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High temperature phase transitions in barium sodium niobate: the wall roughening $1q$ – $2q$ incommensurate transition and mean field tricritical behaviour in a disordered exclusion model

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Received 29 March 2005, in final form 1 August 2005

Published 2 September 2005

Online at stacks.iop.org/JPhysCM/17/5911

Abstract

Barium sodium niobate ($\text{Ba}_2\text{NaNb}_5\text{O}_{15}$) is a tungsten bronze structure that exhibits a complicated sequence of six structural phase transitions, including three incommensurate (IC) phases. The phases are unusual in that all but the highest temperature $P4/mbm$ structure are ferroelectric. Unlike the situation for most incommensurate insulators, in which ferroelectricity develops at low temperatures along the modulation direction, the polarization direction in barium sodium niobate is orthogonal to the modulation(s), permitting some unusual phenomena. In the present study we analyse the thermal and dielectric behaviour at the Curie temperature T_C near 830 K as well as that at the $Ccm2_1$ – $IC(1q)$ transition near 543 K, the $IC(1q)$ – $IC(2q)$ transition near 565 K and the $IC(2q)$ – $P4bm$ transition at 582 K. The entropy change at 565 K is related to the wall roughening model of Rice *et al* (1981 *Phys. Rev. B* **24** 2751). Data near $T_C = 830$ K indicate close proximity to a tricritical point, and discussions of critical exponents are presented, all of which are found to be mean field. Because of Na vacancies, transition temperature variation is found among specimens $\text{Ba}_2\text{Na}_{1-x}\text{Nb}_5\text{O}_{15}$ ($830 \text{ K} < T_C(x) < 865 \text{ K}$), and the system appears to be describable by the disordered exclusion model as a slightly first-order intrinsic system whose dynamics are suppressed by weak disorder. Near T_C the specific heat $C(T)$ is compared with the random bond prediction of Harris (1974 *J. Phys. C: Solid State Phys.* **7** 1671): $C(T) = C_0(T)/[1 + bx^2C_0(T)]$, where $C_0(T)$ is the intrinsic specific heat of the vacancy-free crystal varying as $(T_C - T)^{-1/2}$ and x is the sodium vacancy concentration. In agreement with Harris's model, the shifts in $T_C(x)$ are to lower T with increasing x and scale as x ; the broadening scales as x^2 ; and the effective critical exponent remains unchanged at $\alpha = 1/2$.

1. Introduction

The situation with regard to critical exponents describing thermodynamic quantities near structural phase transitions in ferroelectrics and related oxides is at present rather unsatisfactory, both theoretically and experimentally. Very few ferroelectrics actually exhibit continuous, second-order phase transformations; most are slightly first order, that is, near tricritical points. The exponent α' that describes the divergence of specific heat just below a tricritical point has been calculated in mean field theory to be zero (logarithmic or step discontinuity) in one standard textbook [1] and to be $1/2$ in an equally popular text [2]. It is historically interesting to note that Landau's calculation of $\alpha' = 1/2$ actually predates [3] his classic 'Landau theory' paper of 1937, although this was apparently unknown to the author of [1]. Experimentally, most researchers find these crystalline phase transitions to be mean field, as expected from the fact that strain is long range and unscreened, and the Coulombic interaction (unlike magnetism) also long range; but this is equally contentious, with Kleeman *et al* claiming [4] SBN (tungsten bronze structure strontium barium niobate) to be a perfect example of random field Ising dynamics (RFID), Schranz *et al* recently clarifying the earlier controversy that ferroelectric Lawsonite near T_C is a mean field and *not* an Ising system [5] but maintaining that the antiferrodistortive transition in the same material is not mean field but a [3D] Ising system (this paper clarifies earlier results [6, 7]) and finally Harris arguing that calcite and NaNO_3 are [2D] XY -systems and not mean field [8]. Many authors do not recognize that structural phase transitions may yield 'apparent' or 'effective' exponents (such as $\beta \ll 1/2$ for the temperature dependence of the order parameter), not from true critical fluctuations and the consequent failure of mean field theory, but instead from some slight order-disorder character; structural phase transitions should give $\beta = 1/2$ (second order) or $\beta = 1/4$ (tricritical) only in the displacive limit, not in a system with mixed order-disorder and displacive dynamics. It is unlikely that claims of non-mean field behaviour extending over many degrees can be compatible with the 'Ginzburg criterion' [9] (actually derived by Levanyuk [10]), simply because true universal, fluctuation-dominated 'critical' dynamics require that $\langle \phi^2 \rangle \gg \langle \phi \rangle^2$, where ϕ is the order parameter; and this condition is unlikely to prevail several degrees or more from the phase transition temperature. Indeed, even for SrTiO_3 where the well-known EPR results of Mueller produced [11] a critical $\beta = 0.332$, newer birefringence results from Oxford [12] yield perfectly mean field results of $\beta = 0.50$. We emphasize that in the present case the values of the primary critical exponents $\alpha, \beta, \gamma, \delta$ are all self-consistent, and we draw no conclusions based upon $\beta = 1/4$ alone. Further, we stress that although our barium sodium niobate specimens have weak static disorder due to Na vacancies, the *dynamics* of the ferroelectric phase transition are displacive.

Part of the problem is that among ferroelectrics with displacive phase transitions (as opposed to order-disorder ones) there are very few, if any, for which all of the basic critical exponents $\alpha, \beta, \gamma, \delta$ have been measured near tricritical points. (Here, in the usual notation, α refers to the divergence of the specific heat; β describes the order parameter evolution with reduced temperature $t = (T_C - T)/T_C$ (i.e., spontaneous polarization in a ferroelectric $P(T) = P(0)t^\beta$); γ is the isothermal susceptibility exponent $\varepsilon(t) = \varepsilon(1)t^{-\gamma'}$; and δ , that describing the dependence of displacement vector D or polarization P with applied conjugate field E along a critical isotherm $E = D^\delta$; primes denote values below the Curie temperature T_C .) The behaviour of critical exponents in ferroelectrics near tricritical points has been of special pedagogic interest for more than thirty years, because as claimed by Stanley [1], mean field theory predicts values ($\alpha = \alpha' = 0$, yielding a step discontinuity or logarithmic divergence; $\beta = 1/4$; $\gamma = \gamma' = 1$; $\delta = 5$) that fail to satisfy the Rushbrooke inequality [13], which is satisfied as an equality with $\alpha = 1/2$ in scaling theory (the Griffiths inequality [14, 15]

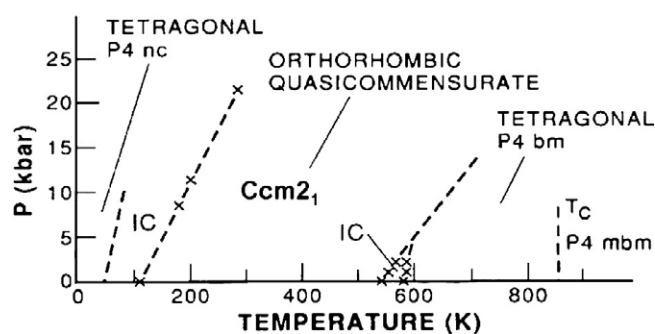


Figure 1. Phase diagram for barium sodium niobate: $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$. The room temperature phase is nominally a commensurate orthorhombic $Ccm2_1$ structure [36] and not the previously assigned [37] $Ccm2$; but a small residual incommensurate quality is found in most samples and generally attributed to Na vacancies pinning antiphase boundaries [38].

is also not satisfied by Landau theory at tricritical points with $\alpha' = 0$, but requires $\alpha' = 1/2$). However, Strukov and Levanyuk [2] disagree with Stanley, following Landau's original 1935 work and deriving $\alpha' = 1/2$ from the simplest $G(P, T) = A(T_C - T)P^2 + BP^4 + CP^6$ Landau–Devonshire free energy. Values of α' have been discussed by Scott [16] (various measurements of α' near tricritical points in ferroelectrics are given in [17–23]) and are also of considerable interest and controversy experimentally in the case of strontium barium niobate (SBN) [3, 24], typically doped with Ce. Adding to the interest is the fact that barium sodium niobate is normally not stoichiometric, owing to the presence of Na ion vacancies, which vary strongly from sample to sample (thus giving T_C from 830 to 863 K). This kind of weak disorder arising from vacancies at only one kind of lattice site probably satisfies the description of ‘disordered exclusion models’, which can change [25, 26] the critical behaviour of nominally second-order phase transitions, according to the Harris criterion [27–32], and also suppress the first-order character of phase transitions [33]. Hence in the present study we wish to reconcile disparate specific heat measurements on $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ and see whether we can describe it in terms of these models; some specific heat data have been presented recently by others, but not fitted to any models [34]. Previously we have shown that our experimental values of β , γ and δ for barium sodium niobate satisfy the thermodynamic Widom equality [35]

$$\gamma' = \beta(\delta - 1), \quad (1)$$

which yields experimentally $1.1 \pm 0.1 = (0.31 \pm 0.05)(4.0 \pm 0.1) = 1.2 \pm 0.1$; but this relationship, unlike those of Griffiths, does not involve the specific heat exponent α . It is useful to point out, parenthetically, that the early but very precise values of $d_{15}(T)$ reported by Byer *et al* [36] show no discontinuity at T_C and are compatible with $1/4 < \beta < 1/2$, and therefore support the value of $\beta = 0.31$ given by Shieh *et al* [36]. Although Byer *et al* did not attempt to fit a value of β from their data, our fit to their data yields $\beta = 0.41 \pm 0.05$, in fair agreement with 0.31 ± 0.05 from Sheih *et al* on a different sample; note that near the exact tricritical point but on the continuous side, β will lie between $1/4$ and $1/2$ from mean field tricritical theory.

The accepted P – T phase diagram for this material is shown [37, 38] in figure 1.

The order parameter for the incommensurate phase is four dimensional, which is unusual but not unique (e.g., BaMnF_4) [39]. This actually causes some serious consequences: unlike systems with order parameters of dimension 1, 2 or 3, four-dimensional cases are those for which the dimensionality is not sufficient to specify the critical behaviour, which also in this case depends upon the symmetry of the order parameter. In some cases [39] the effects

of fluctuations prevent continuous transitions. Toledano and Toledano [39] find that for four-dimensional order parameters the critical exponent β should be 0.39. There has been particular interest in the interaction of mobile point defects with incommensurate antiphase boundaries [38–42]; Toledano *et al* have shown [38] that these are sodium vacancies (as verified by Oliver and Scott [36]), and Schneck has shown [41] that the vacancy concentration can exceed 10%, depressing T_C . These antiphase kinks can propagate very rapidly and give rise to a diffusivity of $1.3 \text{ cm}^2 \text{ s}^{-1}$ [42, 43], approximately 65 times faster than the thermal diffusion at the same temperature, and compatible with theory [44]. Additional studies show [45, 46] that this diffusion is hydrodynamic, with a dynamic central mode linewidth whose width is proportional to q^2 , the square of the momentum transfer in laser spectroscopy experiments. The lowest temperature $P4nc$ phase was determined from a spallation neutron study [47] and is the most recent phase characterized, with its space group in accord with the PhD Thesis prediction of Schneck [41]; note, however, that one group of authors (Uesu *et al* [48, 49]) have found no evidence of any transition near 40 K or in fact below 110 K. This point is reviewed by Buixaderas *et al* [50]. The $1q-2q$ transition near 565 K was analysed by Raman spectroscopy [51]. The same 12% modulation of NbO_6 octahedra angles in the IC phase was found independently by Oliver *et al* [52, 53] and Labbe *et al* [54]. Whereas the $1q$ orthorhombic modulation is long range, the $2q$ tetragonal modulation is only short range [55–62] as shown especially by electron microscopy studies [58–62], and therefore we will describe it in the present work as a wall roughening phenomenon [63]. In general, it is expected that ferroelectric incommensurate insulators will *not* undergo wall roughening transitions for the antiphase boundaries in their incommensurate phases; but as pointed out by Levanyuk [64], this should be true only for those in which the ferroelectric polarization is collinear (or coplanar) with the modulation(s). The reason is that the macroscopic strain that is associated with antiphase boundary curvature carries a long-range Coulombic field, so roughening has an energy cost. Since the crystal structure has \mathbf{P} perpendicular to its modulation(s), wall roughening might be expected in $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$.

The original study of specific heat and entropy changes in the high temperature phases of barium sodium niobate was by Toledano and Pateau in 1974 [65]. However, at that time they thought that the three transitions at about 543, 565 and 582 K were a single (continuous) $Ccm2_1-P4bm$ orthorhombic–tetragonal transition. They pointed out that their experimental results were inconsistent with this assumption combined with mean field dynamics in that the measured specific heat anomaly was an order of magnitude larger than calculated.

2. Experiment

In all first-order or tricritical phase transitions it is convenient to denote three different characteristic temperatures. We use below T_0 to designate the actual phase transition temperature. T_C is the ‘Curie temperature’, and it denotes the extrapolated divergence of some physical quantity (such as electric susceptibility or specific heat) measured from temperatures above T_0 . T'_C is an analogous quantity extrapolated from temperatures below T_0 . Thus $T_C < T_0 < T'_C$ and for a nearly tricritical system each of the three temperatures differs from the others by about 2–10 K.

2.1. Specific heat

The specific heat of a 0.1 g mass, gem quality crystal of $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ was measured using a Perkin-Elmer ‘Diamond’ differential scanning calorimeter. Because of the different forms and magnitudes of the specific heat anomalies for the ferroelectric and the incommensurate

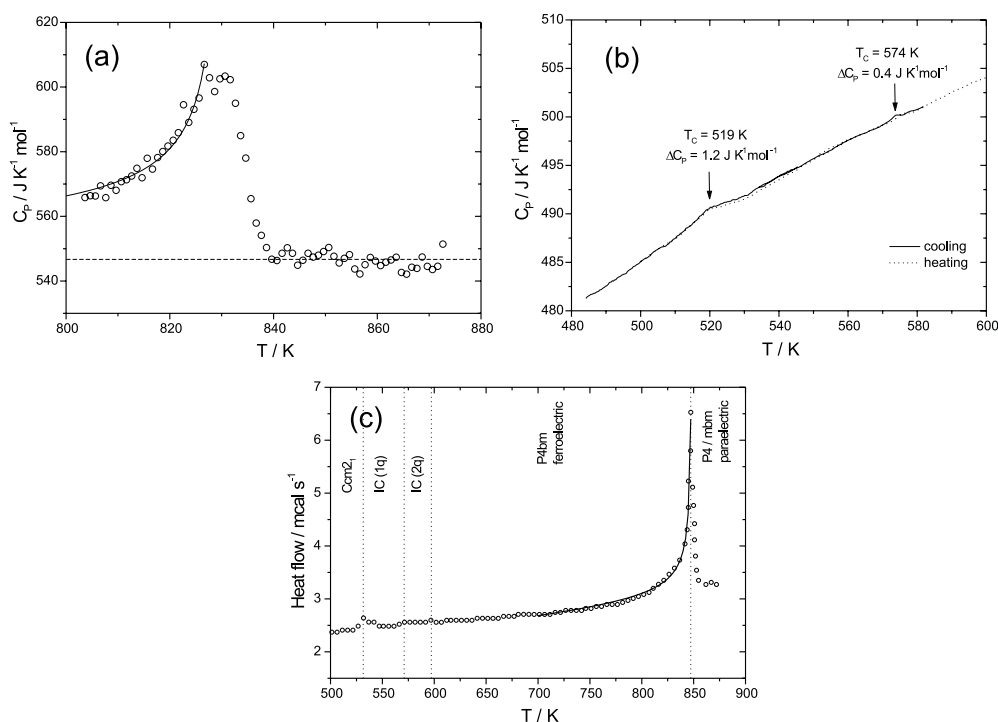


Figure 2. Specific heat: (a) present data on a sample believed to have a high density of sodium vacancies; the solid curve is a fit to the Harris equation (equation (7)) with $\alpha' = 0.50$ and $T_0 = 829.5$ K; (b) present data in the temperature range of the three incommensurate phase transitions, showing the uppermost $2q$ - $P4bm$ and the lowest $Ccm2_1-1q$ (the middle $1q-2q$ is too weak to be seen here but is barely perceptible in (c)); (c) data from [34], fitted by us to a power law $C(T) = A + BT + Dt^{-\alpha}$, with $\alpha = 0.50$, reduced temperature $t = (T'_C - T)/T'_C$ and $T'_C = 848.15$ K.

phase transitions, data were collected using two different calorimetric techniques. For the ferroelectric transition around 830 K, C_P data were collected in step-scan mode; in this method, the sample is repeatedly heated by a standard temperature increment (1 K in this experiment). The heat flow response of the sample is recorded until the sample re-equilibrates. Integrating these data gives the enthalpy change associated with heating the sample, and hence the specific heat, shown in figure 2(a). Measurements in the range $480 \text{ K} < T < 600 \text{ K}$ were made using standard differential scanning calorimeter (DSC) continuous scanning methods, for both heating and cooling scans, with a ramp rate of 20 K min^{-1} . The heat flow data were normalized against a sapphire standard to determine the specific heat, given in figure 2(b). In figure 2(c), we reproduce the raw heat flow data from [34], measured for a different, more stoichiometric sample of $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$.

The fit to the present results for the ferroelectric phase transition shown in figure 2(a) is to the Landau model for a nearly tricritical phase transition, $(T/\Delta C_P^2) \propto (T'_C - T)$, which corresponds to a critical exponent $\alpha' = 1/2$. The fit assumes that the baseline specific heat (shown as a broken line in figure 2(a)) is independent of temperature at sufficiently high T . The temperature T'_C at which ΔC_P would diverge is 831.5 K; the fit shown in figure 2(a) stops at 827 K. (Calibration of our system was made with measurements on quartz and LaAlO_3 , whose transition temperatures are in the same region.) The lower temperature data show two

reasonably clear anomalies, at 519 and 574 K. The most likely interpretation of these data is that these are the temperatures of the $Ccm2_1$ -IC(1 q) and IC(2 q)- $P4bm$ transitions respectively in figure 1, and that the thermal anomaly of the IC(1 q)-IC(2 q) transition is too small to be observed.

The present results shown in figure 2 are compared with previously unfitted data on a different sample from [34]. Note that we see two clear anomalies at the upper and lower incommensurate (IC) phase transitions near 543 and 582 K, and a weaker anomaly at the 1 q -2 q transition at 565 K. The transition near $T_0 = 830$ K, discussed further below, yields a critical exponent $\alpha' = 0.50 \pm 0.05$. We emphasize that this value is expected from scaling theory at tricritical mean field transitions but disagrees with the value (of zero) predicted by Stanley from Landau theory [1]. We show below that it is compatible with the other critical exponents $\beta = 0.31 \pm 0.05$, $\gamma = 1.1 \pm 0.1$ and $\delta = 5.0 \pm 0.1$ determined for this transition. Thus this transition serves as a paradigm for tricritical ferroelectric (mean field) phase transitions. The only other tricritical ferroelectric known to us for which all four of these exponents have been determined is KH_2PO_4 ('KDP'), and that system has been a source of controversy regarding some of its exponents (and even whether the transition is first or second order). The best KDP results are probably those of Schmidt *et al* [17]. The present results also agree with the early values [18] of $\alpha' = 0.50$ in KDP from Reese, and of $\alpha = 0.54$ in BaMnF_4 from Scott *et al* [19], disagree with the non-mean field results from Petzelt *et al* [20] for tris-sarcosine calcium chloride, but agree with the results from Scott and Chen on the same material [21]. Similarly, Lopez-Echarri *et al* find [22] $\alpha' = \alpha = 0.40$ in K_2SeO_4 . Very recently Romero *et al* [23] have also obtained $\alpha' = 0.50$ for the tricritical transition in triglycine selenate.

2.2. Dielectric constant

The original study of dielectric behaviour in barium sodium niobate [66, 67] revealed Curie-Weiss laws in both ferroelectric and paraelectric phases and transition temperatures varying from 833 to 863 K; all samples exhibited slightly first-order transitions, with stoichiometric specimens exhibiting extrapolated Curie-Weiss values of $T_C = 857$ and $T'_C = 859$ K; and the actual transition (Curie) temperature T_0 about midway between at 858 K, at the high T end of the range of samples (less stoichiometric specimens gave T_0 values near 833 K). The more recent data from Zhu *et al* [34] give a slightly lower $T_0 = 848$ K for their specimen. The fitting of T'_C and critical exponent α gives a correlation between these two parameters; therefore in order to provide a value of γ' and also an independent value of T'_C we carried out dielectric measurements on the same sample (B), using an HP4192A impedance analyser. All numerical values quoted are averages of heating and cooling runs. The results are shown in figure 3 and yield $\gamma' = 1.0 \pm 0.1$ and $T'_C = 837.7 \pm 0.1$ K for our sample B; above the transition at $T_0 = 829.5$ K they yield a Curie temperature $T_C = 805.0 \pm 0.1$ K and $\gamma = 1.0$. The large difference of 32.7 K for T_C and T'_C is typical of slightly first-order transitions in ferroelectrics and exceeds the 2 K value from [34] for a perfectly stoichiometric sample. The specific heat data were fitted with this T_0 value as a constraint. Most of the dielectric data were run at 100 kHz; this frequency was chosen after measurements were made at numerous temperatures from 10 Hz to 10 MHz and was picked because it corresponds to a frequency-independent plateau over the temperature range of interest. Both $\epsilon_a = \epsilon_x$ and $\epsilon_c = \epsilon_z$ were measured, where c is the fourfold tetragonal axis. Data very closely resemble the original results of Singh *et al* and Yamada *et al* [66, 67], with ambient $\epsilon_z = 40 \pm 2$ and $\epsilon_x = 230 \pm 5$.

The dielectric loss tangent shown in figure 3(b) exhibits several effects. Below the uppermost incommensurate-commensurate transition temperature at about 582 K, the loss is quite low ($\ll 1\%$). Above the transition to $P4bm$ it abruptly increases and diverges rapidly

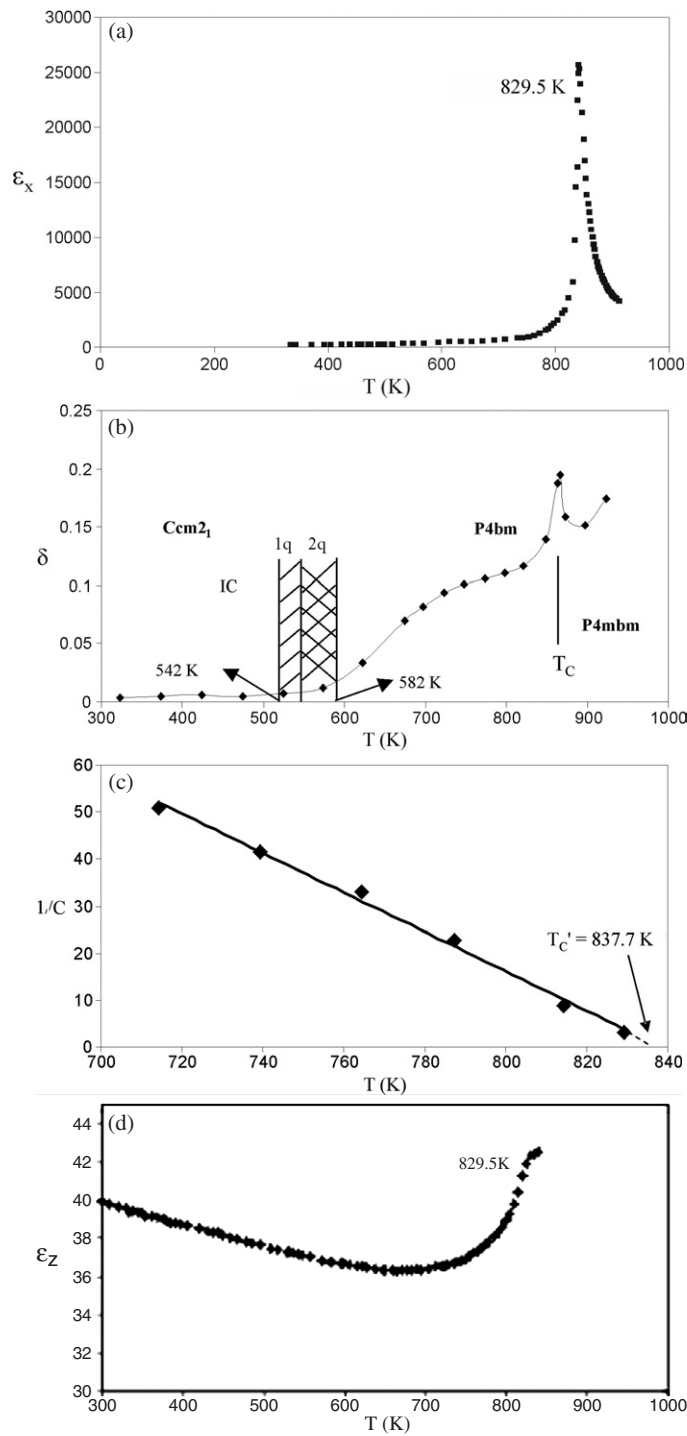


Figure 3. Dielectric constant versus temperature for the present barium sodium niobate sample in the vicinity of its high temperature ferroelectric–paraelectric phase transition temperature (average for heating and cooling). The ratio of $1/\epsilon_x$ above (not shown) and below T_0 is approximately 3.5:1 (see [81] for an explanation of such ratios, which need not be 2:1 even in mean field continuous transitions); (a) ϵ'_x ; (b) $\delta = \epsilon''_x/\epsilon'_x$; (c) $1/\epsilon'_x$ (units are 10^{-5} , dimensionless, and are proportional to reciprocal capacitance $1/C$); (d) non-polar axis susceptibility ϵ'_z ; the minimum near 680 K is not understood but presumably relates to the equally unexplained maximum in the c -axis lattice constant near 675 K [68].

above that temperature, reaching approximately 15% near T_0 . Above 900 K it continues to diverge. This ionic conduction is compatible with other evidence for Na vacancy conduction

discussed elsewhere. We note in addition to this overall increase an unexpected shoulder on the loss beginning at the IC–*P4bm* transition near 582 K and peaking around 700–800 K; this arises slightly above the low temperature limit of the *P4bm* ferroelectric phase and disappears at high temperature for this phase near the *P4bm*–*P4mbm* transition to the paraelectric phase, so it is directly related to the ferroelectric, commensurate state and is absent in the incommensurate state at lower temperatures and the paraelectric state at higher temperatures. Thus, whereas this incommensurate–commensurate transition near 582 K has no measurable effect on the dielectric constant, it has a strong effect, not previously reported, on the loss. It is possible that this loss relates to Na conduction, and we note that there are strong asymmetries in lattice constant expansion [68] at this transition (near 582 K), with the *a*- and *b*-axis expanding at 0.1% per 100 K, but the *c*-axis peaking near 675 K and then contracting at a comparable rate at higher temperatures. These geometric changes alter the Na conductivity. Note in particular that the increase in dielectric loss in figure 3(b) becomes more rapid near about 670 K, the temperature at which the *c*-axis lattice constant peaks [68] (changes from rapidly increasing with temperature to rapidly decreasing).

2.3. Polarization, electro-optic coefficients and exponent β

Our fit to the d_{15} data of Byer *et al* [36] in tetragonal *P4bm* is shown in figure 4. These yield a tricritical transition (no apparent discontinuity) for this Stanford sample at $T_C = 841.6 \pm 0.7$ K, and a critical exponent of $\beta = 0.41 \pm 0.01$ (\pm values are random errors). (The d_{15} values are independent of T in the orthorhombic and IC phases, 300–580 K.) The parameters β and T_C are highly correlated in our least squares fit (89%), so the real uncertainties (systematic errors) are greater than the random errors quoted above. If β is taken as <0.35 or >0.45 the fit becomes visibly worse. Thus, the inferred value of $\beta = 0.41 \pm 0.05$ is compatible with the earlier values of 0.28 ± 0.05 and 0.31 ± 0.05 determined [36] by quite different techniques (on different specimens). The present fit establishes only that the transition is continuous or very nearly continuous (no observed discontinuity at T_C) and that β is $<1/2$, in agreement with a tricritical description.

3. Results and discussion

3.1. Critical exponents and (in)equalities

Having obtained accurate values of α for barium sodium niobate (BNN), together with previously published values [69] of β and δ , and the value of γ from the present work, we can check for self-consistency with the Rushbrooke and Griffiths equalities. In each case these are thermodynamically rigorous inequalities (the left-hand side of each equation below being greater than or equal to the right-hand side) that under the additional assumption of scaling become exact equalities:

$$\alpha' + 2\beta + \gamma' = 2.16 \pm 0.12 \text{ experiment} \quad (\text{Theory} \geq 2; \text{Rushbrooke}) \quad (2)$$

$$\alpha' + \beta(1 + \delta) = 2.18 \pm 0.20 \text{ experiment} \quad (\text{Theory} \geq 2.00; \text{Griffith I}) \quad (3)$$

$$\gamma \geq (2 - \alpha)(\delta - 1)/(\delta + 1) \quad \text{i.e., } 1.1 \pm 0.1 \geq 1.0 \pm 0.1 \text{ experiment} \\ (\text{Theory} : 1.0 \geq 1.0; \text{Griffith II}). \quad (4)$$

We note that in scaling theory α' , β and δ are not independent parameters but are related as

$$\alpha' = 2 - (\delta + 1)\beta = 1/2, \quad (5a)$$

$$\text{and} \quad \alpha' = \alpha. \quad (5b)$$

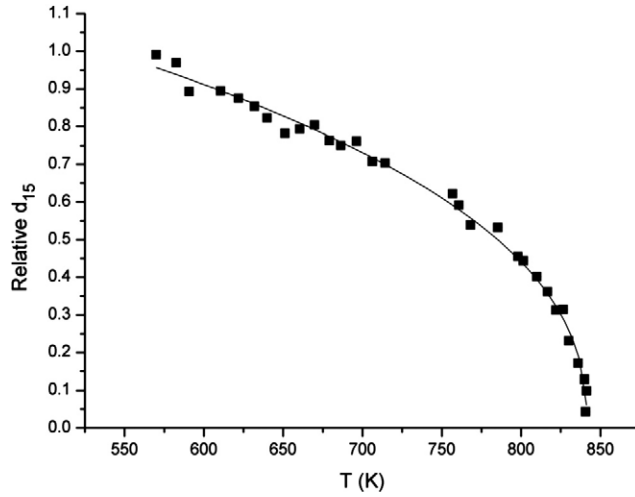


Figure 4. $d_{15}(T)$ electro-optic coefficient in the tetragonal $P4bm$ phase of barium sodium niobate [15], fitted (present work) to $d_{15}(T) = d_{15}(0)[(T_C - T)/T_C]^\beta$, with $\beta = 0.41 \pm 0.01$ and $T_C = 841.6 \pm 0.7$ K (correlation 0.9 between fitted values of β and T_C). Note that the value $\beta = 0.41 \pm 0.01$ agrees, perhaps coincidentally, with the theoretical prediction of 0.39 for a four-dimensional order parameter [39], which is the present case.

With the further assumption (certainly true in the present case) that $2 - \alpha - \gamma' > 0$, Stanley derives [1], by combining equations (3) and (4) to eliminate δ , that

$$\beta(2 - \alpha + \gamma) \geq (2 - \alpha' - \beta)(2 - \alpha - \gamma), \quad (6)$$

an equation of interest because it connects parameters below and above T_C . This relationship does not involve δ and should be satisfied as an equality within the scaling hypothesis. It is the most important (in)equality for the present study. For mean field tricritical values (according to Stanley) $\alpha = \alpha' = 0$, this equation fails even as an inequality. For $\alpha = \alpha' = 1/2$, from scaling it works ($5/8 = 5/4 \times 1/2$). However for $\alpha = 0$ but $\alpha' = 1/2$ [2], it fails as an equality (this is because $\alpha \geq \alpha'$ was assumed by Griffiths in his derivation of the equations leading to equation (6)).

The data on one Chinese sample (sample A; figure 2(c)) from [34] exhibit a ferroelectric transition at 847.18 K, and a critical exponent $\alpha' = 0.50$ (our fit), with a sharp cusp. This is an abrupt, slightly smoothed but discontinuous, first-order phase transition, where the specific heat extrapolated from below diverges at $T'_C = 848.15$ K, about 1.0 K above the actual transition temperature. The data on sample A also reveal small specific heat anomalies at the $Ccm2_1-1q$ transition near 540 K and at the $2q-P4bm$ transition near 582 K, and perhaps just a hint of the $1q-2q$ transition near 565 K. We have examined specimens from CNET (Paris) and from Nanjing; our sample B (figure 2(b)), which was the subject of many earlier studies cited in [69], has an apparent Curie transition temperature of about 829.5 K, a value of $\alpha' = 0.50 \pm 0.05$ and a plateau in specific heat about 10 ± 1 K wide. The data for the incommensurate $1q/2q$ regimes are similar to those in figure 2(a). The differences near T_C can be related to the disordered exclusion model in that they change the transition dynamics from first order (nominally pure) to tricritical (highly Na deficient) and shift the apparent T_C . The shift in Curie temperature is expected to be large (several degrees or more) and quadratic in vacancy concentration, but we have an insufficient number of samples for which Na vacancy concentrations have been determined to check the latter prediction.

3.2. Disordered exclusion model

The specific heat data $C(T)$ shown in figure 2(c) display a peak broadened by 1 K, which is approximately 0.1% of T_C (i.e., about x^2 where x is a few per cent Na vacancy concentration). The peak is also shifted to lower temperatures by about 15 K (i.e., about $x\%$ of T_C) from that of samples [61] with the highest T_C ; however, as T_C is approached from below, the data reveal the $t^{-1/2}$ divergence expected for a pure material. In this section we would like to compare these experimental results with the predictions of Harris [27] and of McCoy and Wu [28] for Ising models with random defects. Their models are qualitatively different: Harris predicts a finite cusp with a significant shift in T_C (about the defect percentage x), rather small broadening (of order x^2), and several non-divergent terms in $C(T)$. This idea, that the main effect of impurities is simply to shift the temperature scale (and hence T_C) originated from Osawa and Sawada [29]. In contrast, McCoy and Wu predict no cusp (complete rounding), zero shift in T_C , but a larger broadening (of order x). Thus, qualitatively, the data in figure 2(c) agree better with those of Harris. However, figure 2(a) exhibits data with larger shifts in T_C , larger broadening and, despite the low T divergence of $C(T)$ as $t^{-1/2}$, an unpredicted plateau. It remains to be shown that Harris's formalism can reproduce the plateau observed in figure 2(a), whereas his leading term in $C(T)$ does not—instead predicting a concave but saturated divergence in $C(T)$ near T_C ; that is, $dC(T)/dT$ in Harris's model is infinite at the renormalized $T_C(x)$, whereas in the data of figure 2(a) it is zero. The probable origin of the plateau in figure 2(a) is the term Harris neglected, of form $\int [d^2U(T)/dT^2] dT$ (his equation (3.28b)), where $U(T)$ is the unperturbed free energy in the pure material, which will add a non-divergent but significant contribution to $C(T)$ between the Curie temperature $T_C(0)$ in the vacancy-free material and the lowered Curie temperature $T_C(x)$ in the samples with vacancies. In this respect it is worth pointing out that Cardy and Jacobsen [30] have considered the critical behaviour of random bond Potts models which are first order or tricritical, rather than the second-order transitions considered by Harris; in such cases, as in $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, there may be large latent heat contributions to $C(T)$ near $T_C(0)$. In addition, Chen *et al* [31] have shown that similar models can give a broadened or even double-peaked specific heat $C(T)$; the broadening of $C(T)$ near T_C in the present work resembles that predicted by Chen *et al* and is not explicitly predicted by Harris.

Harris [27] predicts in a weakly disordered 'exclusion model' (one lattice site having significant vacancy concentration x) in simplified notation

$$\Delta C(T) \cong \Delta C_0(T)/[1 + bx^2\Delta C_0(T)], \quad (7a)$$

where $\Delta C_0(T)$ is the intrinsic specific heat of the vacancy-free crystal with the non-divergent background subtracted off:

$$C_0(T) = d + fT + gt^{-\alpha'} = d + fT + \Delta C_0(T), \quad (7b)$$

with $\Delta C_0(T)$ diverging as reduced temperature $t^{-\alpha'}$. The model predicts a downward shift in transition temperature with increasing disorder and a truncation in the otherwise diverging specific heat cusp. Hence the experimental $C(T)$ will look intrinsic (and give an uncorrected $\alpha' = 0.50$) far below T_C , where the order parameter contribution to the specific heat is only slightly above the linear baseline due to phonons; but nearer T_C , the (normalized) value of $C(T)$ will be saturated. However, equation (7a) does *not* yield a flat plateau, in contradiction to the data; rather, the first derivative of $\Delta C(T)$ diverges, so saturation is achieved as a finite cusp, not a flat plateau. It is of course possible that the plateau in figure 2(a) arises from inhomogeneous broadening of the specific heat due to regions in the sample that have different Na vacancy concentrations; we think this is unlikely because at T_C the Na mobility is sufficiently large to ensure a homogeneous equilibrium distribution.

In general the Harris criterion states that pure critical effects are unstable against weak disorder if $\alpha > 0$, as is the case here; this makes it reasonable to apply his model to ferroelectrics. A second formal relationship from Harris offers a plausible and qualitative check on the use of his equation (7) above; he predicts that a 1% vacancy ratio x will give a shift in T_C downward of about 10 K in the present case (1.3% of T_C):

$$[dT_C/dx]/T_C = -1.3. \quad (8)$$

Our experiments give T_C about 30 K lower than in samples thought to be of lowest Na vacancy concentration [43]. Since the vacancy concentrations in these materials are usually [41] of order 1%–5%, this is in general agreement with the model; i.e., it is of the expected sign and order of magnitude. However, a simple mean field model (which gives -1.0 in equation (8)) is equally applicable.

In concluding this section we note for readers that Harris's model is very appropriate for magnets and is what currently is referred to as a random bond model; for ferroelectrics, random fields are usually as important as random bonds [70–72], and successful models of relaxors usually require both.

3.3. The $1q$ – $2q$ transition and wall roughening model

The transition within the incommensurate (IC) phase from 543 to 582 K occurs near 565 K and is from a long-range low temperature orthorhombic structure with modulation along one axis only ($1q$) to a higher temperature two-dimensional ($2q$) tweed-like modulation [59–62]. Although this upper IC phase is $2q$ modulation, the modulation in the second direction has only short-range ordering and is therefore not tetragonal. We describe it as a wall roughening of the orthorhombic $1q$ structure of the lower phase, on the basis of the TEM studies of Pan and Feng and collaborators [61, 62] which showed directly the onset of wall roughening of the $1q$ antiphase boundaries (APBs). The wall roughening is accompanied by a diffusion process that experimentally peaks [52] at $0.85 \text{ cm}^2 \text{ s}^{-1}$ in accord with theoretical estimates that it exceeds that due to thermal diffusion of entropy fluctuations [53]. Kiat *et al* [73] give the dependences on T of the incommensurate satellite peaks; the full width at half-maximum increases from 0.07° of arc (1.4 mrad) to 0.17° of arc (3.0 mrad) as the $1q$ – $2q$ transition is transited. See also [74–76] for further updates on the low temperature structures and in particular the probable unit cell doubling along the b -axis; reference [76], in particular, also shows that ferroelectricity and incommensurability in this material experimentally do not interact, as argued in a theoretical way in section 1 above and by Levanyuk [64].

A detailed discussion of the strain terms at the $1q$ – $2q$ transition is given by Toledano and Toledano [39], who point out that the effective point group in the $2q$ IC phase is that of the higher C_{4v} phase, whereas that of the $1q$ IC phase is that of the lower orthorhombic phase, and that the $1q$ phase has a spontaneous strain ($e_{xx}-e_{yy}$) purely due to the fact that the order parameter is four dimensional. The number of non-zero tensor components is consequently higher in this phase.

4. Conclusions and comparisons with other critical exponents in ferrodistortive materials

In summary, we determine the critical exponent α' for the ferroelectric transition in barium sodium niobate and show that it is, within a small experimental uncertainty, $1/2$, in agreement with mean field tricritical theory (and in violation of Stanley's derivation which predicts $\alpha' = 0$); we show that the divergence in specific heat near the Curie temperature

agrees quantitatively with Harris's disordered exclusion theory, presumably due to the known Na vacancy concentration; we measure specific heat and dielectric anomalies at two incommensurate transitions; and we obtain an upper limit of entropy change at the $1q-2q$ transition of about $0.1 \text{ J K}^{-1} \text{ mol}^{-1}$ within the IC phase, in agreement with unpublished estimates based upon the wall roughening theory of Rice *et al* [63]. We also determine accurate values of the susceptibility and order parameter exponents γ , γ' and β . All values imply mean field tricritical behaviour [81].

We note in passing that the index of refraction data in disordered ferroelectrics such as lead magnesium niobate (PMN) or strontium barium niobate (SBN) exhibit a flat plateau $n(T)$ within $\pm 5 \text{ K}$ of T_C that has never been explained. The shape of $n(T)$ is very similar [77] to that for $C(T)$ in the present work. This suggests that the same kind of model might be applied. This might resolve some of the disagreements in that material, where some authors [24] infer mean field dynamics, and others [4] find non-mean field RFID (random field [3D] Ising dynamics) behaviour. Note that the values of $\gamma' = 1.85$ and $\beta = 0.14 \pm 0.03$ given [4] by Kleeman *et al* for SBN require a rather implausible (and as yet unmeasured) value of $\delta = 14$ to satisfy the Widom relationship (equation (1)) as an equality and require $\alpha' \leq 0$ to satisfy the Griffiths equation (equation (2)) as an equality; although the standard [2D] Ising model predicts $\delta = 15$, the work of Kleeman *et al* assumes [3D] Ising dynamics, not [2D], and the usual [3D] Ising model has $\delta = 5$ (as at a mean field tricritical point). As Perez-Mato's group has pointed out [78–80], apparent non-mean field critical exponents β can arise from some order–disorder character in nominally displacive transitions, which could be misinterpreted as true 'critical' exponents due to critical fluctuations [82].

As an example of recently published work which does not explicitly consider thermodynamics requirements, Dec *et al* [83] have given the values $\beta = 1.2$ (regarded as 'suspicious' by those authors), $\gamma = 2.01 \pm 0.04$ and $\delta = 2.6 \pm 0.1$ for SrTiO_3^{18} . Partly because they are from the quantum critical regime, in which γ changes from 1.0 to 2.0, these values fail to satisfy the Griffiths and Rushbrooke relationships as equalities for any positive value of α , and would require from equation (5a) (scaling theory) a negative value of both α' and α (equation (5b)). In fact, as shown by Schneider *et al* [84], the values of α' , δ and γ in the quantum critical regime for three dimensions are $\alpha' = -3$ for three dimensions (and -2 for two dimensions); $\delta = 3$; and $\gamma = 2$. Note that $\alpha' < 0$.

The results [83] of Dec and Kleeman for SrTiO_3^{18} [85] therefore give from equation (3)

$$\alpha' = 2 - (\delta + 1)\beta = (2 - 3.6 \pm 0.2)(1.2 \pm 0.1) = -2.3 \pm 0.6 \quad (9)$$

in relatively good agreement with the -3 predicted by Schneider *et al*. This agreement, not previously pointed out, adds support to the quantum critical conclusions of [83] and helps justify their unusual value of β .

The classical derivation of the Rushbrooke inequality assumes positive specific heat C_P at constant polarization P ; hence the thermodynamic identity [1]

$$\chi(T)[C_E(T) - C_P(T)] = T[(\partial P/\partial T)_E]^2 \quad (10)$$

implies (adding $C_P(T)$ to each side)

$$C_E \chi(T) \geq T[(\partial P/\partial T)_E]^2. \quad (11)$$

Taking logarithms of both sides, with $P = P(0)[(T_C - T)/T_C]^\beta$, and $\log(\partial P/\partial T)$ varying as $\beta - 1$, yields the Rushbrooke inequality equation (2):

$$-\alpha' - \gamma' \leq 2(\beta - 1). \quad (12)$$

However this derivation assumes in equation (9) that the electric isothermal susceptibility $\chi(T) = -(\partial^2 G/\partial^2 E)_T$, where G is the Gibbs free energy, and that $C_E = T[(\partial S/\partial T)_E]$,

which may not be true exactly at $T = 0$, where S is a constant and its temperature derivatives C_E and C_P , according to the third law of thermodynamics, are zero. Hence in applying equations (9) and (10) one must be careful to avoid dividing zero by zero.

Although Dec himself expressed scepticism about his value of $\beta = 1.2$ [83] and suggested that β should be < 1.0 (otherwise the order parameter versus T is concave at T_C ; moreover, $\beta = 0.65$ for all known soluble models), setting it less than unity would make their values of $\delta = 2.6$ and $\gamma = 2.0$ fail the Widom equation (equation (1)), which is satisfied as an equality for their values, including $\beta = 1.2$. Thus, the values of Dec and Kleeman for SrTiO_3^{18} satisfy both the Rushbrooke and Widom relationships, when quantum criticality is included [84].

For completeness, however, we suggest a third possibility for the data on SBN:Ce: in the *defect* theory of Levanyuk and Sigov, the electric susceptibility near a ferroelectric phase transition diverges as $N\chi(p)r_c^3$, where $\chi(p)$ is the susceptibility of the pure crystal and varies as $(T_C - T)^{-1}$; N is the concentration density of defects; and r_c (the range over which a defect induces lattice distortions) varies as $(T_C - T)^{-1/2}$. This implies $\gamma_{\text{eff}} = 5/2$. Hence we see that values of γ near 2 or even larger could arise from defect models, and not just from quantum critical fluctuations or a random field Ising model. Figure 5.2 of [96] shows that the effective exponent γ will vary from 1.0 to 2.5 as the transition temperature is approached and the system changes from a fluctuation-dominated regime to a defect-dominated regime, so an average value over a temperature interval near T_C of about $\gamma = 1.8$ – 2.0 is quite plausible, particularly for SBN:Ce [4, 24], which has a high density of Ce dopants as defects. We also note in this context that *defect* models predict extremely unusual numerical values for other ‘effective’ exponents near structural phase transitions [86] such as $\alpha_{\text{eff}} = 2 - 2\beta = 1.0$ – 1.5 and $\alpha_{\text{eff}} = 2 - \nu = 1.5$ (ν is the exponent describing the correlation function and $\nu = \nu' = 1/2$ in the mean field) and the exponent describing ultrasonic attenuation divergence $\eta = 5\nu = 2.5$. Such values have been reported experimentally but generally misinterpreted for KMnF_3 [87], CsH_2PO_4 [88] and BaMnF_4 [89, 90], and a defect explanation of their occurrence (e.g., $\alpha'_{\text{eff}} = 1.1$ in BaMnF_4) given by one of us [91, 92]. Note that the *defects* responsible for values of $\alpha' = 1.1$ can be domain walls, so multidomain BaMnF_4 satisfies [19] intrinsic mean field theory with $\alpha = 0.54 \pm 0.05$ above T_C (where the domain walls vanish) but a defect model with $\alpha'_{\text{eff}} = 1.1 \pm 0.1$ below T_C . SrTiO_3 with some O^{18} percentage behaves like a mass defect system, and thus defect exponents may be involved. We note that even for ordinary O^{16} – SrTiO_3 , Hoehli and Bruce have shown [93] that the critical exponent describing the elastic coefficient and the specific heat near $T_0 = 105$ K (tetragonal–cubic antiferrodistortive) is not intrinsic, and that its experimental numerical value [94, 95] of 1.5 ± 0.2 satisfies the defect theory of [96], which predicts exactly $3/2$; so extrinsic mechanisms for effective critical exponents seem established for strontium titanate near its tetragonal–cubic transition at about 105 K. Unfortunately, this result contradicts the earlier conventional wisdom regarding intrinsic critical exponents in this perovskite family [97]. Finally, we emphasize that the exponents in the defect theory need not satisfy the Widom, Griffiths or Rushbrooke relationships, because they are not valid asymptotically as $T \rightarrow T_C$.

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