Reversal of Ferroelectric Domains by Ultrashort Optical Pulses

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The response of a soft-phonon ferroelectric material subjected to a high-intensity optical pulse of duration much shorter than the period of the phonon is modeled using a classical, finite-temperature simulation. It is found that complete, permanent reversal of the orientation of the ferroelectric domains may occur even when the energy per atom imparted by the light pulse is much less than the average thermal energy. The result raises the possibility of using the effect to create optical switches or data storage media with switching times less than 10 psec.

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In recent years it has become feasible to excite coherent, large-amplitude vibrations in a crystal, using an intense light pulse of duration (typically less than 1 ps) much shorter than the period of the phonon [1–3]. On the time scale of the atomic vibration, the primary effect of the light pulse is to impart (through an appropriate nonlinear photon-phonon coupling, e.g., Raman coupling) an approximately instantaneous impulse to the motion of the atoms in the relevant mode of vibration—thus giving rise to the name "impulsive scattering" for this process [1]. The resulting oscillations in the atomic positions, following the application of the light pulse, can be probed in real time by observing their effect on the reflectivity of the material as atoms moving back and forth modulate the electronic response [2,3]. Since the duration of the optical pulse is very short and does not modify the subsequent, intrinsic dynamics of the atomic system, impulsive scattering has provided a useful tool for the time-domain investigation of phonon motion. In particular, because of the large amplitude of atomic motion attainable, it is a natural means for investigation of anharmonic effects [3].

In ferroelectrics, antiferroelectrics, and other soft-phonon materials, the formation of domains is associated with the development of a permanent nonzero phonon displacement below the transition temperature T_c [4]. In the vicinity of T_c, the phonon branches associated with the phase transition show a very low frequency in a small region of the Brillouin zone near the wave vector of the soft mode, and anharmonic effects become important at relatively small amplitudes. Below T_c, the phonon modes can be visualized as vibrations about the potential energy minima of a double-well structure, each well corresponding to a different domain orientation of the material [5]. The soft modes, particularly in ferroelectrics and antiferroelectrics, often couple strongly to scattered light, so that conventional light scattering has provided an effective tool for studying such soft phonons [6], and impulsive scattering is especially effective in producing large-amplitude motion [1,3].

Our purpose in this paper is to analyze the large-amplitude response of a soft-phonon material to impulsive light scattering, using a finite-temperature, classical model of the phonon dynamics. For very large-amplitude light pulses, it will be shown that *the domain structure is not destroyed, but undergoes a coherent switching behavior where entire domains have their orientation reversed, without fragmentation.* This coherent domain reversal occurs for values of the light amplitude which lie within broad windows, giving the effect a robustness which suggests that the behavior is not dependent on the precise details of the model used in the simulations presented here, but should occur generally in soft-phonon materials below T_c. The switching of domain orientation occurs within a few phonon periods, which is typically of the order of 10 psec, raising the possibility of using the effect in fast optical switches. The effect can persist even when the energy per atom required for domain reversal is less than 1% of the average thermal energy per atom. This indicates that the domain reversal can be achieved without substantial heating of the material. Indeed, the physical process involved here is quite distinct from a heating-reannealing effect.

The simplest model [5] containing the essential features of a phonon branch associated with a soft-mode transition is a set of harmonically coupled, damped oscillators (nearest-neighbor coupling spring constant k, damping constant γ, and mass $m = 1$), each in an anharmonic double-well potential $u(x) = x^4 - ax^2$. (The barrier height between the wells is $a^2/4$, the minima occurring at $x = \pm\sqrt{a/2}$.) In this model the position of each oscillator represents the local amplitude of the optical mode associated with the phase transition.

By taking a nearest-neighbor coupling only, we are neglecting, for example, the important long-range coupling to the polarization field present in ferroelectrics [5,7]. However, for the purposes of the present general discussion, such a coupling does not affect our qualitative conclusions. The essential feature we wish to represent is

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the softening of the phonon branch near the center of the Brillouin zone. Throughout this paper we will assume that we are considering the material below the structural phase transition temperature, where the soft-phonon mode of the high-temperature structure has acquired a permanent nonzero amplitude.

In the one-dimensional case of this model, the small-amplitude, harmonic oscillations about the well minima have a dispersion relation given by

$$\omega^2 = 4a + 2k[1 - \cos q],$$

where q is the phonon wave vector, measured in units of the inverse atomic spacing. Thus, the phonon branch is substantially softened (i.e., has a frequency less than twice the lowest frequency $\omega_{\min} = 2\sqrt{a}$) over a fraction approximately $\sqrt{a/k}$ of the entire Brillouin zone [8]. In the real materials of interest, this fraction is typically 10%–30% in a given direction in the Brillouin zone [9], as long as we are not too close to the transition temperature, so that it is reasonable for illustrative purposes to use a ratio $k/a = 20$ in our simulations. Parenthetically, we note that, even within the model, the phonon frequencies are temperature dependent, due to the anharmonicity of the potential $u(x)$ [8]. This choice of parameters places the model in the "displacive" regime [10].

The fraction of the Brillouin zone over which softening occurs is closely related to the equilibrium thickness of a wall between domains of opposite orientation. Such domain walls have a thickness of order $\sqrt{k/a}$ unit cells [8]. We will make use of this point in the qualitative interpretation of the coherent domain reversal found in the numerical simulations.

The choose an appropriate value for the damping γ to model the real system, we note that typically the soft phonons are strongly damped [1,3,9] (as determined by the phonon linewidth), so that a Q factor of 10 or less is to be expected. For the zone-center mode in our model, the Q factor is $\sqrt{a}/\gamma$, suggesting a value of γ of the order of $\sqrt{a}/10$ or larger to be appropriate. It will turn out that γ plays a crucial role in determining the width of the windows of values for the pulse energy which give coherent domain reversal, larger values of γ giving wider energy windows.

In order to examine numerically the collective dynamics of the system, we have performed finite-temperature simulations on large arrays of oscillators (approximately 10^4–10^5) with nearest-neighbor coupling. The equations of motion for the system are

$$\dot{v}_i = -4x_i^3 + 2ax_i + k\sum_j (x_j - x_i) - \gamma v_i + \eta, \quad (1)$$

where $v_i = \dot{x}_i$, j varies over nearest neighbors of i, and η is a random force term (proportional to $\gamma k_B T$) satisfying the fluctuation-dissipation theorem [11] for temperature T. The damping and random force terms represent the anharmonic coupling of the modes in the phonon branch under consideration with all the electronic and vibrational degrees of freedom of the crystal not explicitly contained in the model.

We achieve an initial thermalization of the system at a specified temperature by evolving the system under thermal forces after starting with all atoms at the positive minimum ($x_i = \sqrt{a/2}$) of the double-well potential. Note that the thermalization time, though sufficient for relaxation of the positions within one domain, is not long enough to allow substantial domain-wall creation or annihilation at low temperature, so that it is necessary to set up the initial condition of the system with a definite polarization.

Having reached thermalization of the positions and velocities of the particles, the effect of the optical pulse is reproduced [1] by adding an impulse V to the velocity of each particle; i.e., $v_i \rightarrow v_i - V$. For a large system, this increases the average kinetic energy per particle by $V^2/2$. As we will see below, this increment to the average energy per particle may be large or small compared to the average thermal energy, but it is important to note that the impulse contributes initially only to the motion associated with the zone-center vibrational mode.

Shown in Fig. 1 is the final average polarization (i.e., the average value of x_i) of a two-dimensional system of 200×200 oscillators, having evolved according to the equations of motion for a time $5/\gamma$ after an initial velocity pulse V, for various values V. The temperature $k_B T = 0.25$ is equal to the barrier height for the single-particle potential $u(x)$, which is approximately a factor of 20 smaller than the paraelectric transition temperature found in simulations of the system. (Note that a time of $5/\gamma$, which is of the order of 10 psec for many materials of interest, is long enough for the initial pulse of energy to be damped, though not necessarily long enough for annealing of any domain walls formed.) Also shown in Fig. 1 is the variance of the final positions. A large variance indicates the presence of multiple domains in the system at the end of the evolution time.

The original domain is not permanently altered until the pulse energy $V^2/2$ approximately equals the barrier height

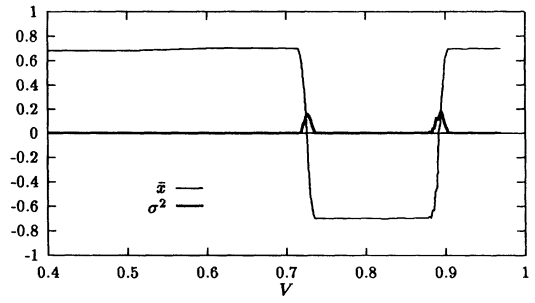

FIG. 1. Final average polarization $\bar{x}$ and variance σ^2 of position versus initial pulse velocity V for a system of 200×200 oscillators evolving according to Eq. (1). The parameters are $\gamma = 0.1$, $k = 20$, $a = 1$, and $k_B T = 0.25$.

in $u(x)$. Very close to this value of V, we see a sudden increase in the variance of the final positions of the atoms, indicating that fragmentation of the initial single-domain structure has occurred. This fragmentation is permanent on the time scale of our simulation. However, as the pulse velocity V is increased slightly, the fragmentation decreases again and the entire single domain remains intact but undergoes a reversal of direction. Over a window of values between $V = 0.74$ and 0.88, essentially no fragmentation occurs. At a higher threshold near $V = 0.89$, fragmentation again occurs before the final domain orientation returns to its initial value for a range of values of V above 0.90.

To understand this behavior, let us first consider a system at zero temperature. Since an identical velocity pulse is given to each particle, the entire system merely follows the dynamics of a single particle in the potential $u(x)$, with the damping γ. In this situation, the final state of the particle is either at $\sqrt{a/2}$ or at $-\sqrt{a/2}$. Which value it finally takes depends on how many times the particle can climb over the barrier in $u(x)$ before damping reduces its energy below the barrier height. If it can pass the barrier an odd number of times, it has a final value of $-\sqrt{a/2}$. Otherwise, it has a final value $\sqrt{a/2}$. The width of the first energy window above the first threshold is equal to the energy lost due to damping during one half-period of the motion, i.e., the energy lost to damping in moving from $x = 0$, $\dot{x} > 0$ back to $x = 0$, $\dot{x} < 0$ (see Fig. 2). For small damping γ, the motion is approximately periodic and the first energy window above threshold has a width $W = \gamma 2a\sqrt{2a}/3$. Note that this width is proportional to the damping γ, so that a broader phonon line width gives a broader energy window.

This pattern of windows of values of V giving intact domains of alternating orientation, separated by narrow thresholds where substantial domain fragmentation occurs persists as the temperature is increased. The most notable aspect of the behavior shown in Fig. 1 is the fact that the energy threshold over which fragmentation occurs is much smaller than the temperature of the system. Thus, although in the example the temperature equals the barrier height and the thermal kinetic energy of each particle is comparable to the energy barrier in $u(x)$, with an associated fluctuation in its velocity, this does not give rise to a comparable uncertainty in the value of V entering into the "single-particle" analysis of barrier passage given above.

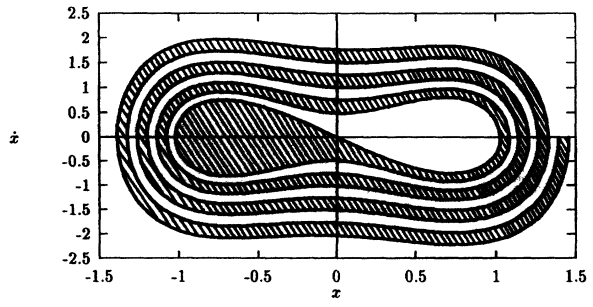

FIG. 2. Phase-space $(x, \dot{x})$ diagram for the single particle in an anharmonic potential $u(x) = x^2 - x^4$ with damping $\gamma = 0.1$, showing the trajectories separating regions of initial conditions which lead to opposite final polarization $x = \pm\sqrt{2}/2$.

This behavior can be understood when we realize that the coupling of neighboring atoms prevents an individual atom from changing its displacement too much from that of its neighbors. Thus, it is not possible to form a long-lived domain fragment less than a certain critical size. We would expect the linear dimension of this critical domain fragment to be proportional to the thickness of a static domain wall and, certainly, the critical fragment must have a size at least twice the domain wall thickness. In the present model, this means that we would expect the critical domain fragment size to be proportional to $\sqrt{k/a}$ and the number of atoms in this fragment to be proportional to $(k/a)^{d/2}$, where d is the dimension of the system.

This allows us to give a qualitative analysis of the fragmentation and the average final polarization near the threshold, as follows: We assume that there is a typical domain fragment size N_D which acts as an independent entity, i.e., for which the coupling to the rest of the system can be approximately ignored. The velocity of the center of mass of this unit has a Gaussian fluctuation ΔV with a standard deviation equal to $\sqrt{k_B T/N_D}$, where k_B is Boltzmann's constant. We now treat this entity as in a single-atom problem (ignoring its coupling to other parts of the system), but with the temperature reduced by a factor of N_D. We assume that if the initial (center of mass) velocity of this unit (the impulse velocity V plus the given value of the random thermal velocity ΔV) is greater than a threshold value V_t, the final polarization of the unit will be negative. It is then straightforward to show that a large system will have a final average polarization near threshold,

$$\bar{x}(V) = x_0 \,\mathrm{erf}\left[\frac{V_t - V}{\sqrt{2k_B T/N_D}}\right], \tag{2}$$

where x_0 is the full polarization value. Equation (2) gives an excellent fit to the simulation results near threshold. We find a value of $N_D = 12\sqrt{k/a}$ for one-dimensional systems and $N_D = (30\sqrt{k/a})^2$ for two-dimensional systems. Three-dimensional systems of appropriate size require much larger computations and have not been performed yet. However, we expect much larger values of N_D in 3D systems, with correspondingly sharper thresholds.

Shown in Fig. 3 is the average final polarization versus impulse velocity V for a temperature $k_B T = 4.5$, comparable to the paraelectric transition temperature (which is slightly larger than 5 in our simulations). We see a substantial renormalization of the barrier energy $V_t^2/2 = 0.03$ (a factor of 8 smaller than the low-temperature barrier)

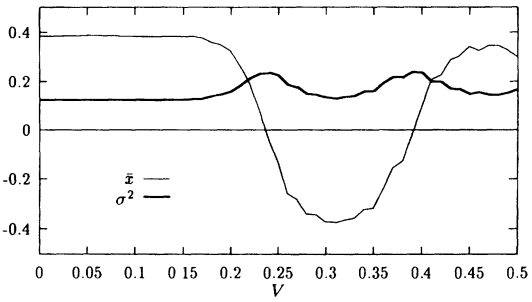

FIG. 3. Final average polarization $\bar{x}$ and variance σ^2 versus initial pulse velocity V, as in Fig. 1, but for a 400 × 400 system with temperature $k_BT = 4.5$.

and of the domain polarization, as expected. It is remarkable that, although the average energy added per particle is less than 1% of the thermal energy, the domain reversal threshold remains quite sharp and clear windows of alternating final polarization persist in Fig. 3. At this temperature, the width of the first energy window is comparable to the threshold energy $V_t^2/2$, so that a substantial fractional error can be tolerated in the applied pulse energy without seriously degrading the reliability of the domain reversal. Since the average energy per particle in our simulation is only increased by about 1%, the heating effect of a single pulse is small. In a material with many phonon branches, this heat is distributed over all modes and the temperature rise in the material is correspondingly reduced.

In the following, we estimate the energy of the optical pulse necessary to flip a domain. From the expression giving the change in energy density, $\delta U = -(\delta\chi/2)E^2$, one obtains the effective force per unit cell $F = (\partial\chi/\partial x)E^2$. Here, $\delta\chi$ is the susceptibility change due to the phonon displacement x and E is the electric field of the light. For pulse widths shorter than the phonon period, the velocity impulse is given by

$$V = \frac{\partial\chi}{\partial x}\frac{Pv_c}{2Mc}, \tag{3}$$

where P is the total pulse energy per unit area, v_c is the cell volume, M is the phonon effective mass, and c is the speed of light. Since domain reversal requires that $MV^2/2 \approx 0.01k_BT_c$, an estimate for P is

$$P_{\text{flip}} = \frac{\sqrt{8Mc^2k_BT_c}}{10v_c(\partial\chi/\partial x)}. \tag{4}$$

Values for $\partial\chi/\partial x$ can be obtained from measurements of the Raman scattering cross section. In the region of transparency, we find that $\partial\chi/\partial x \approx 0.1-10$ Å^{-1} [12]; this range is consistent with the relative reflectivity changes $\Delta R/R = 10^{-6}-10^{-2}$ observed in impulsive scattering experiments [1–3]. For typical values of the remaining parameters, we obtain the conservative estimate $P_{\text{flip}} \approx 0.01-1$ J/cm^2. Since standard femtosecond laser systems give pulse energies in the range $10^{-2}-10^3$ nJ and spot sizes are limited only by the diffraction limit, it appears that our mechanism should operate in a range accessible to experiments. We emphasize that the kinetic energy per particle required to flip a domain decreases with T, especially near the phase transition temperature T_c (see Fig. 3). In addition, we note that $\partial\chi/\partial x$ can be enhanced by using laser frequencies in the vicinity of the material's energy gap. These considerations suggest that experimental realizations of our proposal may be feasible at the lower end of available energies.

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Note added.—After this manuscript was accepted for publication, the authors became aware of a preprint by Nelson [13], where the reversal of ferroelectric domains by impulsive excitation of coherent phonons is also considered.

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