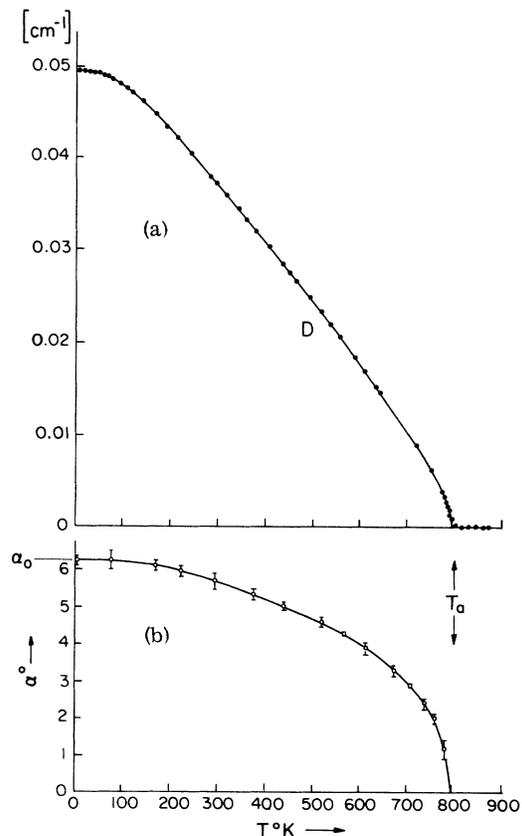


FIG. 1. (a) Axial splitting D of the Fe^{3+} EPR spectrum, and (b) trigonal rotation angle of the AlO_6 octahedra in LaAlO_3 as a function of temperature below T_a .

The Fe^{3+} has a ${}^6S_{5/2}$ ground state and a fourth-order term in the Hamiltonian of the form

$$a(S_{\xi}^4 + S_{\eta}^4 + S_{\zeta}^4) \quad (1)$$

is present. The $\xi\eta\zeta$ axes define an orthogonal system of axes in the directions of the octahedral oxygens around the Fe^{3+} . From this term the orientation of the octahedra with respect to the crystalline axes can be obtained.⁹ It was found that below the phase transition, the oxygen octahedra rotate around a cubic $[111]$ axis.¹⁰ Because in the perovskite structure the BO_6 octahedra have common oxygen corners, half of them rotate by an angle $+\alpha$ and the other half by an angle $-\alpha$. The unit cell is then enlarged. A glide plane along the trigonal axis is present and the structure is $R\bar{3}c$.¹⁰ In a hexagonal triple cell, the oxygen parameter x is

$$x = \frac{1}{2}[1 \pm 3^{-1/2} \tan \alpha]. \quad (2)$$

This first structure determination using EPR was well confirmed by a neutron diffraction study of Tsoucaris and coworkers,¹¹ where the determined oxygen parameter $x = 0.53 \pm 0.01$ was, within the experimental accuracy, the one obtained by EPR at 300°K . Since then we have determined the rotation angle α in the whole range from 800 to 4.2°K . The results are shown in Fig. 1(b).

After the observation of a slight anisotropy of the dielectric constant in SrTiO_3 below 100°K by Gränicher,¹ an EPR study on Fe^{3+} first established the existence of a cubic-to-tetragonal phase transition by means of line splitting resulting from the presence of domains.² This finding has been confirmed by EPR with eight different paramagnetic impurity ions¹² and a considerable number of other experiments.¹³ Sawaguchi¹⁴ observed the domains optically and showed that they are unaffected by an applied electric field, thus the low-temperature phase is nonpolar. Using the large axial EPR splitting of Gd^{3+} below the transition, Rimai and de Mars¹⁵ confirmed the second-order nature by measuring $D(T)$, which varies near T_a as $(T_a - T)^{1/2}$. In the meantime, we have measured the smaller $D(T)$ parameter of Fe^{3+} with better crystals. The data illustrated in Fig. 2(a) show that $D(T)(\text{Fe}^{3+}) \sim (T_a - T)^{1/2}$ near $T_a = 103 \pm 1^\circ\text{K}$. Figure 2(a) also shows the rhombic splitting of an axial Fe^{3+} spectrum attributed to a substitutional Fe^{3+} -oxygen vacancy complex ($\text{Fe}^{3+}-\text{VO}^{2-}$) due to local charge compensation.^{16,17}

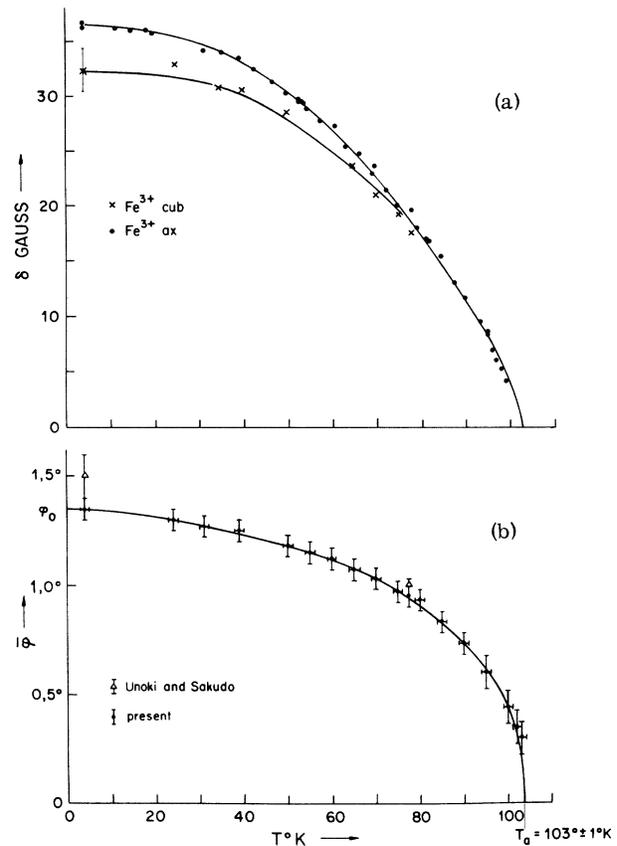


FIG. 2. (a) Axial splitting of the "cubic" Fe^{3+} and rhombic splitting of the ($\text{Fe}^{3+}-\text{VO}^{2-}$) spectrum. (b) Tetragonal rotation angle $\bar{\varphi}$ of the $\text{Fe}^{3+}-\text{VO}^{2-}$ complex in SrTiO_3 as a function of temperature below T_a .

Already in the first study, the possibility of a rotation of the TiO_6 octahedra around a tetragonal axis below the phase transformation in SrTiO_3 was discussed.² The $\text{Fe}^{3+}-\text{VO}^{2-}$ defect pair defines an axial ζ direction in the crystal. Thus, below 103°K if the octahedra rotate, certain distinct maxima and minima of the EPR spectrum will not occur along the tetragonal directions of the crystal. This has indeed been found to be the case and the tetragonal rotation angle $\bar{\varphi}(T)$ has been measured down to 4.2°K as shown in Fig. 2(b). In this figure, two data points of a remarkable study of Unoki and Sakudo¹⁸ are reproduced which agree with ours within the experimental accuracy. These authors were also able to resolve the rotation of the charge-noncompensated Fe^{3+}O_6 octahedra using the term (1), with crystals of Japanese origin. They find that the angle $\varphi(T)$ derived from the charge-noncompensated Fe^{3+} is proportional to the charge-compensated one at the two temperatures they measured, and

obtain

$$\varphi(T) = 1.4\bar{\varphi}(T). \quad (3)$$

They also made the first structure determination of the low-temperature phase of SrTiO_3 and found it to be probably $I4/mcm$. We agree with this assignment which is thus the second such determination using EPR.

In Fig. 3, the rotation angles of the octahedra around the tetragonal axis in SrTiO_3 and around the trigonal axis in LaAlO_3 are plotted in reduced units, $t = T/T_a$, $\varphi' = \alpha' = \varphi/\varphi_0 = \alpha/\alpha_0$. Despite the fact that the transition temperatures differ by a factor 8 and that the maximum rotations differ by a factor 3, the fit of the two curves is very good. Thus there can be little doubt that the order parameter is the rotation angle and the physical origin is the same in both cases. Because LaAlO_3 is a normal oxide, it is unlikely to have a soft ferroelectric TO mode tending towards zero at $k=0$. Thus, the soft ferroelectric mode known to exist in SrTiO_3 cannot be the primary cause for its phase transition at T_a . Such a possibility was suggested by Cowley³ to result from an accidental degeneracy of this TO mode with the longitudinal acoustic one.

Our findings are in agreement with those of Rupprecht and Winter¹⁹ who have carefully investigated the electric field dependence of T_a in SrTiO_3 ²⁰ and who expressed doubts in the above explanation.³ Further, Horner⁴ finds on theoretical grounds that Cowley's mechanism cannot lead to this transition. Horner proposes a two-phonon bound state instead, in which the soft TO mode at $k=0$ plays a major role. However from

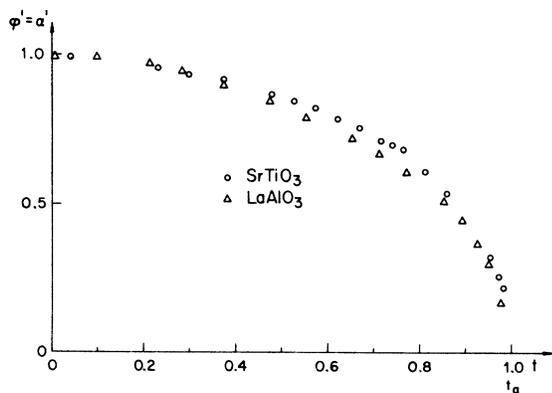


FIG. 3. Trigonal and tetragonal rotation angle of AlO_6 and TiO_6 octahedra in LaAlO_3 and SrTiO_3 as a function of temperature in reduced units, $t = T/T_a$, $\varphi' = \alpha' = \varphi/\varphi_0 = \alpha/\alpha_0$.

our evidence, all the explanations involving the dielectric anomalies are excluded as primary cause. The SrTiO_3 phase transition is thus typical for compounds crystallizing in the perovskite structure. LaAlO_3 is to our knowledge the cleanest and most characteristic example of such a transition.

Using the EPR structure determination of LaAlO_3 , Cochran and Zia²¹ show that the phase transition may be of second order. This conclusion is well supported by our $D(T)$ data on Fe^{3+} [Fig. 1(a)]. They further find that in LaAlO_3 there should be only one TO mode becoming soft near T_a at the $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ point of the Brillouin zone. Thus, there can obviously be no interaction of an acoustic mode with another soft TO mode at $k=0$. A coupling of an acoustic mode with the one soft TO $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ mode may, however, be important.

We can now assume these findings in LaAlO_3 to hold also for SrTiO_3 , where there is actually a soft TO mode at $k=0$. Therefore we can stipulate that in SrTiO_3 there are at least two TO modes tending to zero, one near T_a and a second one with characteristic temperature $T_c \sim 40^\circ\text{C}$ at $k=0$. From the structure of SrTiO_3 we conclude that the former becomes soft at the $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ corner point of the zone.

After the present manuscript had been submitted, a paper by Fleury, Scott, and Worlock²² appeared in this journal on their Raman scattering experiments in SrTiO_3 below T_a . Their data and arguments strongly support the existence of a phonon soft mode at the corner point of the zone for $T > T_a$ which has now been observed with neutron scattering by G. Shirane (see Ref. 22).

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CORRELATED-UNCORRELATED REACTION KINETICS IN A DISCRETE LATTICE

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(Received 26 July 1968)

A new technique is introduced which provides a unified formalism for treating diffusion-controlled reaction kinetics in a discrete lattice. Illustrative calculations are presented for vacancy-interstitial reactions in a fcc lattice.

Diffusion-controlled reaction kinetics were first treated by Smoluchowski.¹ His treatment has been extended and applied in a number of fields, but we will be concerned with radiation damage where such an approach to the recombination kinetics of vacancy-interstitial (Frenkel) pairs was first employed by Fletcher and Brown.² The theory was developed in a unified, closed form by Waite,³ whose work has been extended by others.⁴⁻⁸ The theory, particularly in the Waite form, has found a number of applications in both semiconductors^{5,9-13} and metals,^{7,8,14-20} with probably the most extensive test coming in copper.^{7,8,14,17} The Waite theory, and its derivatives, has the deficiency of being a continuum theory, whereas the experiments are on discrete lattices which exhibit well-resolved recovery stages.²¹ Thus the theory has limited utility in aiding in the identification and the understanding of specific defect configurations and recovery mechanisms. Moreover, the theory employs a spherically symmetric function for the distribution of the interstitial about the vacancy, whereas numerous experiments indicate an anisotropy in the damage threshold and production rate²² which should be manifest in the distribution function of the interstitials as well. Further, an important parameter obtained from fitting the theory to experiment, the volume about a vacancy

for the capture of interstitials, seems too large^{14,17,18,20,24} (containing well over 500 lattice sites) in view of both the calculation by Johnson,²⁵ which gave a capture volume of less than 50 lattice sites, and the observation of relatively few recovery stages due to bound vacancy-interstitial pairs.²¹

In this paper we consider a new computational technique and demonstrate its use in treating diffusion-controlled reaction kinetics in discrete lattices. For convenience, but with no significant detriment, we consider the vacancies immobile and the interstitials the mobile defect. We let \vec{C} be a vector,²⁶ the i th component of which, C_i , will be the concentration of interstitials at the i th site about a vacancy site; $(C_i)_0$ will be the initial distribution. We let P be the matrix whose components P_{ji} are the probabilities per time increment for transition from the i th to the j th site,^{27,28} where the time increment (which we refer to as a "jump") is chosen so that the P_{ji} are conveniently small. The absorbing boundary condition at the sites on the surface of the vacancy capture volume requires $P_{ji} \equiv 0$ for transitions out of the capture volume. Next we establish a hierarchy of difference equations: After the first jump the concentration vector is $\vec{C}_1 = P\vec{C}_0$; the second jump, $\vec{C}_2 = P\vec{C}_1 = P^2\vec{C}_0$; \dots , $\vec{C}_N = P^N\vec{C}_0$. Thus far we have simply described