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CLUSTER MODEL FOR TRIS-SARCOSINE CALCIUM CHLORIDE (TSCC) DESCRIBING
ORDER-DISORDER AND DISPLACIVE FEATURES OF ITS FERROELECTRIC TRANSITION
AND ITS PRESSURE-INDUCED TRANSITION TO AN ANTIFERROELECTRIC PHASE

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Abstract-Features of the TSCC phase diagram and its polarization and soft mode behavior are explained by a model having two-particle ferroelectric and anti-ferroelectric clusters in which the interacting particles reside in ϕ^4 potential double-minimum wells.

INTRODUCTION

TSCC has a second-order^{1,2} ferroelectric (FE) phase transition at 131 K which exhibits both order-disorder and displacive features. Within about 10°C of T_c , electron paramagnetic resonance results exhibit anomalies attributed³ to the order-disorder nature of the transition. Farther below T_c there are Raman soft modes characteristic of a displacive transition which become over-damped and disappear about 10°C below T_c .^{4,5} Hydrostatic pressure increases T_c quite rapidly, but the paraelectric-ferroelectric (PE-FE) phase boundary is terminated at a triple point at 5.03 kbar and 176.8 K by a first-order phase transition line with even steeper slope which bounds a third, antiferroelectric (AFE) phase.⁶ Windsch⁷ found that the PE-FE transition becomes first-order at a tricritical point near the triple point.

The PE phase structure of TSCC is orthorhombic $Pnma$, with $Z=4$ formula units per unit cell.⁸ The FE phase is assumed⁹ to be orthorhombic $Pn2_1a$ with $Z=4$, but cell doubling has been suggested.⁴ The four calcium ions and four of the twelve sarcosine molecules in the unit cell lie (statistically, at least) in mirror planes perpendicular to $\underline{b}$ in the PE phase. They can order without cell doubling in 4 ways, one with the above FE space group and the other 3 with AFE ordering.⁶ The present model assumes that the AFE phase has the orthorhombic and piezoelectric $P2_12_12_1$ space group, in which the sarcosine dipoles linked by $N-H \cdots Cl$ hydrogen bonds into chains running along $\underline{b}$ are aligned as in the FE phase, while the sarcosines lying in zigzag chains along the pseudo-hexagonal $\underline{a}$ axis have pressure-induced AFE ordering.

MODEL

Dipoles with interaction energy $\pm J$ are assumed for simplicity to occupy simple cubic (SC) lattice sites. They are assigned to clusters as described in Table 1.

Because the n_i sum to 1, there are only three independent populations, which are chosen as the fractional polarization $p=n_+-n_-$, the fractional antiferroelectric order parameter $q=n_1-n_2$, and the fractional nonpolar cluster population $n=n_1+n_2$. To eliminate n , the probability that two adjacent dipoles along the $\underline{a}$ axis are anti-aligned is required to be n whether or not the two dipoles are in the same cluster.

This gives the relation $n = \frac{1}{2}(1+q^2-p^2)$. The internal energy then is

$$U = -NJ(3p^2+q^2), \quad (1)$$

TABLE 1. Description of two-particle clusters employed in TSCC model.

Location and orientation of dipoles in cluster relative to TSCC $\underline{a} \uparrow$ and $\underline{b} \rightarrow$ axes	Cluster type	Cluster energy	Cluster fractional population
	FE	-J	n_+
	FE	-J	n_-
	AFE	J	n_1
	AFE	J	n_2

where N is the number of dipoles. This is the first of three terms in the Gibbs free energy $G=U+PV-TS$.

The -TS term in the Gibbs free energy is

$$-kT \ln W = (NkT/8) \{ -8 \ln 2 + [(1+p)^2 - q^2] \ln [(1+p)^2 - q^2] + [(1-p)^2 - q^2] \ln [(1-p)^2 - q^2] + [(1+q)^2 - p^2] \ln [(1+q)^2 - p^2] + [(1-q)^2 - p^2] \ln [(1-q)^2 - p^2] \}. \quad (2)$$

This term is symmetric in p and q, and simplifies for $q=0$ to

$$-kT \ln W(q=0) = \frac{1}{2} NkT [-2 \ln 2 + (1+p) \ln(1+p) + (1-p) \ln(1-p)], \quad (3)$$

which is identical to that for the Ising model. Accordingly, for zero pressure this model has a second-order FE transition at $T_c = 6J/k$, because U in Eq. (1) favors the FE state, so that $q=0$ and G is the same as for the mean-field SC Ising model.

The PV term in G is important when hydrostatic pressure P is applied. To explain the first-order FE and AFE transitions, negative terms in p^4 and q^4 are obtained by assuming that the change in volume V is a cooperative effect; in other words, each of the 4 cluster types requires less volume when surrounded by similar clusters. The probability that neighboring clusters are similar is proportional to p^2 for a FE cluster and q^2 for an AFE cluster. Because there is a fraction $\frac{1}{2}(1+p^2-q^2)$ of polar clusters and $\frac{1}{2}(1-p^2+q^2)$ of nonpolar clusters, the PV term can be written (ignoring a constant) as

$$PV = -\frac{1}{2} NJ \phi [(1+\alpha)(1+q^2-p^2)q^2 + (1-\alpha)(1+p^2-q^2)p^2] \\ = -\frac{1}{2} NJ \phi [(1+\alpha)(q^2+q^4) + (1-\alpha)(p^2+p^4) - 2p^2q^2]. \quad (4)$$

Here ϕ is bilinear in the pressure and the strength of the cooperative volume decrease common to both the FE and AFE phase, while α is proportional to the difference in these strengths for the two phases. One finds p and q by minimizing G, but first it is helpful to find as many features as possible of the phase diagram as a function of the dimensionless parameters $\phi, \tau = kT/J$, and α , in order to choose an α which agrees well with the TSCC phase diagram in pressure-temperature (ϕ, τ) space. A necessary condition for a second-order FE transition is $\partial^2 G / \partial p^2 = 0$, which yields $\tau_c = 6 + \phi(1-\alpha)$. Thus $\alpha < 1$ is required to predict positive $d\tau_c/d\phi$ as observed for TSCC. By comparing free energies at $T=0$, one finds that the FE phase having $G = -NJ[3 + \phi(1-\alpha)]$ is stable for $\phi < \alpha^{-1}$, above which pressure the AFE phase having free energy $-NJ[1 + \phi(1+\alpha)]$ is stable, as shown in Fig. 1. In that Figure, α is restricted to $0 \leq \alpha \leq 1$ to allow both an AFE phase and positive $d\tau_c/d\phi$. The dashed lines show where the T-independent free energy for the stable completely ordered phase ($p=1$ or $q=1$) is equal to the free energy $-NkT_c \ln 2$ of the PE phase at the PE-FE second-order transition. To the right of these lines a second-order transition is impossible. The first-order transition actually occurs at lower pressure

(TP line in Fig. 1), because at finite T a partly ordered phase will have lower free energy than a completely ordered phase. The tricritical point (TCP line in Fig. 1) is located from the requirement that $\partial^4 G / \partial p^4$ vanish as well as $\partial^2 G / \partial p^2$, yielding $\phi_{TCP} = 6/5(1-\alpha)$.

Fig. 1 shows that in order to have a PE-FE tricritical point near the PE-FE-AFE common point as reported by Windsch,⁹ α must be near 0.5. This value also gives a surprisingly good fit to the slopes dT_C/dP and dT_N/dP near the triple point, as shown in Fig. 2. The observed curvature of the PE-FE transition line is not predicted, while the curvature of the FE-AFE phase boundary is overestimated.

At zero pressure the polarization curve is predicted to obey the mean-field SC Ising result $p = \tanh(6Jp/kT)$, which has an effective β exponent near the mean-field value of $1/2$ most of the way down to $T=0$, in disagreement with experiments^{1,9,11} which yield effective β near $1/3$ starting about 10°C below T_C . Fairly good agreement with these zero-pressure experimental results is obtained from the model predictions at 3.2 kbar. Perhaps this model overestimates the rate at which the transition moves away from tricriticality as pressure decreases, because the PV term in G is the only one giving the possibility of a first-order transition.

The possibility of temperature-dependent J must be considered, because TSCC seems to be on the borderline between displacive and order-disorder behavior.

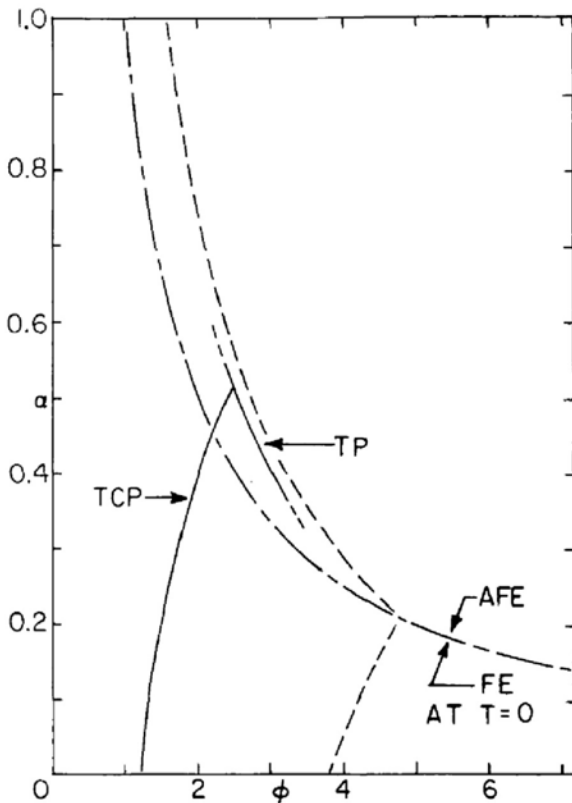


FIGURE 1. Effect of α on phase diagram for TSCC model.

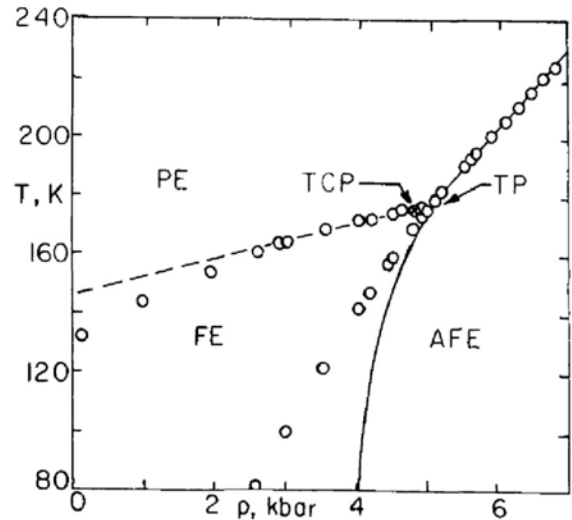


FIGURE 2. Phase diagram for TSCC comparing experimentally determined phase boundaries (circles; Ref. 6) with those predicted by two-particle cluster model with $J/k=24.34$ K, $\phi=2.53$, and $\alpha=0.5$. Solid and dashed lines represent first- and second-order transitions respectively.

Displacive behavior such as soft modes has been explained in terms of particles in potential wells having dipolar interactions.¹⁰ In TSCC the spontaneous polarization is quite small, so in this model the nature of the interaction is not specified. Each sarcosine dipole is assumed to lie in its own biased " ϕ^4 " potential well with internal energy

$$U = U_0(y^4 - 2y^2) - 3J_0\bar{y}y. \quad (5)$$

Here U_0 is the barrier height in the absence of bias, y is displacement normalized to ± 1 at the unbiased well minima, and $\pm J_0$ is the interaction energy of a particle with any of its 6 neighbors if both particles are at $y = \pm 1$. In the order-disorder limit that $U_0 \gg J_0$ the correspondence $J_0 = J$ can be made. Each well is biased in proportion to the average displacement $\bar{y}$ of all the other particles, assuming $\bar{y} = \bar{y}_r p$. The calculation of $\bar{y}_r$ is made classically using the Boltzmann factor:

$$\bar{y}_r = \frac{\int_0^\infty y \exp(-U/kT) dy}{\int_0^\infty \exp(-U/kT) dy}; \quad U' = U_0(y^4 - 2y^2) - 3J_0\bar{y}_r y. \quad (6)$$

The two-particle-cluster model with $J = J_0\bar{y}_r$ is used to calculate p , so this model must be solved self-consistently with the above relations. For $U_0 < kT_c$ which is roughly the range in which displacive transition phenomena such as soft modes are expected to occur, J increases by about 20% from T_c down to zero temperature. This causes only modest changes in the shapes of the phase diagram (drawn for fixed J in Fig. 2) and in the polarization vs. T curve.

DISCUSSION

A possible objection to this model is that if U_0/J_0 is taken small enough to get strongly temperature-dependent soft mode frequency dependence, the thermal energy kT will be larger than U_0 near T_c , so a two-state order-disorder model becomes less applicable when each dipole has a continuum of states (positions y) available to it. In any event, the agreement of this model with the observed phase diagram is quite good.

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