

Microscopic Origin of the Two-Sublattice Model for Antiferroelectric State

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The macroscopic model proposed by Kittel for antiferroelectrics assumes two interpenetrating sublattices with antiparallel polarizations. Although the model can explain many properties, it does not provide microscopic lattice displacement patterns associated with these sublattices since the order parameter in the model is a volume-averaged quantity. We propose a model based on microscopic positioning of symmetry elements and use an order parameter field directly associated with the local dipoles, which can provide a more transparent definition for the sublattices used in the Kittel model. We also include nonlocal gradient interactions to model multidomain structures and domain walls in ferroelectrics.

Keywords: antiferroelectric; Landau theory of phase transitions; sublattice model; microscopic symmetry

INTRODUCTION

The antiferroelectric (AFE) state was modeled by Kittel based on the Landau theory and use two interpenetrating sublattices with equal but opposite polarizations.¹ This model can successful describe the double hysteresis loops² observed in antiferroelectrics, but contains no mechanism to describe the spatial relationship between the two

sublattices. In other words, there is no mechanism to guarantee the two sublattices to exist alternately in space to form the antiferroelectric state.

We propose a microscopic model for the AFE state, which not only provides the origin of the Kittel sublattices, but also gives the fixed spatial relationship between them. This model is based on microscopic symmetry and group theoretical methods. By adding the gradient energy associated with the AFE state, it can also be used to describe inhomogeneous structures, i.e., orientation twins and antiphase configurations.

In describing this model, we will use ammonium dihydrogen phosphate, or ADP, as a prototype. The method itself is quite general, and can be applied to any other antiferroelectric species.

MICROSCOPIC SYMMETRY

The high-temperature paraelectric phase³⁻⁶ of ADP is tetragonal, with space group $I\bar{4}2d$. At $T_C = -125^\circ\text{C}$, a transition to an orthorhombic AFE phase⁴⁻⁷ with space group $P2_12_12_1$ occurs, with a doubling of the primitive unit cell.

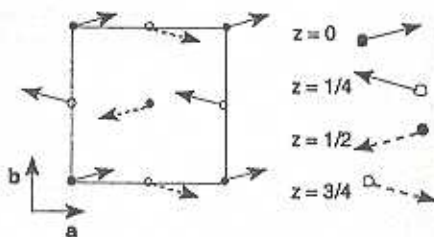


Figure 1 Dipole moments within the AFE unit cell.

The transition is driven by an M-point soft mode corresponding to the M_3M_4 physically irreducible representation.⁸ The antiferroelectric state consists of four individual molecular dipole moments, parallel to the a - b plane, within the unit cell of the AFE phase as shown in Fig. 1. The transition can be described by a two-component order parameter

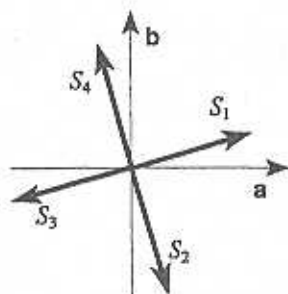


Figure 2 Directions of (000) dipole moment in the four AFE domains.

that corresponds to the components of the molecular dipole at the (000) position. There are four energetically equivalent orientations for this dipole, as shown in Figure 2, and so there are four distinct domains in the AFE phase, with the two-component order parameters as listed in Table I. For convenience, we assume $p_a > p_b$ in the low temperature orthorhombic structure with space group $P2_1 2_1 2_1$.

TABLE I. Values of the order parameter for the four different domain states.

Domain	Order Parameter
S_1	(p_a, p_b)
S_2	$(p_b, -p_a)$
S_3	$(-p_a, -p_b)$
S_4	$(-p_b, p_a)$

Since the space groups of the two phases and the irreducible representation are known, the symmetry allowed distortions, based on the positions of the microscopic symmetry elements, can be calculated. This is done using the ISOTROPY computer program⁹, and the results for the Wyckoff *a*-sites are shown in Table II. Using the distortions in this table, the dipole arrangement can be reproduced for any single domain state given in Table I (similar to the arrangement shown in Fig. 1 for S_1). The relationship between these allowed

distortions and the positions of the microscopic symmetry operations is illustrated for domain S_1 in Fig. 3

TABLE II. Group-theoretically allowed distortions at Wyckoff a -sites in domain S_1 .

Position	Distortions
$(0,0,0)$	$p_a (1,0,0) + p_b (0,-1,0)$
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$p_a (-1,0,0) + p_b (0,1,0)$
$(0, \frac{1}{2}, \frac{1}{4})$	$p_a (-1,0,0) + p_b (0,-1,0)$
$(\frac{1}{2}, 1, \frac{3}{4})$	$p_a (1,0,0) + p_b (0,1,0)$

RELATIONSHIP TO THE KITTEL SUBLATTICES

Our model has focused on the microscopic structure of the AFE state. In order to understand the macroscopic behavior (in particular, the double hysteresis loops observed when the antiferroelectric material is placed in an external electric field), we must make a connection

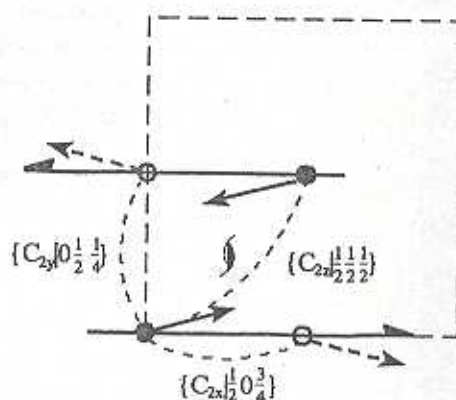


Fig. 3 Actions of symmetry elements generate dipole arrangement

between our microscopic model and the Kittel macroscopic model. Since polarization is an average of molecular dipole moments over a given volume, the sublattice polarizations P_1 and P_2 in the one-dimensional Kittel model can be defined, in terms of the molecular dipole moments, as

$$P_1 = \frac{1}{V} \sum_{(p_i > 0)} p_{ai}, \quad P_2 = \frac{1}{V} \sum_{(p_i < 0)} p_{ai}. \quad (1a,b)$$

In other words, in the AFE state those dipole moments with a positive component in the a -direction form one sublattice with polarization P_1 , and those dipole moments with a negative component in the a -direction form the other sublattice with polarization P_2 , as shown in Fig. 4.

On a unit cell level, we can further define the sublattices in terms of symmetry operations. Referring to the positioning of symmetry operations in Fig. 3, define p_+ and p_- as

$$p_+ = p + \{C_{2x} | \frac{1}{2} 0 \frac{1}{2}\} p$$

$$p_- = \{C_{2x} | \frac{1}{2} \frac{1}{2} \frac{1}{2}\} p + \{C_{2y} | 0 \frac{1}{2} \frac{1}{2}\} p \quad (2a,b)$$

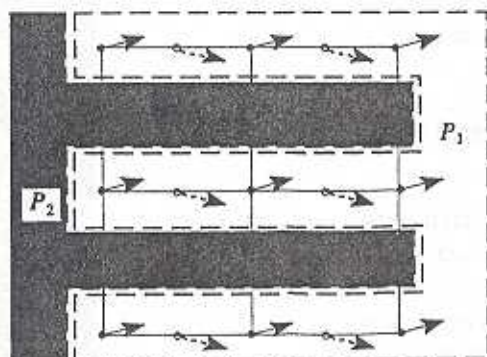


Figure 4 Defining the macroscopic Kittel sublattices in terms of the microscopic dipole moments.

These two quantities, when volume averaged over all unit cells, naturally recreate the Kittel sublattices on the microscopic scale.

Our microscopic theory presented here not only can derive the macroscopic Kittel model, but also can account for the spatial relationships among dipoles of adjacent cells. More importantly, it also gives the dipole tilt, which occurs in the ADP system, leading to the observed unit cell doubling associated with the antiferroelectric phase transition.

FREE ENERGY DENSITY

The free energy originally incorporated in the Kittel model included only local terms:

$$F = \alpha_1 (P_1^2 + P_2^2) + \alpha_2 P_1 P_2 + \alpha_3 (P_1^4 + P_2^4) \quad (3)$$

In our model, however, knowledge of the irreducible representation involved in the transition allows non-local terms to be added in the form of gradient invariants. For the ADP case being considered, this free energy density can be written as

$$\begin{aligned} F = & A(p_1^2 + p_2^2) + B_1(p_1^2 + p_2^2)^2 + B_2(p_1^4 + p_2^4) \\ & + B_3(p_1^2 p_2 - p_1 p_2^2) + C_1(p_1^2 + p_2^2)^3 + C_2(p_1^4 p_2^2 + p_1^2 p_2^4) \\ & + C_3(p_1^2 p_2 - p_1 p_2^2) + D_1 \left[\left(\frac{\partial p_1}{\partial x} \right)^2 + \left(\frac{\partial p_2}{\partial y} \right)^2 \right] \\ & + D_2 \left(\frac{\partial p_1}{\partial x} \frac{\partial p_2}{\partial x} - \frac{\partial p_1}{\partial y} \frac{\partial p_2}{\partial y} \right) + D_3 \left[\left(\frac{\partial p_1}{\partial y} \right)^2 + \left(\frac{\partial p_2}{\partial x} \right)^2 \right] \end{aligned} \quad (4)$$

where p_1 and p_2 refer to the two components of the order parameter, i.e., the *a*- and *b*- components of the (000) molecular dipole moment. All coefficients are temperature independent except $A = A_0(T - T_0)$. With the addition of the order parameter gradient terms, this free energy can be used to describe the change in order parameter across a

domain wall in an inhomogeneous structure. For example, the change in order parameter across the domain wall in an orientation twin formed by domains S_1 and S_2 can be calculated by normalizing the order parameter using the following change of variables:

$$p_1 = p_a^{(0)} f_1 + p_b^{(0)} f_2 = p_a^{(0)} (f_1 + \kappa f_2) \quad (5a)$$

$$p_2 = p_b^{(0)} f_1 - p_a^{(0)} f_2 = p_a^{(0)} (\kappa f_1 - f_2). \quad (5b)$$

This leads to a coupled set of differential equations upon energy minimization,

$$f_{1,x''} = -\tau f_1 - f_1^3 + f_1^5 + b' f_1 f_2^2 + c' (2f_1^3 f_2^2 + f_1 f_2^4) \quad (6a)$$

$$f_{2,x''} = -\tau f_2 - f_2^3 + f_2^5 + b' f_1^2 f_2 + c' (f_1^4 f_2 + 2f_1^2 f_2^3), \quad (6b)$$

with the boundary condition

$$f_1 = \begin{cases} \sqrt{\frac{1}{2} + \sqrt{\frac{1}{4} + \tau}}, & x'' \rightarrow -\infty \\ 0, & x'' \rightarrow +\infty \end{cases}, \quad f_2 = \begin{cases} 0, & x'' \rightarrow -\infty \\ \sqrt{\frac{1}{2} + \sqrt{\frac{1}{4} + \tau}}, & x'' \rightarrow +\infty \end{cases} \quad (7)$$

where τ describes the temperature dependence. These equations can be solved numerically, and solutions for three temperatures are shown in Fig. 5. Further details of this process are reported elsewhere.¹⁰⁻¹¹

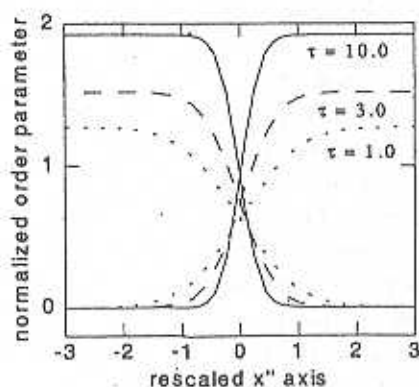


Fig. 5 Calculated profiles for a representative orientation twin for three different temperatures.

CONCLUSION

We proposed a Landau-Ginzburg type model for the antiferroelectric state based on microscopic symmetry and group theory. The order parameter corresponds to the local dipole moment within the unit cell, instead of the macroscopically averaged polarization conventionally used. Our model can rigorously derive the sublattices of the model proposed by Kittel and address the dipole tilt and cell doubling in the antiferroelectric transition. The so derived sublattices are intrinsically linked, which resolved the confusion encountered in the Kittel model.

The model is also extended to include order parameter gradient terms. These nonlocal interaction terms allow inhomogeneous structures, such as, orientation twins and antiphase walls, to be modeled.

Acknowledgements

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