SBN is mean field and first-order:

K. Wokulska, P. Pacek, J. Dec, T. Łukasiewicz, and M. Świrkowicz, Characterisation of phase transition in strontium barium niobate by Bond method, Sol. St. Phenomena 163, 264-7 (2010).

Volume discontinuity of delta V = 0.6989 A3 and mean field lattice expansion exponent 0.53 +/- 0.15.

Experiments of Hilczer and Theory of Levanyuk and Sigov

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Abstract

The pioneering breakthrough of Bozena Hilczer and her coworkers showed that so-called critical phenomena in many ferroelectric crystals are entirely produced by defects. She studied GASH, lithium ammonium sulphate, lithium hydrazinium sulphate, PZT, barium titanate, and especially TGS, via neutron irradiation, X-ray irradiation, and e-beam electron irradiation, which showed that the divergences in specific heat or dielectric constant near the Curie temperature T_c are not caused by “critical” fluctuations but by static defects, which can be annealed out and subsequently reproduced by irradiation. This work is rarely cited (modern physicists often feel that literature searches are optional), leading to frequent rediscovery and generally spurious claims of true “critical” phenomena near T_c.

Introduction

The study of hydrogen-bonded ferroelectrics has waned; commercial device interests have a priority for oxides, which are more robust and easier to fabricate into thin-film devices with standard silicon technology. In part the present author has to take some of the blame for that,[1] but the process began in 1945 with the independent discovery of $BaTiO_3$ and related perovskites in Japan, the USA, and Russia, and was accelerated by the invention of transparent PLZT.

From a strictly scientific point of view this is a great pity, because hydrogen-bonded ferroelectrics are very subtle and educational systems for physicists, chemists, and materials scientists. Here I review briefly one particular topic made clear by work on them: notably the experiments of Bozena Hilczer and her Polish colleagues [2-13] and the theory of Sasha Sigov, Arkadiy Levanyuk, and their students.[14-28] (Sigov and Strukov also added gamma-ray irradiation [29] to the other studies by Hilczer.) These show that so-called critical phenomena (unusual exponents) in various thermodynamic properties near the Curie temperatures (specific heat, electric susceptibility, thermal expansion, ultrasonic attenuation) arise not from true critical fluctuation phenomena, but instead from static defects. These old papers (some > 50 years old) were breakthroughs, but they are seldom read and even more rarely cited. As a result, on an almost annual basis there are new claims that some ferroelectric satisfies the three-dimension Heisenberg model, or some xy-pseudo-spin model, or a two-dimensional Ising model, or some equally inapplicable spin model borrowed naively from magnetism. The present author's view is that ferroelectrics almost always are mean-field, and that defects can create effective exponents for thermodynamic quantities near T_c that are misleading. A good relatively recent review on this topic is given by Hilczer herself.[28]

Early experiments

The best, most quantitative early experiments verifying defect models of effective critical exponents were by Ian Fritz.[30,31] Ian found very large exponents for ultrasonic attenuation. See [21, 22, 26]. These are qualitatively outside the range permitted by intrinsic theories. Initially it was unclear what these exponents arose from, since the transition is an unusual incommensurate-commensurate transformation; but in retrospect, it fits the same values as those of Bobnar et al. on PMN-PT, so it is almost certainly defect-driven, where the defects are the discommensurations.

Theory of Sigov, Levanyuk et al.[14-28]Experiments by Fritz [30,31]

Throughout the 1970s and 80s Arkadiy Levanyuk, Alexander Sigov and others produced a long series of papers showing how defects would influence phenomena in ferroelectrics near their Curie temperatures. In general, these models predict effective exponents that are much larger than those arising from true critical fluctuations: For example, the specific heat exponent α is between 1 and 3/2; the ultrasonic attenuation exponent is 5/2. Recently the latter has been found by Bobnar et al. in PMN-PT, with rather exact values of 2.52, but unfortunately they chose an exotic model for its explanation. This seems odd to me, since relaxors such as PMN-PT have very large numbers of “defects.” The same argument can be made about $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN).

Experiments by Lashley et al. [32,33]

Jason Lashley at Los Alamos recently measured thermal expansion in TSCC (tris-sarcosine calcium chloride) doped with 3% Br. He confirmed for the first time another predicted exponent from the Sigov-Levanyuk theory and found a value of -1.51, in perfect agreement with the predicted -3/2. Here the Br-ions may act as the dominant defects, and it would be useful to repeat the experiments on pure undoped TSCC.

Claims of Kizhaev, Smolenskii, and Tagantsev: JETP Lett. [34]

Kizhaev et al. reported some interesting exponents in $KMnF_3$, which Tagantsev modeled as an xy-pseudospin result. However these data also satisfy the defect model predictions, as shown in their reinterpretation by Scott. [35]

Experiments by Kleemann on $SrTiO_3$[36]

An interesting set of experiments on ^{18}O $SrTiO_3$ were reported by Dec et al. who inferred a critical exponent for the order parameter P (polarization) as β = ca. 2. Unfortunately this arose from an algebraic error. Values of $\beta > 1$ are not possible,[37] as detailed by Scott, Pirc, et al.

There have been many arguments and counter-arguments concerning the “critical” exponents in SBN.[38-40] It is not necessary to go over all of them again. But a simple summary is this:

(1) The published values by Kleemann et al.[38] violate hyperscaling and the Fisher equality. This alone is sufficient to make them extremely unlikely, since no other phase transition is known to do this.

(2) Most measurements have been reported on SBN:Ce, not on undoped SBN, and the cerium dopants are certainly defects, implying that the most likely theoretical models are those of Levanyuk and Sigov.

(3) There is clear evidence that at least some (perhaps all) SBN samples have a discontinuous first-order transition.[39] In mean field, the exponent gamma for isothermal electric susceptibility (dielectric constant) is ¼ near tricritical points, at which transformations change from second order to first order. Such exponents are very easily confused with model predictions for non-mean-field systems.

(4) The earlier work on domain precursors within the paraelectric phase also suggests a first-order transition: J. Dec, V. V. Shvartsman and W. Kleemann, Appl. Phys. Lett. 89, 212901 (2006). This is not wholly self-consistent with their own model.

New experiments on PZT by Ye and Bokov [41]

In the past two years Z-G Ye and A. Bokov have reported very careful measurements of all the main exponents at T_c in single-crystal PZT. Their results for specific heat, dielectric constant, and order parameter are all self-consistent with regard to thermodynamic inequalities, which become equalities under scaling theory, and none of the values are mean-field. This is very puzzling, because measurements are made over a temperature range of degrees Kelvin, which seems incompatible with the Levanyuk-Ginzburg criterion discussed below.

Theory by Kornev et al [42]

The puzzle deepens based upon the theoretical results of the Kornev-Bellaiche group, who find similar non-mean-field exponents. Their work seems technically faultless, but raises the same Ginzburg-criterion question.

Present situation: Levanyuk-Ginzburg Criterion [43,44]

In almost all structural or magnetic phase transitions the range of applicability of mean field theory can be estimated by the so-called Ginzburg criterion (although it was actually published by his student Levanyuk a year earlier – it was never unusual for Russian theoreticians to publish their students' work as sole author). This is a self-consistent estimate of the temperature regime over which the rms value of the order parameter $<\theta^2> >> <\theta>^2$. It varies as L^{-6}, where L is the interaction length. For magnets, L is nearest-neighbor and ca. 0.1 nm; whereas for ferroelectrics, L is dominated by Coulombic long-range interactions, or even longer unscreened strain. Thus for magnets, the true fluctuation-dominated critical regime might be of order 1 K, but in ferroelectrics it should be << 1 mK. It is therefore unclear how the experiments or theory of non-mean-field exponents in PZT circumvent this.

Summary

The study of so-called critical exponents near T_c in ferroelectrics began with the pioneering experiments of Bozena Hilczer on TGS, which established unambiguously that these were entirely extrinsic. Other systems are summarized in Table I. Her work is rarely cited in recent similar studies, which seem unwisely influenced by critical exponent results in magnets, partly misled by the heavily influential work of Cowley and Bruce.[45] The topic is still moot, with very recent theory and experiment on PZT unchallenged yet in the literature. But claims in ^{18}O $SrTiO_3$, in $KMnF_3$, in PMN-PT, and in $Sr_{0.61}Ba_{0.39}Nb_2O_6$ are not holding up well, and those systems seem to satisfy the detailed predictions of Levanyuk, Sigov et al.

Table I: Experimentally confirmed Topological defect-dominated exponents near T_C [t = reduced temperature (T-Tc)/Tc]

Exponent	Topological defect model	Material
Isothermal susceptibility γ	5/2	PMN-PT(c),$BaMnF_4$
Specific heat α	1.0-1.5	$KMnF_3$(a), CsH_2PO_4(b),$BaMnF_4$(f)
Ultrasonic attenuation η	5/2	$BaMnF_4$ (d)
Thermal expansion n	3/2	TSCC (e)

Refs: (a) S. A. Kishaev, G. A. Smolensky, A. K. Tagantsev, Pis'ma Zh. Eksp. Teor. Fiz. 43, 445 (1986).

(b) E. D. Yakushkin, A. I. Baronov, and L. A. Shuvalov, Pis'ma Zh. Eksp. Teor. Fiz. 33, 27 (1981).

(c) V. Bobnar et al., J. Appl. Phys. 107, 084104 (2010); J. F. Scott, J. Appl. Phys. 108, 086107 (2010).

(d) Refs. [30,31]

(e) Refs. [32,33]

(f) J. F. Scott, F. Habbal, M. Hidaka, Phys. Rev. B 25, 1805 (1982).

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