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LETTER TO THE EDITOR

Resolving the quantum criticality paradox in O-18 isotopic $SrTiO_3$

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Abstract

Recently there has been considerable interest in the displacive ferroelectric phase transition near $T = 28$ K in O-18 isotopic strontium titanate. Special efforts have been made to combine the quantum criticality exponents $\alpha = -2$ (2D) or -3 (3D), $\delta = 3$, and $\gamma = 2$ with the thermodynamic inequalities of Rushbrooke, Griffiths, Widom *et al*, which become exact equalities under the hypothesis of scaling. In particular, these have led others to the inference that $\gamma = 2.0$ and $\beta = 1.2$ in $SrTiO_3$. First we show that this is mathematically incorrect and explain why (quantum criticality is exact only at $T = 0$, whereas the thermodynamic (in)equalities are valid everywhere except $T = 0$). Second, we show that the inferred values strongly violate a new equality, $\gamma - 2\beta = \nu(4 - d - 2\eta) > 0$, we derive from hyperscaling. Third, we show that the existing soft mode frequency data $\omega(T)$ from Takesada *et al* (2006 *Phys. Rev. Lett.* at press) yield above T_c (from the Lyddane–Sachs–Teller relationship) $\gamma = 1.0$. Fourth, we remeasure β from the polarization $P(T)$ and find $\beta = 0.50 \pm 0.02$. Fifth, we remeasure the electric susceptibility and find that it perfectly satisfies the Salje–Wruck–Thomas equation, which requires $\gamma = 1.0$. The important conclusions are: (a) O-18 $SrTiO_3$ near T_c is mean-field; (b) the thermodynamic scaling equalities of Rushbrooke, Griffiths *et al* are mathematically incompatible with quantum criticality theory; (c) a new hyperscaling relationship makes $\beta = 1.2$ and $\beta > \gamma/2$ impossible.

1. Introduction

Recently there has been a series of publications in which authors fit experimental data on ferroelectrics to infer critical exponents describing the behaviour near the Curie temperature, especially for strontium titanate with oxygen isotope 18 [1–5]. Some of these were shown to be compatible with those predicted from quantum criticality theory [6]. Although not all of the commonly measured exponents $\alpha, \beta, \gamma, \delta$ were measured, the authors used thermodynamic inequalities, which become equalities under the widely accepted hypothesis of scaling, to calculate the remaining exponents. Here α describes the specific heat divergence; β, the order parameter evolution with temperature; γ, the electric susceptibility evolution with temperature;

and δ, the electric displacement vector D (or polarization P) with conjugate field E. This procedure yielded some extraordinarily unusual exponents, such as $\beta = 1.2$. In fact, no analytical theory produces $\beta > 0.65$. It is especially suspicious that $\gamma - 2\beta = -0.4$ is negative; we show below that this violates hyperscaling [7].

2. Theory

2.1. Quantum criticality theory

As initially developed by Schneider *et al* [6], quantum criticality theory is applicable only at $T = 0$. It calculates critical exponents $\delta = 3$, $\alpha = -d =$ (minus) dimensionality (-2 or -3); and $\gamma = 2$. It is important to note that it does not calculate β at all. Since β is defined only for $T < T_c$, and $T_c = 0$, β is not defined in the theory. Therefore Schneider and co-workers assumed that for real systems where T_c is near zero but finite, $\beta = 1/2$; however, this value is taken not from mean-field, but from the spherical quantum model [8]. It is also very important to note that $\gamma = 2$, when found experimentally, would not in itself imply quantum criticality, because $\gamma = 2$ is also predicted from the quantum spherical model [8]. Finally it is important to note that the sign of α is negative, unlike many statistical mechanical models (e.g., $\alpha = +1/2$ at mean-field tricritical points and $+1/8$ for (3D) Ising models). We emphasize that quantum criticality theory is not valid for finite temperatures.

2.2. Thermodynamic (in)equalities

There are a number of famous inequalities among the thermodynamic critical exponents, such as those of Griffiths, Rushbrooke, Widom, Fisher, etc. These all become equalities under the further assumption of scaling [8]. However, these generally are valid only for finite temperatures and are untrue at $T = 0$. This is well illustrated with the Rushbrooke (in)equality, whose derivation is short and simple [9].

Using the more familiar notation of magnetism, Rushbrooke started with

$$\chi_T(C_H - C_M) = T(\partial M/\partial T)_H^2, \tag{1}$$

where C_M, C_H are the specific heats at constant magnetization M and constant field H (in the ferroelectric case these become C_D and C_E, where D is the displacement vector and is nearly the same as the polarization P; E is electric field).

Assuming that specific heats are not negative quantities (physically necessary), he rewrites (1) as

$$\chi_T C_H \geqslant T(\partial M/\partial T)_H^2, \tag{2}$$

from which, using the definitions $C_H \approx t^{-\alpha'}$, $\chi_T \approx t^{-\gamma'}$, and $(\partial M/\partial T)_H \approx t^{\beta-1}$ (here t is the reduced temperature $(T_c - T)/T_c$)), the relationship (2) becomes

$$\alpha' + 2\beta + \gamma' \geqslant 2, \tag{3}$$

where primes designate values below T_c. The scaling assumption makes (3) an equality and also requires $\alpha = \alpha'$ and $\gamma = \gamma'$, so we may rewrite (3) as

$$\alpha + 2\beta + \gamma = 2. \tag{4}$$

If we naively insert the values from quantum criticality theory for $SrTiO_3$, which are $\alpha = -2$ and $\gamma = 2$, we predict from (3) that

$$\beta = 1. \tag{5}$$

However, we note in (1) that the left-hand side of the equation is zero at $T = 0$, because $C_H = C_M$. Similarly the right-hand side is zero for two reasons: $T = 0$ (first term), and

also $(\partial M/\partial T)_H = 0$ (second term) at $T = 0$ (Third Law of Thermodynamics). Therefore equations (1) and (2) cannot be applied at $T = 0$, for they yield zero divided by zero, and hence equation (5) is an error (even as an inequality as from (3)) obtained by mathematically inconsistent assumptions of quantum criticality and the Rushbrooke equation.

Note that this error in obtaining $\beta = 1$ in (5) is independent of any experimental data. It is a simple mathematical mistake.

2.3. Hyperscaling

In addition to the scaling arguments above, one may invoke arguments from hyperscaling. Hyperscaling involves the dimensionality d of models and usually the critical exponents ν and η. One important hyperscaling relationship is

$$\gamma = (2 - \eta)\nu. \tag{6}$$

This is equation (12.29) of Stanley's text [8] and equation (5.4.10) of the text by Chaikin and Lubensky [10].

A second important hyperscaling relationship is

$$d - 2 + \eta = 2\beta\nu \tag{7}$$

which is equation (12.28) in Stanley and equation (5.4.15) in Chaikin and Lubensky.

Here ν is the exponent describing the temperature evolution of the correlation length ξ in the pair correlation function $G(r) \approx (e^{-r/\xi})/r$; η is the exponent describing the wavevector dependence of the structure factor $S(q)$ at T_c: $S(q) \approx q^{-2+\eta}$.

From (6) and (7) we immediately get

$$\gamma - 2\beta = \nu(2 - \eta) - \nu(d - 2 + \eta) \tag{8}$$

whence

$$\gamma - 2\beta = \nu(4 - d - 2\eta). \tag{9}$$

Equation (9) is the most important result of the present paper, and although it follows simply from Stanley or Chaikin and Lubensky, it seems not to have been published explicitly before. Note that Chaikin and Lubensky emphasize that these equations are not generally valid for $d \geqslant 4$, except that for mean-field $d = 4$, the upper critical dimensionality, is required. We note that (9) is satisfied by the (2D) and (3D) Ising and Heisenberg models, using the most recent values of γ, β, ν, and η. For all realistic models, the right-hand side of (9) is $\geqslant 0$. Therefore, the experimental values from Kleeman *et al* of $\gamma = 1.97$–2.01 and $\beta = 1.2$ are impossible, since they require a negative value -0.4. Thus, the values of γ and β published by Kleeman *et al* [1–5] strongly violate hyperscaling, a point not made previously.

3. Experiment

The experiments on oxygen-18 isotopically enriched strontium titanate all require mean-field theory for their correct interpretation.

3.1. Raman data

The recent Raman results from Yagi's group [11] show an underdamped soft mode from about 400 to 20 GHz in the paraelectric phase whose temperature dependence is given by

$$\omega(T) \approx (-t)^{\gamma/2}, \tag{10}$$

with $\gamma = 1.0$ and where the proportionality to $\gamma/2$ follows rigorously from the Lyddane–Sachs–Teller relationship [12]. (Note that $\omega(T)$ does NOT involve β, a common misconception.) This is of course a mean-field result.

3.2. Polarization and susceptibility data

Levstik and Filipic have shown [13] by direct measurement below $T_c = 28$ K in 95% O-18 $SrTiO_3$ that

$$P(T) \approx t^{\beta} = t^{0.50}, \tag{11}$$

another mean-field result, and that the electric susceptibility satisfies the Salje–Wruck–Thomas equation, which assumes $\gamma = 1$; hence that

$$\chi(T) \approx t^{\gamma} = t^{1.0}, \tag{12}$$

another mean-field result. Others who have tried to apply the Salje equation and deduce $\gamma = 2$ from fitting data to it apparently do not recognize that this equation assumes $\gamma = 1$ in its derivation.

3.3. Artefacts in experimental fitting of $\gamma = 2$

Although ideal ferroelectrics with second-order phase transitions have dielectric constants that diverge at T_c, all real crystals exhibit finite maxima with flat or rounded peak values. This occurs because of: (a) inhomogeneous strain; (b) finite applied electric fields (true divergence requires $E = 0$); (c) atomic-scale disorder; etc. Thus a graph of reciprocal dielectric constant $1/\varepsilon(T)$ will exhibit a flat base at T_c, followed by rapid curvature that is *always* best approximated as quadratic, and farther away from T_c, a linear behaviour. Thus, a naive fitting of such data always yields $\gamma = 2.0$ near T_c. But this is a complete artefact of the fitting procedure and has nothing to do with true critical (fluctuation-dominated) phenomena.

4. Conclusions

We show that analyses combining quantum criticality exponents with thermodynamic inequalities that become equalities under the assumption of scaling are mathematically inconsistent, since they combine theories whose temperature ranges of applicability do not overlap. We further show that the experimental relationship $\gamma - 2\beta = -0.4$ published for the ferroelectric transition in $SrTi^{18}O_3$ strongly violates hyperscaling. And we show that the actual experimental values of $\gamma = 1.0$ and $\beta = 0.50$ measured in several independent ways are mean-field. Fitting of $\varepsilon(T)$ in real ferroelectrics always gives a value $\gamma = 2.0$ near T_c, but this is a fitting artefact arising from pedestrian causes such as inhomogeneous strain and finite probe fields E, unrelated to critical (fluctuation-dominated) dynamics.

References

[1] Lehnen P, Kleemann W, Woike Th and Pankrath R 2000 *Eur. Phys. J.* B **14** 633
[2] Dec J, Kleemann W, Boldyreva K and Itoh M 2005 *Ferroelectrics* **314** 7
[3] Dec J, Kleemann W and Itoh M 2005 *Phys. Rev.* B **71** 144113
[4] Zhang L, Kleemann W, Dec J, Wang R and Itoh M 2002 *Eur. Phys. J.* B **28** 163
[5] Zhang L, Kleemann W, Wang R and Itoh M 2002 *Appl. Phys. Lett.* **81** 3022
[6] Schneider T, Beck H and Stoll E 1976 *Phys. Rev.* B **13** 1123
[7] Kadanoff L P 1966 *Physics* **2** 263
[8] Stanley H E 1971 *Introduction to Phase Transitions and Critical Phenomena* (Oxford: Clarendon)
[9] Rushbrooke G S 1963 *J. Chem. Phys.* **39** 842
[10] Chaikin P M and Lubensky T C 1995 *Principles of Condensed Matter Physics* (Cambridge: Cambridge University Press)
[11] Takesada M, Itoh M and Yagi T 2006 *Phys. Rev. Lett.* at press
[12] Lyddane R H, Sachs R G and Teller E 1941 *Phys. Rev.* **59** 673
[13] Levstik A and Filipic C 2006 *Phys. Rev.* B at press