

Photoinduced changes in the nature of ferroelectric phase transitions

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For phase transitions in ferroelectric semiconductors subjected to illumination, there may be two tricritical points and also regions of a self-excited oscillatory instability of the ferroelectric phase.

The properties of photostimulated ferroelectric phase transitions are determined in many ways by the mutual effects of the electron and lattice subsystems. As a result, the width of the band gap is increased through the onset of a spontaneous polarization, and there is a shift in the Curie temperature because of a change in the population of capture centers.¹ Experiments on these^{2,3} and related⁴ effects have led to several problems involving the kinetics of photostimulated phase transitions. We analyze these problems in this letter and show that illumination changes the dynamics of the order parameter and can lead to a qualitatively new type of ferroelectric transition.

We consider a ferroelectric which is subjected to continuous illumination that generates conduction electrons. These electrons may be captured by capture centers. The thermodynamic potential of the ferroelectric can be written as a Landau expansion which depends on the number of electrons at capture centers.¹⁾ Since the processes associated with them are slow, we can use the following relaxation equation for a single-component order parameter P :

$$\frac{dP}{dt} = -\Gamma \{ [\alpha' (T - T_0) + am] P + \beta P^3 + \gamma P^5 \}. \quad (1)$$

Here Γ is a kinetic coefficient; α' , β , and γ are the coefficients in the expansion of the lattice energy (for first-order phase transitions we would have $\beta < 0$); m is the number of electrons at capture centers; T is the temperature, in energy units; and a is a coefficient in the expansion of the electron energy, in which we retain only the term $\sim P^2$. We show below that in our model this approach is sufficient for correctly describing the behavior of the thermal hysteresis. For the electron system we adopt a unipolar model with a single attachment level, which is filled through an exchange of electrons with the condition band (the c -band).⁵ The corresponding balance equations are

$$\frac{dn}{dt} = \beta_0 kI - \frac{n}{\tau_n} - \gamma_n n(M - m) + A(P)m, \quad (2)$$

$$\frac{dm}{dt} = \gamma_n n(M - m) - A(P)m, \quad (3)$$

where n is the number of conduction electrons; M is the density of attachment levels; I

is the intensity of the light; k is its absorption coefficient; β_0 is the quantum yield; $A(P) = \gamma_n N_c \exp[-\epsilon(P)/T]$ is the probability for a thermal scattering into the c -band; τ_n and N_c are the lifetime and state density in the c -band; and $\epsilon(P) = \epsilon_0 + \tilde{a}P^2$ is the interval from the bottom of the conduction band to the attachment level. Under the assumption that the conduction electrons can keep up with the instantaneous value of the number of electrons in capture centers [$\gamma_n \tau_n (M - m) \ll 1$, $\tau_n A \ll 1$], we can reduce (2) and (3) to a single equation,

$$\frac{dm}{dt} = J(M - m) - A(P)m, \quad J = \gamma_n \tau_n \beta_0 k I. \quad (4)$$

System of equations (1), (4), which describes the kinetics of the transition, reflects both a change in the potential due to the capture of electrons by capture centers and a decrease in the thermal scattering into the c -band due to the appearance of a polarization. A qualitative analysis⁶ of this system of equations leads to the phase diagram in Fig. 1. The solid line is the boundary of absolute instability of the paraelectric phase (P):

$$J = \alpha'(T_0 - T)A(P=0)[\alpha'(T - T_0) + aM]^{-1}. \quad (5)$$

For a sufficiently high density of attachment levels, under the condition

$$M \geq M_0 = -4\beta T_0 \tilde{a}(\alpha')^2 / a(\tilde{a}\alpha' - \beta)^2, \quad (6)$$

there is a region of second-order phase transitions on curve (5), bounded by the two tricritical points A and B :

$$T_{A,B} = T_0 - \frac{aM}{2\alpha'} \left(1 - \frac{\beta}{\alpha'\tilde{a}}\right) \left(1 \pm \sqrt{1 - \frac{M_0}{M}}\right). \quad (7)$$

The dashed lines are lines of the absolute instability of the ferroelectric phase (F); and regions I and II are regions of a coexistence of phases (a thermal hysteresis). At $aM > \alpha'\epsilon_0 T_0^2 \times [(T_0 + \epsilon_0/2)^2 - T_0^2]^{-1}$, a region with a positive slope can appear on line (5).

Under the condition that the maximum shift of the Curie point is significantly greater than the hysteresis, i.e., under the condition

$$aM \geq \Gamma\beta^4 T_0 / \gamma^2 A(0)[\epsilon(P) - \epsilon(0)] \sim \Gamma\beta^4 / \gamma^2 A(0), \quad (8)$$

there is a closed region of an instability of the ferroelectric phase near line AB (the hatched region in Fig. 1). At the boundary of this region, we have $J + A(P) + 2\Gamma(\beta P_0^2 + 2\gamma P_0^4) = 0$, where P_0 is the steady-state value of the polarization. In this region the paraelectric phase is also unstable; because of the global stability of system (1), (4), this instability of the paraelectric phase is evidence that there is a limiting cycle. This limiting cycle corresponds to self-excited oscillations of the polarization and of the number of electrons in capture centers. The mechanism for the self-excited oscillations can be described as follows: For a system in the ferroelectric phase, the pumping leads to an increase in the number of electrons at capture centers. This increase lowers the transition temperature, and the system remains in the para-

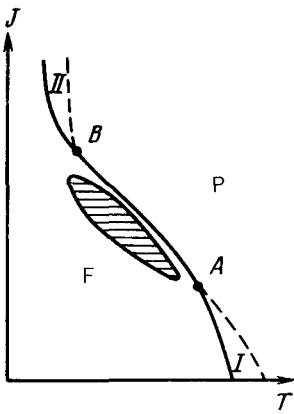


FIG. 1. Temperature-(illumination intensity) diagram of stationary states of the semiconductor. A self-excited oscillation occurs in the hatched region.

electric phase. There is an increase in the probability for thermal scattering into the c -band, and the capture centers become emptied. This effect results in an increase in the transition temperature and a return to the ferroelectric phase, etc.

A similar picture with a periodic change in phase during illumination has been observed in diffractometric studies² of a ferroelectric phase transition in proustite (Ag_3AsS_3) at 25–30 K. According to Ref. 7, the components of the order parameter for proustite transform under a two-dimensional representation of the C_{3v} group. Since there is no third-order invariant, the expansion of the thermodynamic potential takes a form which is the same as the lattice part of the potential in (1). Accordingly, in a situation in which the equilibrium value of the phase of the order parameter is established more rapidly than its modulus relaxes, Eq. (1) describes a relaxation of the polarization in proustite. It is only necessary to allow for the circumstance that the conductivity of proustite is a p -type conductivity, and m corresponds to the number of holes at capture centers. According to indirect experimental evidence,⁸ the nearest attachment level lies a distance $\epsilon_0 \sim 0.08$ eV from the top of the valence band. Using the known values of the polarization jump ($\Delta P = 2 \times 10^{-2} \mu\text{C}/\text{cm}^2$; Ref. 7), of the jump in the band gap ($\Delta E_g = 5 \times 10^{-2}$ eV; Ref. 3), and of the Curie-Weiss constant ($C \sim 10^5$ deg; Ref. 1) for proustite, and assuming $M \sim 10^{14} - 10^{18} \text{ cm}^{-3}$, we find the maximum shift of the Curie point to be $aM = \Delta E_g CM / \pi(\Delta P)^2 \sim 6 - 6 \times 10^4$ deg. In the case of such a large shift, inequalities (6) and (8) are satisfied, indicating that there are two tricritical points and a region of self-excited oscillations for proustite. We can thus link the unusual critical behavior of proustite with our model. The observed period (~ 1.5 s) is due to the small value of the probability for thermal scattering. The decrease in the thermal hysteresis with intensifying illumination which was observed in Ref. 2, culminating in the complete disappearance of the hysteresis, apparently corresponds to the attainment of the tricritical point $T_A \cong 27$ K, $I_A \cong 5 \times 10^6$ lx.

In summary, we have demonstrated that illumination can change the nature of a ferroelectric phase transition. This result helps explain the nature of the anomalies observed in proustite. It would thus be particularly interesting to carry out experiments at high illumination intensities in order to observe the second tricritical point, while infrared illumination is used to empty the capture centers.

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