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Dielectric Hysteresis Loops of First-order Antiferroelectrics

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Landau-Devonshire free-energy expression is applied to study the dielectric hysteresis loops of a two-sublattice antiferroelectric undergoing a first order phase transition from the paraelectric phase. This expression for the antiferroelectric sublattices corresponds to the free energy expression of ferroelectric bilayers of equal thicknesses. The pattern of the dielectric hysteresis loops is characteristic of the value of temperature t relative to the three critical temperatures and the limit of field induced temperature t_2. The interlayer coupling term J, assumed to be antiferroelectric, is also an important factor that affects the patterns of dielectric hysteresis loops. Despite their complicated appearance the dielectric hysteresis loops can be classified in terms of a small number of types of minimum.

Formalism

Dielectric hysteresis loops (DHLs) of the first-order antiferroelectric have been mentioned in the monographs [1, 2], however, the details of the rather complicated behaviour in different temperature ranges are not available. Here, therefore, we give those details. We have previously used a Landau-Devonshire model to discuss the DHLs of ferroelectric bilayers and superlattices with an assumed antiferroelectric coupling at the interfaces [3, 4]. A main parameter is the ratio $l = L_1/(L_1 + L_2)$, where L_1 and L_2 are the thicknesses of the individual layers. The free energy used here is the same as the special case $l = 1/2$ and the

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results to be presented here correspond to equal-thickness bilayers.

The free energy expression of a first-order antiferroelectric, AFE, is described as

$$F=\frac{1}{2}\frac{A}{\varepsilon_0}\left(P_1^2+P_2^2\right)+\frac{1}{4}\frac{B}{\varepsilon_0^2}\left(P_1^4+P_2^4\right)+\frac{1}{6}\frac{C}{\varepsilon_0^3}\left(P_1^6+P_2^6\right)+JP_1P_2-E\left(P_1+P_2\right) \qquad (1)$$

where the coefficient A is $a(T-T_0)$, B is negative but C is positive. For J positive, the forth term describes antiferroelectric coupling since it favours $P_1P_2<0$. The last term describes the coupling to the electric field E.

We introduce dimensionless variables in the same way as for first-order ferroelectrics [1,5], namely $t=4aC(T-T_0)/|B|^2$, $p_n=P_n/P_0$ for $n=1$ and 2 with $P_0^2=\varepsilon_0|B|/2C$, $j=J/J_0$ with $J_0=|B|^2/4\varepsilon_0C$, $e=E/E_0$ with $E_0^2=|B|^5/32\varepsilon_0C^3$ and $f=F/F_0$ with $F_0=|B|^3/8C^2$. In terms of these variables, we have

$$f=\frac{1}{2}t\left(p_1^2+p_2^2\right)-\frac{1}{2}\left(p_1^4+p_2^4\right)+\frac{1}{6}\left(p_1^6+p_2^6\right)-e\left(p_1+p_2\right)+jp_1p_2 \qquad (2)$$

It can be shown that for the antiferroelectric critical temperatures values for the ferroelectric [5] are simply offset by j:

$$t_{SC}=j,\ t_C=0.75+j,\ t_{SH}=1.0+j,\ t_2=1.8+j \qquad (3)$$

where t_{SC} is the supercooling limit of the paraelectric, PE, phase, t_C the thermodynamic transition temperature, t_{SH} is the superheating limit of the AFE phase and t_2 as the upper limit of the field-induced phase.

we are concerned with the minima of f, given by (2), so to find the DHL we find numerical solutions of the simultaneous equations

$$tp_1-2p_1^3+p_1^5-e+jp_2=0 \qquad (4)$$

$$tp_2 - 2p_2^3 + p_2^5 - e + jp_1 = 0 \qquad (5)$$

Patterns of Hysteresis loops

The DHL is plotted as $(p_1 + p_2)$ versus e. We find that the form of the DHL depends mainly on where the temperature t is located relative to the critical temperatures in (3). We take as a starting value $j = 1.0$ for which $t_{SC} = 1.0$, $t_C = 1.75$, $t_{SH} = 2.0$ and $t_2 = 2.8$. An example of the DHL for a temperature below t_{SC} is shown in Fig. 1. There are three branches labeled A, B and C. For $e = 0$ the PE phase $p_1 = p_2 = 0$ is not stable and, this point on line A corresponds to the AFE phase $(p_1, -p_2)$. It can be shown that in fact $p_1 = p_2 = 0$ is a saddle point. As seen in Fig. 1, the A line persists to some value e_C of e, above which it disappears and only the C line $p_1 = p_2 \neq 0$ is stable (we describe the qualitative forms of the various minima by the same letters). An additional line B is seen for a small range of intermediate field values. The nature of the B line corresponds to a minimum point with p_1 large and $p_2 \approx 0$, or vice versa.

The qualitative form of the DHL shown in Fig. 1 persists up to $t = t_{SC}$, but it changes as follows for increasing t. First, the C line begins at higher field value. Second, e_C decreases; the A line becomes shorter. Third, the B line becomes longer. The converse is true: with decreasing t, the C line appears at a lower value of e, the A line becomes longer, i.e. e_C increases, and the B line becomes shorter and eventually disappears. These changes are summarized in Fig. 2 for j = 1.0 and the two t values 0.0 and 0.8. In addition, it is also seen from Fig. 2 that for a fixed value of j the size of the hysteresis loops, shown by the marked arrows, shrinks as the temperature is increased.

Some indications of the effects of changing j at constant temperature are given by Fig. 3, which shows two DHLs at the same temperature but for different values of j. For larger j,

since the coupling term favours antiparallel p_1 and p_2, the C minimum at $e = 0$ is absent with the C line starting only at non-zero e. For the smaller value of j, although the C minimum does exist at $e = 0$, it is much shallower than the A minimum. In other words, the AFE phase is stable at zero field and the aligned phase is at best metastable. The effect of j on the A line is also clearly shown in Fig. 3; it is longer at higher j, again because the coupling term favours antiparallel p_1 and p_2. In addition, the B line is absent for larger j. Since at a B point $p_1 p_2 \approx 0$ larger j disfavours B compared with A.

Fig. 4 is for $t = 1.5$ ($t_{SC} < t < t_C$). The main difference from Fig. 1 is the appearance of a second line, labelled P, in the low-field region. From our plots, we notice that in the whole range $t_{SC} < t < t_{SH}$ both the PE and AFE phases are locally stable and the appearance of the P line is to be expected, as shown in Fig. 4 for $t = 1.5$.

As t increases towards t_{SH} the AFE phase becomes relatively less stable and on the DHL the A line becomes shorter and the P line longer. At temperature t above t_{SH}, the AFE phase is not locally stable for $e = 0$ and consequently the A line no longer appears; this is illustrated in Fig. 5. A distinct quadruple-loop-DHL like that in Fig. 5 is seen throughout the temperature range $t_{SH} \le t < t_2$. This is the region of the field-induced ordered phases and we have confirmed from contour plots that the three segments of the DHL have P, B and C characters as noted in Fig. 5. For small j, the quadruple-loop DHL is most distinct for t very close to t_{SH}.

Conclusions

As far as we know, the possible forms of the DHL for a first-order antiferroelectric have not been discussed in detail before. Here we have carried out a numerical investigation of these forms, using as a basis the Landau-Devonshire free energy f of (1). Like the first-

order ferroelectric, the first-order antiferroelectric has three critical temperatures: t_{SC}, t_C and t_{SH}. In addition, the fourth temperature is at t_2, the upper limit of the field-induced phase. The broad generalization that can be made about the DHL is that its qualitative form is characteristic of the position of the temperature relative to the three critical temperatures and t_2.

At a sufficiently high field in all temperature ranges the only minimum of f is the fully aligned state in which the sublattice polarizations p_1 and p_2 are equal and lie along the field e; the corresponding line is marked C, as before. A new form of minimum in which one of p_1 and p_2 is near zero and the other is not appears for the first-order antiferroelectric and is denoted B on the DHLs where it appears.

The DHL, as we have calculated it here, is the locus of minima of the free energy and therefore it may be used to assess possible forms of the hysteresis loop that could be observed in practice. However, there are some questions that cannot be answered on the basis of a static theory like the present. As an example, in graphs like Fig. 2 is the curve B observable, that is, does switching occur direct from A to C and vice versa or does switching pass through the line B? To answer this we need to extend the model to include dynamics and this can be done by means of the Landau-Khalatnikov equation of motion

$$\gamma \frac{\partial P_n}{\partial \tau} = -\frac{\partial F}{\partial P_n} \qquad n = 1,2 \tag{6}$$

where τ is time and γ determines the switching speed. The numerical solution of this has been applied to investigate switching in step fields and hysteresis loops in sinusoidal fields for both second-order [6] and first order [7] ferroelectrics. Similar calculations should be possible for second-order and first order antiferroelectrics and the present investigation of the static DHL establishes the framework for such studies.

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Figure captions

Fig. 1. Dielectric hysteresis loop $p=(p_1+p_2)$ versus e for a first-order antiferroelectric; $t=0.5$ ($t<t_{SC}$) and $j=1.0$. The coercive field e_C is indicated.

Fig. 2. Dielectric hysteresis loops $p=(p_1+p_2)$ versus e for a first-order antiferroelectric with $j=1.0$ for $t=0.0$ (solid line) and $t=0.8$ (dashed line).

Fig. 3. DHLs for $t=0.2$: A_1, B_1, and C_1 and solid lines $j=0.6$; A_2 and C_2 and dashed lines $j=1.6$.

Fig. 4. DHLs for $j=1.0$ and $t=1.5$.

Fig. 5. DHL for $j=0.4$ and $t=1.4$ ($t=t_{SH}$). The extremes of the hysteresis loops are indicated.

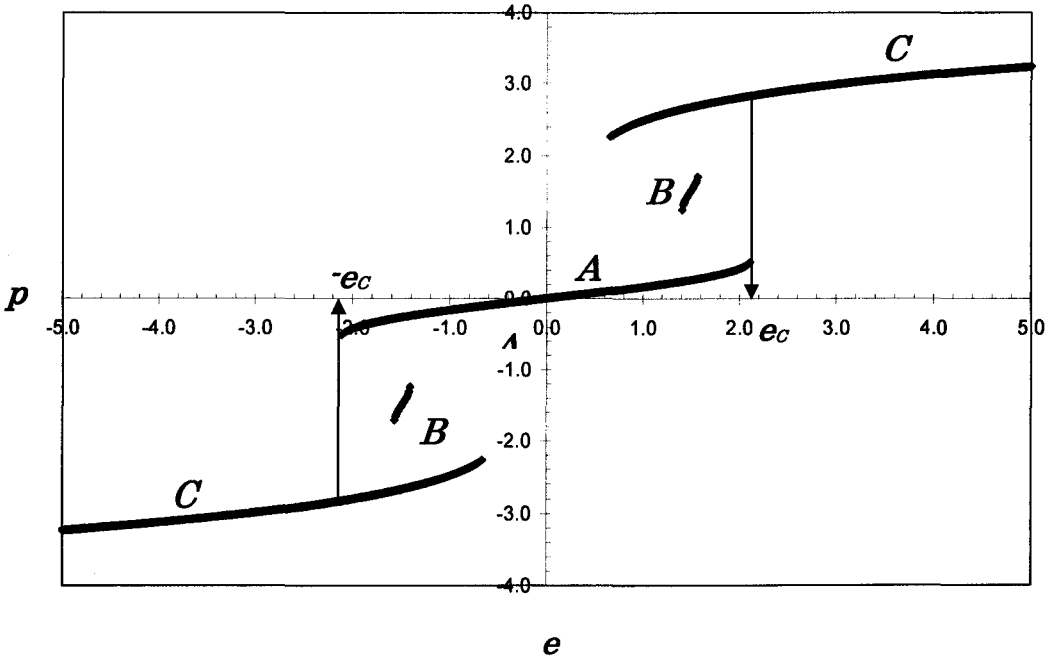


Fig. 1

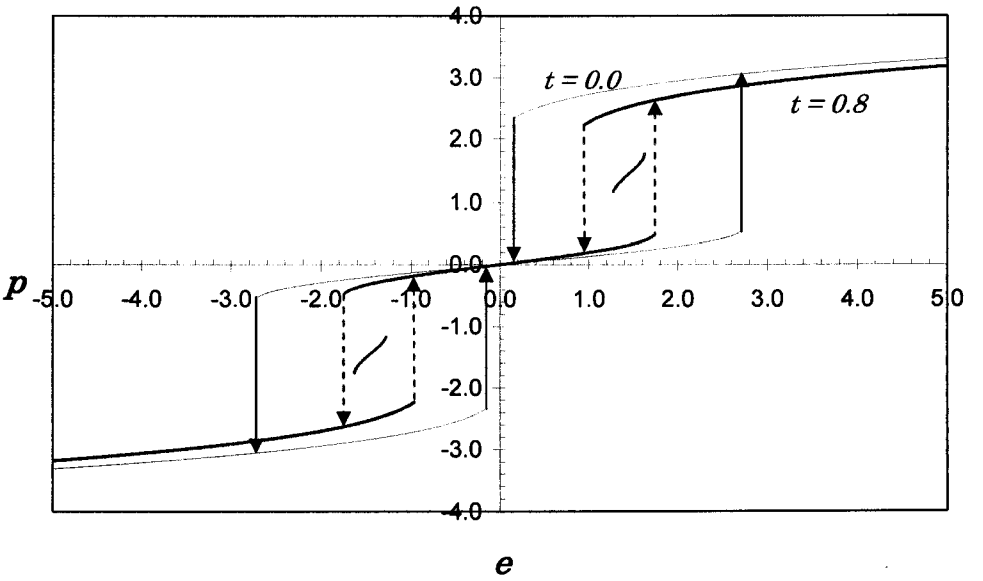
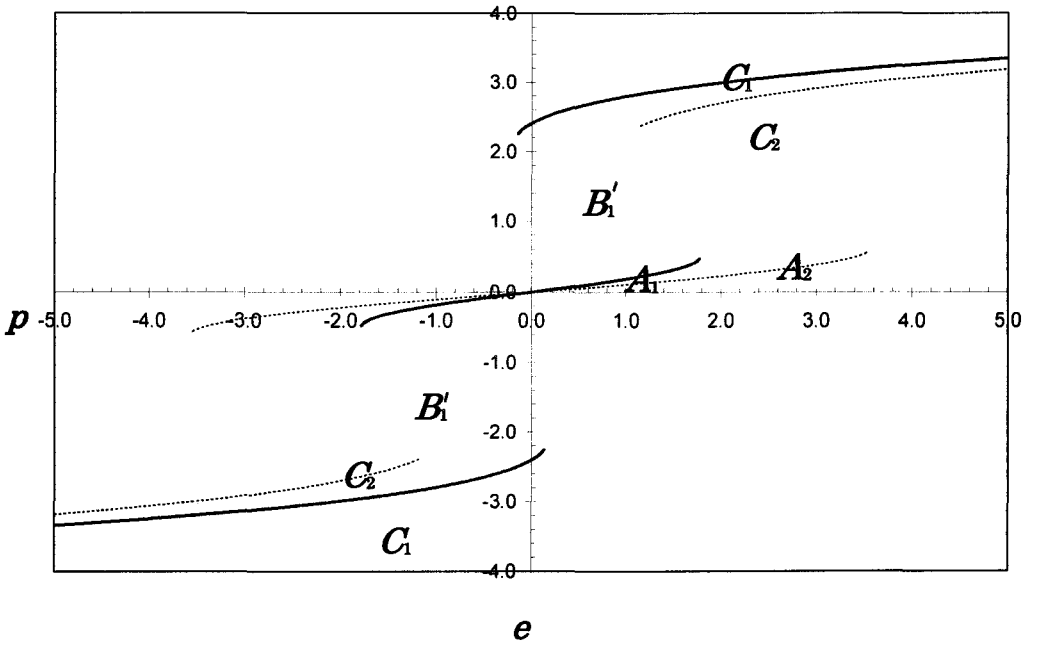


Fig 2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C1

Fig. 3

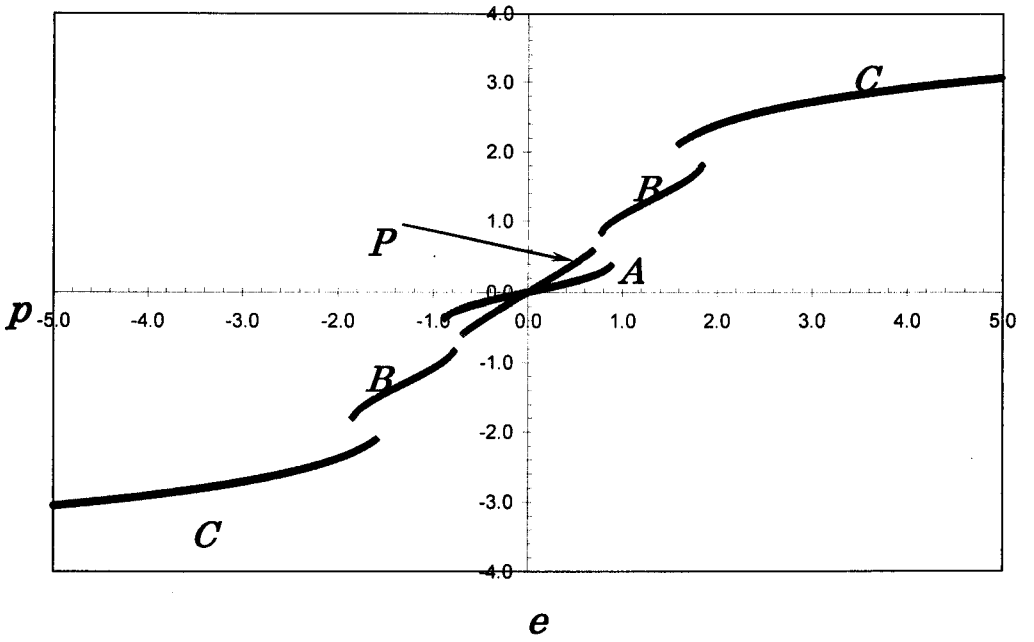

Fig 4

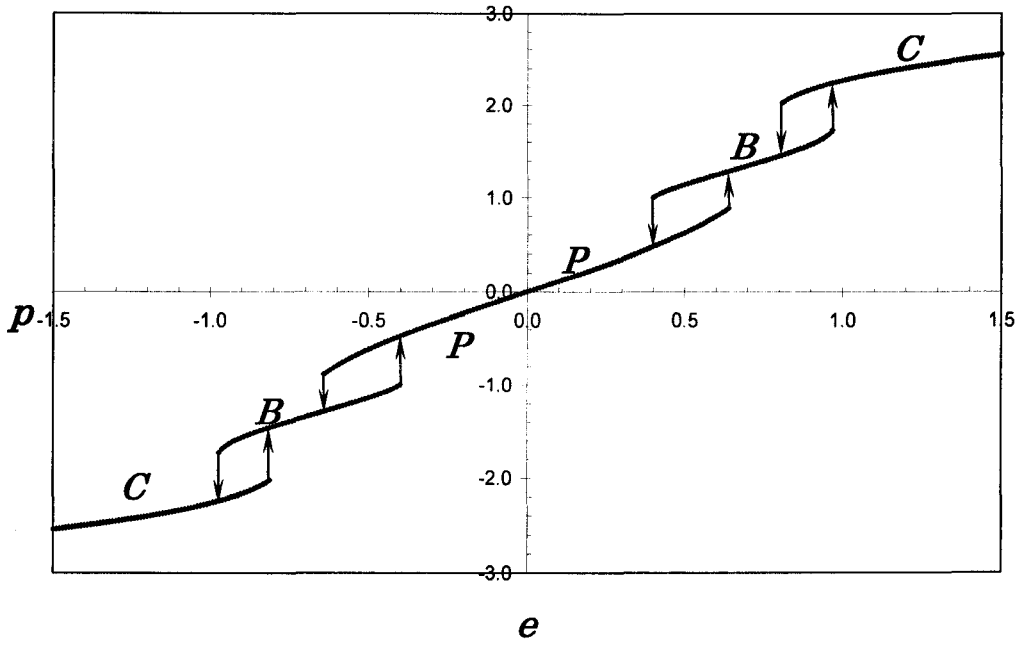

Fig 5