# Dielectric anomalies in nonferroelectric phase transitions

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A defect model is presented as an alternative explanation to the two-dimensional fluctuation theory of Kitaev *et al.* for the changes in the dielectric constant near the antiferrodistortive phase transition temperature of $KMnF_3$. It is further suggested that a similar explanation may be given for the unusual critical exponents reported for $CsH_2PO_4$.

Recently Kizhaev *et al.*[1] have reported very interesting experimental data for the changes in dielectric constant that occur near the antiferrodistortive structural phase transition temperature (188.6 K) in $KMnF_3$. They measured a logarithmic change in the dielectric constant over a wide temperature range (10 K to 60 K from $T_0$ rather far from the transition temperature, which they related theoretically to the specific heat divergence

$$\frac{\partial \Delta \epsilon}{\partial T} = -\frac{1}{4\pi}\frac{\Delta c}{T_c}\frac{\partial^2 T_c}{\partial E^2}. \qquad (1)$$

They then relate their observed critical exponent $\alpha = 1.0$ to the equivalent relationship for elastic moduli observed in $KMnF_3$ by Melcher and Plovnick and Holt and Fossheim, i.e., $C_{ij} = A(T - T_c)^{-1}$, through the Pippard relationship.[2,3] The critical exponents observed yield an extremely unusual exponent, $\alpha = 1.0$, which although compatible with a logarithimic divergence in $\epsilon$ in Eq. 1 above, is not compatible with most intrinsic statistical mechanical models.[4] The purpose of the present Letter is to suggest that defect mechanisms at structural phase transition temperatures can provide a simple explanation of the observed data, and that therefore the interpretation of the $KMnF_3$ results as proof of two-dimensional fluctuation phenomena is still open to question. Indeed, it would be quite unexpected, a priori, that fluctuation phenomena would be dominant as much as 10 K from a structural phase transition.[5]

There is a long and somewhat colorful history to the theoretical and experimental study of dielectric anomalies at non-ferroelectric phase transitions; this is most explicit in the case of dielectric anomalies at magnetic phase transitions. The first detailed theoretical treatments were by Rado[6] (see also Samokhvalov,[7] who made explicit application to $Cr_2O_3$. However, experimental results were widely disparate (Lal *et al.*[8] and Fang and Brower[9]), disagreeing among themselves as well as with theoretical predictions and generally giving experimental values many orders too large, in comparison with theoretical predictions. This variance itself suggests extrinsic defect mechanisms. Rather recently this dielectric phenomenon at magnetic ordering temperatures has received study[10] in $BaMnF_4$, but as with earlier work on $Cr_2O_3$, there is no real understanding of the quantitative observations.

The primary purpose of the present Letter is to point out that the presence of a dielectric divergence near $T_0$ in a nonferroelectric phase transition, and the inference of a critical exponent $\alpha \simeq 1.0$, is not prima facie evidence of 2D fluctuations. Several related defect models predict such unusual values of $\alpha$. Hoechli and Bruce,[11] Levanyuk *et al.*,[12] and Rehwald[13] all describe model systems with very large values of $\alpha$, near unity. Hoechli and Bruce[11] calculate $\alpha = 1.3$. Levanyuk *et al.*[12] assume a model in which a distribution of immobile defects dominate the specific heat divergence through the correlation length $\xi(T)$. $\xi(T)$ diverges as $T \rightarrow T_0$ until it is approximately equal to $r_d$, the average distance between defects. This produces a plateau in the specific heat divergence and is the reason values of $\alpha \geqslant 1.0$ are permitted in the theory (i.e., it is a nonasymptotic theory and as such permits $\alpha = 1.0$, which would yield unphysical divergences in internal energy at $T_0$). This theory predicts that the ultrasonic attenuation exponent $\eta$ is given by

$$\eta = (2\beta - \gamma) + 5\nu, \tag{2}$$

which in mean field ($\beta = 1/2$; $\gamma = 1$; $\nu = 1/2$) yields 2.5. Since dynamic scaling predicts[14] $\alpha = \eta - 1$, this yields $\alpha = 1.5$, which, like the 1.3 value of Hoechli and Bruce, is in reasonable agreement with experiment.

A slightly different value of $\alpha = 1.25$ can be obtained by combining Rehwald's relationship $\eta = 2\alpha$ with Eq. 2 above.

It would be important in comparing the defect model above with other explanations of unusual dielectric divergences in nonferroelectric phase transitions to show self-consistency between several quantities, especially between dielectric constant (or, through the Pippard relationships, sound velocities) and ultrasonic attenuation temperature exponent. Note that Strukov *et al.*[14] have shown that these relationships remain valid even in extrinsic, defect-dominated systems.

As a peripheral comment, let us observe that the defect models provide an explanation of other unusual exponents reported at structural phase transitions. In particular, the values $\alpha = 1.00 \pm 0.05$ and $\eta = 2.30 \pm 0.05$ reported by Yakushkin *et al.*[15] in $CsH_2PO_4$ and also interpreted, like the $KMnF_3$ results in Ref. 4, as arising from lowdimensionality, can equally easily be reinterpreted as due to defects. They agree with Eq. 2 and with dynamic scaling, as do experimental data[16] for $BaMnF_4$, for which $\alpha = 1.1$ and $\eta = 2.2$ (LA phonon).

The conclusion from these observations is that large values (near unity) of critical exponent $\alpha$, inferred from data several degrees away from $T_0$ in structural phase transitions, may be more likely to arise from defect contributions than from low-dimensional critical fluctuations, and that, in general, it is necessary to show self-consistency with other exponents, particularly that ($\eta$) describing ultrasonic attenuation.

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