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# Static Critical Exponents at Structural Phase Transitions

K. A. Müller and W. Berlinger
*IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland*

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The temperature dependence of the rotational displacement parameters below the second-order phase transitions in $SrTiO_3$ and $LaAlO_3$ at $T_a = 105.5$ and 797°K is described by an exponent $\beta = 0.33 \pm 0.02$ down to $t = T/T_a = 0.95$. For smaller $t$'s there occurs a change to Landau behavior approximately followed between $t = 0.9$ and 0.7. The observation of static critical exponents near displacive phase transitions confirms now the notion of universality in this field.

The static scaling theories introduced for fluids and for the Ising model have been quite successful in describing phase transitions[1-4] in the critical region. The critical exponents deduced for magnetic systems and fluids are close to one another[4,5] and the notion of universality has been advocated[6]; its essence being that, in the critical region, physically measurable variables become, to a substantial extent, independent of interatomic interactions. Due to the cooperative phenomena the correlation lengths are much larger than the range of forces between particles making the phenomena nearly independent of them.

Although the universality notion is quite suggestive and successful in most of the order-disorder transformations, an important void existed to fully confirm its validity. This concerns the large group of order-order transformations such as displacive purely structural or ferroelectric ones. Indeed up to recently these have all been analyzed within the framework of the Landau approach or the mean-field approximation, which yields critical exponents $\alpha = 0$, $\beta = \frac{1}{2}$, $\gamma = 1$, etc. (for a definition see Ref. 4). However, very recently it was found that the uniaxial stress dependence of the order parameters in $SrTiO_3$ within one degree of the transition $T_a$ of the unstressed crystal deviated from the classically computed value.[7] In $LaAlO_3$ the temperature dependence of the EPR parameter $D(T)$ of $Fe^{3+}$ substitutional for $Al^{3+}$ deviated for $T < T_a$ near the structural phase transition from the straight line it should have followed if the system had behaved Landau-like[8] (see below). Hereafter it will be shown quantitatively that in both crystals the exponent $\beta$ of the displacement parameter differs indeed from the mean field result ($\beta \neq \frac{1}{2}$).

The phase transitions in $SrTiO_3$ and $LaAlO_3$ set in when, in the cubic crystals, alternate static rotations of nearly rigid $TiO_6$ and $AlO_6$ octahedra occur around the [100] and [111] axes, respectively.[7] The rotation angle $\varphi$ is a measure of the oxygen displacement, and corresponds to the order parameter of an order-disorder transition.[9] Its temperature dependence has been determined with limited accuracy by paramagnetic resonance of $Fe^{3+}$ ions substitutional for $Al^{3+}$ in $LaAlO_3$ and $Ti^{4+}$ in $SrTiO_3$.[8] In the latter case there is a charge misfit, and in addition to the $Fe^{3+}$ spectrum due to nonlocal charge compensation, one with a nearest-neighbor oxygen vacancy ($Fe^{3+}$-$V_O$) is observed.[8] Very recently proper shaping of $SrTiO_3$ crystals led to samples which became nearly monodomain below the phase transitions.[10] These samples allowed us a heretofore unattained accuracy in the determination of $\varphi$. The $c$ axis of the monodomain was aligned parallel to the rotation axis of the magnet. Under this geometry there are essentially two $Fe^{3+}$ spectra rotated relatively to each other by $2\varphi$, the difference in $TiO_6$ sublattice rotations. Due to local distortion the corresponding $Fe^{3+}$-$V_O$ spectra are rotated by the smaller amount $2\bar{\varphi}$; $\varphi = (1.59 \pm 0.05)\bar{\varphi}$.[7] For temperatures very close to $T_a$, where $\varphi$ is small, the field splitting of the lines proportional to $\varphi$ or $\bar{\varphi}$ was scanned on a recorder and analyzed. Maximum sensitivity occurs for maximum slope of the resonance magnetic fields versus field angle, i.e., ~30° away from [100] for the $Fe^{3+}$ and along [110] for the $Fe^{3+}$-$V_O$ spectrum ($H_c$ in Fig. 1 of Ref. 7). For the latter an ultimate accuracy of $1 \times 10^{-2}$ angular degrees was achieved corresponding to a determination of relative oxygen position by $\Delta x = 4\times 10^{-12}$ cm. The temperature was determined with a gold-2.1% cobalt-copper thermocouple, a constant-voltage source, and a Keithley model No. 149 millimicrovolt null detector to a relative accuracy of 4/100 of a degree.

To determine $\beta$ in the exponential relation

$$\varphi \propto \epsilon^{\beta}, \quad \epsilon = (T_a - T)/T_a, \tag{1}$$

we plotted $\varphi^{1/\beta}$ as a function of $T$ with assumed exponents $\beta$ for two data sets; one obtained for the "cubic" $\mathrm{Fe}^{3+}$ and the other for the $\mathrm{Fe}^{3+}$-$V_{\mathrm{O}}$ center. A near straight line was obtained for $\beta = 0.33$ rather than 0.32 or 0.34. Extrapolating this line back to $\varphi^{1/\beta} = 0$ yields the transition temperature $T_a = 105.50 \pm 0.04$. With this we obtain $t = T/T_a$ and $\epsilon = 1 - t$ to an accuracy of $4\times 10^{-4}$. From Fig. 1 one sees that down to $t = 0.94$ the straight line is well followed, but afterwards it deviates. To estimate the range of $\epsilon$ in which (1) is valid a least-squares fit (LSF) computed for the first eleven points with the more precise data of the $\mathrm{Fe}^{3+}$-$V_{\mathrm{O}}$ center gives $1/\beta = 3.004$, and for the first thirteen points (down to $t = 0.92$) $1/\beta = 2.991$. With a range in $\epsilon$ of $5\times 10^{-2}$ to $1.5 \times 10^{-3}$ we estimate the absolute limit $\beta = 0.33 \pm 0.02$. The determined $T_a$ is of value only for the particular sample. Due to differences in the oxidation and impurity content, deviations as large as 3°K have been observed for certain crystals.[7]

In $\mathrm{LaAlO_3}$, determination of $\varphi$ necessitates a rotation of the monodomain sample around the domain axis (inclined by ~60° to the magnetic field). It is far too imprecise for present needs, as is also a measurement of appropriate line splittings, due to large EPR line widths. These are narrowest for $H$ parallel to the domain axes. There the lines are insensitive to $\varphi$ but sensitive to $D$, the accurately determined crystalline field parameter,[8] which reflects the local distortion of the octahedra along the trigonal axis. $D$ must be proportional to an expansion in even powers of $\varphi$ because the trigonal $R\bar{3}c$ structure has a center of inversion. Thus for small $\varphi$, $D \propto \varphi^2$. Assuming the critical exponent of $\varphi$ is close to $1/\beta = 3$ as in $\mathrm{SrTiO_3}$, $D^{3/2}$ should be proportional to $t$. In Fig. 2 this is seen to hold for the first seven points down to $t = 0.94$ with $T_a = 797$°K for our sample. An LSF for these gave $1/\beta = 3.03$.

In our opinion it is remarkable how well the critical exponents $\beta$ coincide in magnitude as well as in range of validity for $\mathrm{SrTiO_3}$ and $\mathrm{LaAlO_3}$, despite one crystal being tetragonal and the other trigonal. In addition, the transition temperature for $\mathrm{LaAlO_3}$ is eight times higher than that of $\mathrm{SrTiO_3}$. However it should be noted that in both cases the transformations occur from a cubic structure. In this context is it interesting that the value of $\beta$ is, within the experimental error, the same as the one determined by Heller and Benedek[11] in ferromagnetic EuS although this is an order-disorder system. The high-temperature phase of EuS is also $O_h^{1}$ as in $\mathrm{LaAlO_3}$ and

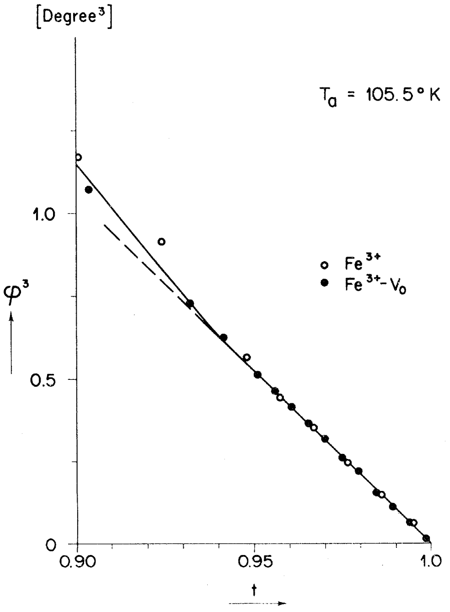

FIG. 1. The cube of the rotational parameter $\varphi$ versus reduced temperature $t = T_a$ in $\mathrm{SrTiO_3}$.

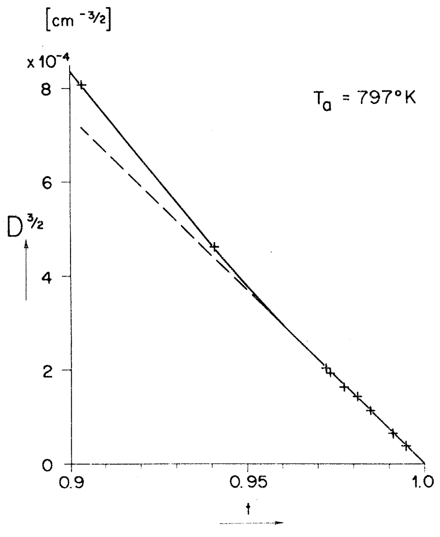

FIG. 2. EPR parameter $D^{3/2}$ versus reduced temperature $t$ in $\mathrm{LaAlO_3}$.

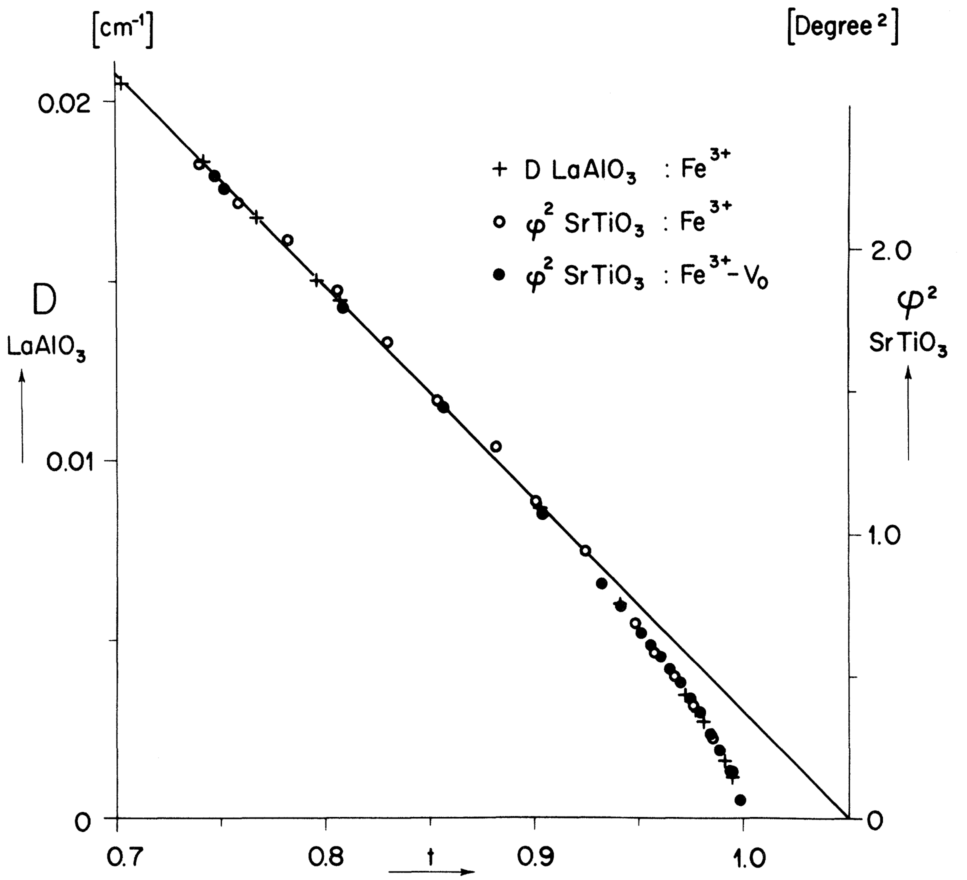

FIG. 3. $\varphi^2$ of $SrTiO_3$ and $D$ of $LaAlO_3$ vs $t$ between 0.7 and 1, showing the changeover from Landau to critical behavior.

$SrTiO_3$. The $\beta$'s observed in this group appear to deviate slightly from the ones in noncubic $CrBr_3$ and isotypes as well as the gas-liquid systems[5]. It is common to all static scaling theories that the critical exponents of two physical variables remain undertermined.[1-4] Apart from $\beta$ obtained here, a measurement of specific heat possibly yielding $\alpha$ or $\alpha'$ could be of value.

To obtain the limit beyond which the behavior becomes classical, $\varphi^2$ of $SrTiO_3$ and $D$ of $LaAlO_3$ were plotted as a function of $t$. If the systems behaved Landau-like, a straight line should result. From Fig. 3 it is seen that this is approximately the case for $0.7 \leq t < 0.9$ in both systems. Furthermore $\varphi^2$ ($SrTiO_3$) and $D$ ($LaAlO_3$) are proportional to each other to an appreciable extent, also outside the critical region, thus their respective rotational parameters are, too. From this a number of conclusions can be drawn.

In scaling, the critical region extends equally above and below $T_a$, i.e., $t_\pm = 1 \pm \epsilon_c$. With $\epsilon_c \simeq 0.1$ from Fig. 3 it becomes clear why the Landau analysis of Slonczewski and Thomas[12] on several $SrTiO_3$ experiments gave good results except near $T_a$. Using their calculated specific-heat jump $\Delta c_p = 8.1 \times 10^{-4}$ cal/deg g at $T_a$ and $\rho = 5.13$ g cm$^{-3}$ in the expression of Ginzburg,[13]

$$l = (k/\rho \Delta c_p)^{1/3} \epsilon_c^{-1/6}, \qquad (2)$$

which defines a zero-temperature coherence length $l$, we obtain $l \approx 13$ Å, which is of the order of the distance between equivalent octahedral units (8 Å) as expected. Thus for the structural transitions $l$ is quite short range as evidenced from the large $\epsilon_c$. Further (2) is more quantitative than anticipated and agrees with findings for $l$ in the ordering $CdIn_2S_4$ spinels.[14]

In the megahertz region a strong ultrasound absorption has been observed especially in near-monodomain $SrTiO_3$ peaking at $T_a$.[15] The absorption clearly occurs in the critical region between $t_+$ and $t_-$ and thus is due to critical absorption and cannot be explained by classical theories.

The soft optic mode $\omega_0$ associated with these structural phase transitions is underdamped in $SrTiO_3$[16] and overdamped in $LaAlO_3$.[17] From our data it follows that static scaling is independent of mode damping. Using the fluctuation-dissipation theorem, one derives that the intensity $I'$ of the diffraction peaks, which are observed below $T_a$, is proportional to $T\omega_0{}^2 \propto T\varphi^2$. Thus $I'/T$ should behave like[17] $\varphi^2$ or the EPR parameter $D$. This is observed for the (331) Bragg reflection[18] in $KMnF_3$ undergoing the same transition as $SrTiO_3$ at 184°K, and in $LaAlO_3$ for the (711) reflection as measured by Plakhty and Cochran.[19] In both cases a straight line is followed by a rounding down near $T_a$. With the more precise data in $LaAlO_3$, an LSF yielded $1/\beta = 2.6$ and 3.5 for the first three and four points, respectively, bracketing our value of 3.0. The classical straight line overshooting $T_a$ as in Fig. 3 was also obtained from Raman[20] and neutron data[17] in $LaAlO_3$ and has been discussed in terms of a possible first-order transition. From the present work it is now assigned in a quantitative way to nonclassical behavior.

It also becomes clear why deviations from Landau behavior are more difficult to discern in displacive ferroelectrics: For perovskite materials the ferroelectric transitions are all first order with $\epsilon_T = (T_0 - T_c)/T_0$ typically of several percent. We can assume that the dipolar forces are rather longer in range than those leading to purely structural transitions, thus we can set $\epsilon_c(\text{ferro}) \lesssim \epsilon_c(LaAlO_3)$ and obtain $\epsilon_c(\text{ferro}) \lesssim \epsilon_T$. This agrees with the results of Vaks,[21] who estimates correlations $\xi$ of the order of unity at $T_0$. However due to strong soft Cochran-mode-acoustic-mode coupling he concludes that $\xi$ is sufficiently large to induce the first-order ferroelectric transitions. The small rotational-mode-strain coupling in $SrTiO_3$ and $LaAlO_3$[13,22] allows a near-second-order transformation to take place to such an extent that most of the critical region associated with large fluctuations is observable.

Our work suggests a large variety of high-precision experiments to be undertaken to test the static and dynamic scaling laws near the order-order phase transitions of these compounds as well as in crystals undergoing similar transitions as $KMnF_3$[18] or $NdAlO_3$[20] and possibly then allowing systematics in their critical exponents.

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