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One-dimensional behavior of ferroelastic domain arrays in neodymium pentaphosphate

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Domain structures in ferroelastic neodymium pentaphosphate NdP_5O_{14} of small *a* and *b* dimensions have been observed to be nearly periodic domain arrays of quasi-one-dimension sandwiched by parallel domain walls along the (001) lattice plane. Based on a continuous order-parameter profile along the wall normal, a positive temperature-dependent wall energy was obtained from Landau's theory of second-order phase transitions. Then a one-dimensional spin system, with the spins corresponding to the shear strains of the two orientation states of NdP_5O_{14}, has been developed to describe statistically the effect of thermal energy exciting the fluctuation of the wall number. The theoretical deductions were well consistent with the actual drastic increase of walls on approaching the phase transition temperature and the dynamical behavior of the domains in external stress fields.

I. INTRODUCTION

A great number of crystals discovered and synthesized in recent years have been shown to be ferroelastic (or coelastic) and the unique ability of these crystals to break into domains, which are usually switchable under the influence of mechanical stresses or temperature variation, has attracted many investigators' attention.[1-3] However, though many experimental observations of domain patterns are available, little theoretical work has been performed to understand the principles governing these patterns in the important class of ferroelastic materials.

In this class, neodymium pentaphosphate NdP_5O_{14} (NPP) is a pure ferroelastic crystal with two equivalent orientation states of opposite shear strains $\pm e_5$ (Voigt notation[4]) in the ferroelastic phase.[5] One of the remarkable characteristics of the ferroelastic domains is that they are often aligned as nearly periodic domain arrays in a systematic and repeatable way.[6] A typical domain array and its strain configuration are illustrated in Fig. 1, in which the two kinds of domain laminae are repeated alternatively at nearly equal intervals with the shear strain sequence of alternating signs.

In NPP crystals of small *a* and *b* dimensions, the domain patterns are strongly dependent on temperature. The temperature evolution of a domain array in a (010) wafer with dimensions of 2 mm (*a* dimension) by 0.5 mm (*b* dimension) by 8 mm is shown in Fig. 2. In the initial state at room temperature, the plate consists of only several domains. At $T > 350$ K, thin domain laminae begin to emerge from the thick domains with the wall intervals decreasing. When the temperature is raised further, the wall density increases drastically till the plate is filled with numerous thin domain stripes. It was observed that, although the local wall density fluctuates when T is very close to the Curie point T_c ($\simeq 417$ K), the average wall density distinguishable within the resolution limit in a polarizing microscope does not increase indefinitely but becomes saturated. At $T = T_c$, the walls disappear gradually as the crystal undergoes the second-order transition from monoclinic $P2_1/c$ to orthorhombic *Pncm*.

In Figs. 1 and 2, the walls running through the crystals are invariably parallel to the (001) lattice planes due to the strain compatibility condition between adjacent

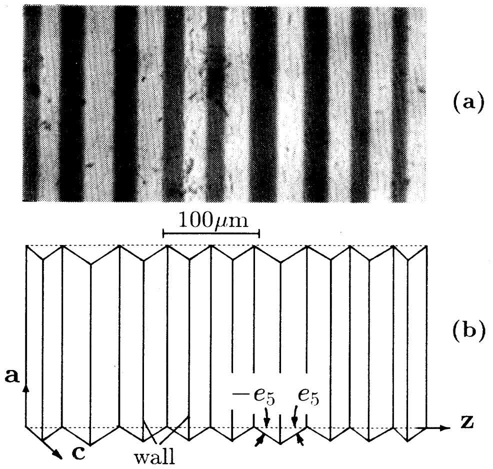

FIG. 1. A nearly periodic domain array consisting of *a*-type twins in a ferroelastic NPP plate [*b*-type twins with (100) walls rarely occur due to their higher interfacial energy than that of *a*-type ones]. (a) Domain pattern observed under a polarizing microscope; the domains are visible due to their birefringence. (b) Spontaneous strain configuration; strains e_5 ($\simeq 8.4 \times 10^{-3}$ at room temperature) exaggerated; twin relationship verified by synchrotron-radiation topography (Refs. 9 and 10).

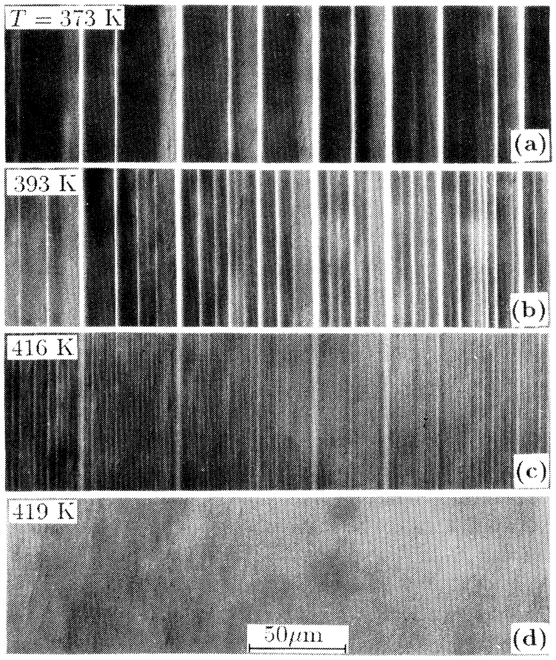

FIG. 2. Evolution of the domain array in NPP on heating. The number of domains increases with temperature from (a) to (c), and (d) is taken above T_c with all the domain walls annihilated.

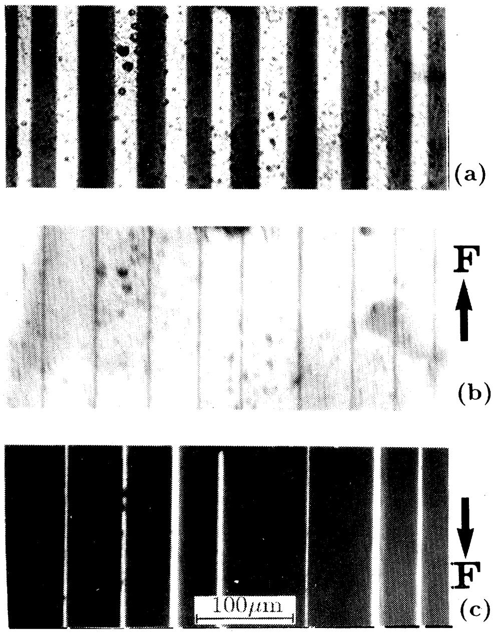

FIG. 3. Variations of the domain array caused by shear forces. (a) Initial state; (b) a positive shear force leading to the lateral growth of positive domains with white contrast; (c) the inverted force leading to the growth of negative domains with black contrast.

domains.[7–10] Therefore, these arrays are quasi-one-dimensional (1D) structures with the spontaneous strain varying only along the z axis, i.e., the direction of the wall normal. The 1D behavior is also characterized by the switching process of domains when mechanical stress ε_5 is exerted on the crystal. As shown in Fig. 3, the small shear force **F** acting on the (001) surface switches the domains in such a way that the walls move laterally along the normal of the wall to keep the 1D array structure.

Similar phenomena can also be observed in other rare-earth pentaphosphates,[11,12] but the mechanisms has not been appreciated completely. In this paper, we attempt to elaborate a 1D statistical model to decipher the interesting dynamical behavior of the domain arrays observed in NPP crystals.

II. 1D STATISTIC MODEL OF DOMAIN ARRAY

A. Domain wall energy

From experiments, it is inferred that the creation and annihilation of domain walls associated with the dynamical properties of domain arrays in rare-earth pentaphosphates are directly dependent on the wall structures and their interfacial energy. However, no systematic conclusions concerning the wall structures have been obtained since it is impossible for rare-earth pentaphosphates to be examined by the only available technique, high-resolution transmission electron microscopy (HRTEM),[3] due to the heavy electron-radiation damage. Here we employ the continuum theoretical modeling[13–15] of the order-parameter profile along the wall normal to obtain the wall energy of NPP.

From the structural viewpoint, the spontaneous strain e_5 can be considered as the order parameter in the second-order phase transition of NPP. Then for the 1D domain structure the free-energy density, added to a term $C[de_5(z)/dz]^2$ corresponding to the local nonuniform distribution of e_5 at the domain wall (see Fig. 1), is written as

$$F=F_0+A(T-T_c)e_5^2(z)+Be_5^4(z)+C\left[\frac{de_5(z)}{dz}\right]^2 , \tag{1}$$

where A, B, and C are positive constants. Minimizing the free energy F with respect to $e_5(z)$ yields the solitary-wave solution of the strain distribution of a wall located at $z=0$:

$$e_5(z)=e_5\tanh\left[\frac{z}{\delta}\right] , \tag{2}$$

where $e_5=[A(T_c-T)/B]^{1/2}$ is the spontaneous strain of a homogeneous crystal (the temperature dependence of e_5 has been verified in Ref. 10), and

$$\delta=\left[\frac{2C}{A(T_c-T)}\right]^{1/2} \tag{3}$$

is the wall thickness. From Eqs. (2) and (3) we can see that the strain changes from $-e_5$ to e_5 across the wall in a smooth way microscopically, which leads to a special structure of the domain wall deviating from the homogeneous crystal, as schematically shown in Fig. 4. In addition, the wall width δ diverges as the temperature approaches T_c.

Generally, the interfaces between different orientation domains are very narrow or even reduce to a single lattice plane from HRTEM observations and crystallographic descriptions.[3,16] So the continuous model of the walls in NPP is a theoretical assumption and has not been corroborated by any direct observations. However, some experimental phenomena in Sec. I may indirectly show the validity of the model: (i) the walls of NPP do not increase indefinitely but become saturated when the temperature approaches T_c, which may result from the divergence of the wall width (x-ray diffraction has shown that the wall width in KH_2PO_4 increases sharply as the transition point is approached from below[17]); (ii) the easy mobility of the walls under small shear stress $\varepsilon_5(\simeq 10^4$ Pa or less at room temperature) also indicates the definite wall width since wider boundaries are generally more mobile than sharp ones.[14]

Based on the continuous model, the interfacial energy density of a domain wall is then the energy deviation from the homogeneous crystal:

$$E_w=\int_{-\infty}^{\infty}\left\{A(T-T_c)[e_5^2(z)-e_5^2]+B[e_5^4(z)-e_5^4]+C\left[\frac{de_5(z)}{dz}\right]^2\right\}dx$$
$$=D(T_c-T)^{3/2}\,, \tag{4}$$

where $D>0$ is an integration constant dependent on A, B, and C. In Eq. (4), the wall energy vanishes asymptotically at $T\to T_c$. It can be seen that during the transition process there always exists a temperature point T_f where the energy of a wall is equal to the thermal energy: $SD(T_c-T_f)^{3/2}=k_BT_f$ (S is the wall area). Above T_f, we have $SD(T_c-T)^{3/2}<k_BT$ and then the fluctuation of domain walls is possible.

B. 1D spin system

The ability of NPP to split into nearly periodic 1D domain arrays at temperature close to T_c (with the periodicity of the arrays in different samples being almost the same) shows that the crystal can be treated as a 1D "spin system" consisting of thin domain lamina of opposite shear strains. Consider a NPP bar with small a and b dimensions. We divide it into a great number of discrete thin domain laminae with the lamina surfaces lying in (001) lattice planes, and term each lamina a *domain unit.* By further assuming that all the domain units have the same thickness, they line up along the c axis into a periodic *domain lattice* in the bar, as shown in Fig. 5. In this 1D domain lattice, the spontaneous strain of each domain unit can be written as se_5 where s is either 1 or -1. When two neighboring domain units have opposite senses of spontaneous strains, they interact by forming a domain wall separating them; otherwise, there is no interaction and they form a thicker domain lamina. Thus the domain lattice has a nearest-neighbor interaction equal to the (temperature-dependent) wall energy.

From the continuous picture of the wall (see Fig. 4), the domain lattice constant d, the thickness of the domain unit, must be not less than the wall width which is greater than the crystal lattice constant. Usually we can choose the width of the thinnest domain lamina possibly existing in NPP at any temperature below T_c as the domain lattice constant.

Then for the system containing N domain units ($N=L/d$ where L is the length of the bar), the Hamiltonian corresponding to the domain wall energy with no external force applied is

$$H=SE_w\sum_{i=1}^{N-1}\tfrac{1}{2}(1-s_is_{i+1})\,, \tag{5}$$

where S is the cross-sectional area of the bar. Equation (5) is very similar to the 1D Ising model of a ferromagnet[18] except that the interaction energy density E_w between two domain units of opposite strain senses is dependent on temperature (stemming from the variation of spontaneous strain with temperature), i.e., it decreases as $|T-T_c|^{3/2}$.

The partition function of this 1D domain lattice is easily obtained as

$$Q=\sum_{s_1=\pm1}\sum_{s_2=\pm1}\cdots\sum_{s_N=\pm1}\exp(-\beta H)$$
$$=[1+\exp(-\beta SE_w)]^N\,, \tag{6}$$

where $\beta=(k_BT)^{-1}$. Differentiating Q with respect to β, we obtain the total energy of the walls:

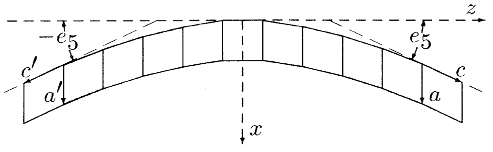

FIG. 4. Schematic picture of a coherent domain wall in NPP indicating the continuous profile of the spontaneous shear strain along the wall normal.

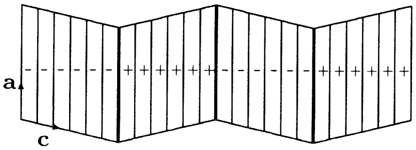

FIG. 5. Schematic representation of division of a NPP bar into a 1D domain lattice, the signs "+" and "−" indicating spontaneous strain senses of domain units and heavy lines representing domain walls.

$$E=-\frac{\partial \ln Q}{\partial \beta}=\frac{NSE_w}{1+\exp(\beta SE_w)} \ . \tag{7}$$

Therefore, the average number of walls in the system is

$$n_w=\frac{E}{SE_w}=\frac{N}{1+\exp(\beta SE_w)}$$
$$=\frac{N}{1+\exp[SD(T_c-T)^{3/2}/k_BT]} \ , \tag{8}$$

As a result of the model, the number of walls increases monotonically as temperature increases.

Figure 6 shows two calculated curves from Eq. (8) together with a set of experimental data of the average density of domain observed in a (010) NPP wafer. From the two curves, we can see that the evolution process is also dependent on the value of the wall area S. For small S, the energy for creating a wall running through the bar is small, and fluctuation of domains can occur in a wide temperature range. When S is larger (corresponding to the macroscopic dimensions of the crystals in the experiments), the wall energy directly proportional to S also becomes larger, and consequently creation of walls is only excited at higher temperature by the higher thermal energy k_BT. It can be seen that the theoretical curves for the larger magnitude of S are consistent with the experimental results.

Equation (8) also leads to $n_w \rightarrow N/2$ which is independent of S in the limit $T \rightarrow T_c$. In reality, when T approaches T_c, the spontaneous strain e_5 tends to be zero, and the difference of two adjacent domain units with opposite strains, hence, becomes very small. Correspondingly, the probability for two adjacent domain units to have opposite strains tends to the probability for them to have the same sign of strains, i.e., they approach $\frac{1}{2}$ from below and above, respectively. Thus numerous domain laminae are bound to emerge from the crystal and form periodic arrays in the temperature range close to T_c, even in the case that the a and b dimensions are very large. At $T=T_c$, the crystal becomes orthorhombic and the walls disappear, so the number of walls $n_w=N/2$ loses it physical meaning.

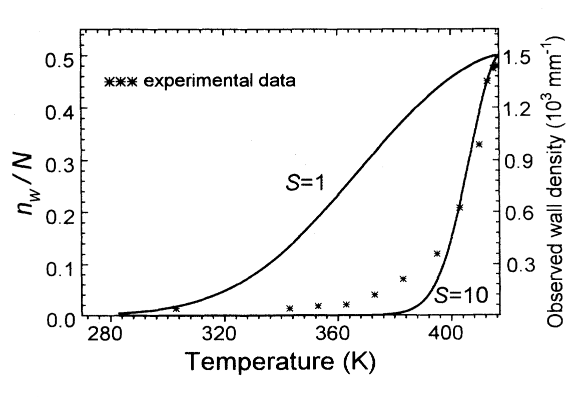

FIG. 6. Temperature dependence of the average number of domain walls. Experimental data were measured in a NPP crystal with dimensions of 2 mm (a dimension) ×0.5 mm (b dimension) ×8 mm during the phase transition process; theoretical curves were calculated from Eq. (8) with $D/k_B=1$.

It should be noted that in the above model the dynamical behaviors of domain arrays are inferred to result from the existence of a positive wall energy and from the effect of thermal energy "populating" excited states of the 1D system (i.e., an effect of increasing entropy). This picture would therefore be different from the situation in ferromagnets in which the domain pattern is determined energetically by the balance between the wall energy and the magnetic energy of the sample surface. The latter energy is decreased by the multiplication of domains[19] (the surface effect is also significant in ferroelectrics[20]). But for pure ferroelastics the spontaneous strains do not produce any charges on the surface, so we assume that the surface effect in NPP is absent or can be neglected. Actually, no investigation has indicated the existence of a similar surface with special structure deviating from the bulk crystal of ferroelastics.

III. INFLUENCE OF STRESSES ON THE 1D SYSTEM

Since the domain arrays in NPP crystals are easily alterable by small external stresses, we must pay attention to the situation that the 1D spin system is put in external stress fields. From the experiments we have demonstrated that the domain arrays maintain their 1D structure in spite of the lateral movements of wall when mechanical stresses are applied. Therefore, we still can consider the crystal in external stress fields as a 1D domain lattice, but the system's Hamiltonian must include the coupling energy between the strains and the stresses in the limit of linear theory of elasticity:[2] $-\sum \varepsilon_i e_i$ $(i=1,2,\ldots,6)$. For simplicity, we discuss the case that only a homogeneous shear stress ε_5 is applied on the system.

For small ε_5, the coupling energy density, or rather the potential of the domain unit in the stress field, is $-\varepsilon_5 s e_5$. Then by taking into account this coupling the system's Hamiltonian at $S=1$ can be written as

$$H=\frac{E_w}{2}\sum_{i=1}^{N-1}(1-s_is_{i+1})-\varepsilon_5 e_5\sum_{i=1}^{N}s_i \ . \tag{9}$$

The partition function is derived to be

$$Q=\{\cosh(\beta\varepsilon_5 e_5)+[\sinh^2(\beta\varepsilon_5 e_5)$$
$$+\exp(-2\beta E_w)]^{1/2}\}^N \ . \tag{10}$$

The energy of the system is, therefore, obtained in the form

$$E=-\frac{\partial \ln Q}{\partial\beta}=-\frac{N\varepsilon_5 e_5\sinh(\beta\varepsilon_5 e_5)}{[\sinh^2(\beta\varepsilon_5 e_5)+\exp(-2\beta E_w)]^{1/2}}+\frac{NE_w\exp(-2\beta E_w)}{\cosh(\beta\varepsilon_5 e_5)[\sinh^2(\beta\varepsilon_5 e_5)+\exp(-2\beta E_w)]^{1/2}+\sinh^2(\beta\varepsilon_5 e_5)+\exp(-2\beta E_w)}\ . \tag{11}$$

The total energy in Eq. (11) contains two kinds of energy: one if the wall energy, and the other is the coupling energy between the spontaneous strain and the stress. Since the average spontaneous strain of each domain unit is

$$\langle e_5\rangle=\frac{e_5}{N}\sum_{i=1}^{N}s_i=\frac{1}{N\beta}\frac{\partial\ln Q}{\partial\varepsilon_5}=\frac{e_5\sinh(\beta\varepsilon_5 e_5)}{[\sinh^2(\beta\varepsilon_5 e_5)+\exp(-2\beta E_w)]^{1/2}}\ , \tag{12}$$

the coupling energy $-N\varepsilon_5\langle e_5\rangle$ of the system is the first term at the right side of Eq. (11). Correspondingly, the second term is the total wall energy, and then the number of domain walls under the influence of ε_5 is

$$n_w=\frac{N\exp(-2\beta E_w)}{\cosh(\beta\varepsilon_5 e_5)[\sinh^2(\beta\varepsilon_5 e_5)+\exp(-2\beta E_w)]^{1/2}+\sinh^2(\beta\varepsilon_5 e_5)+\exp(-2\beta E_w)}\ . \tag{13}$$

It is apparent that Eq. (13) turns into Eq. (8) at zero stress. Also, we have $\langle e_5\rangle=0$ at $\varepsilon_5=0$ from Eq. (12) since the probability for each domain unit to possess positive strain (up-spin, $s=1$) or negative strain (down-spin, $s=-1$) is $\frac{1}{2}$ under this condition.

From Eq. (13) we can see that the average strain $\langle e_5\rangle$ increases with the increase of the stress ε_5. Meanwhile the average wall density n_w decreases monotonically, as illustrated in Fig. 7. In the range of small ε_5, however, there is a remarkable contrast between the behaviors of $\langle e_5\rangle$ and n_w: $\langle e_5\rangle$ rises drastically while n_w declines slightly as ε_5 is increased. In fact, as the applied stress ε_5 of positive sign is increased, more domain units of negative strain are switched to the positive-strain state, which leads to the increase of $\langle e_5\rangle$. At the same time, the applied stress ε_5 of small magnitude can hardly influence the wall number but moves the wall laterally and modulates the structure of the domain array, just as demonstrated in Fig. 3.

At extremely large ε_5, we have $\langle e_5\rangle=e_5$ and $n_w=0$ from Eq. (13). This means that the whole crystal is switched to a single-domain state with all the walls annihilated.

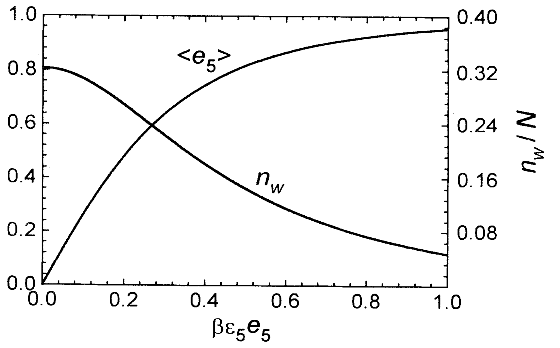

FIG. 7. Shear stress dependences of the domain wall number and the average spontaneous strain $\langle e_5\rangle$ with $\beta E_w=1$.

IV. DISCUSSION

Based on the fact that the domain array in NPP crystal consists of 1D structures along the [001] direction with the walls separating consecutive domains, and by dividing the crystal into a 1D domain lattice with each domain unit having an up- or down-spin (corresponding to the positive or negative sign of spontaneous shear strains), we have designed a 1D spin model (with the spins corresponding to the shear strains of the two orientation states of NPP) to describe statistically the dynamical behavior of the domain arrays during the second-order ferroelastic phase transition, i.e., the rapid decrease of the distance between domain walls on approaching the transition temperature. However, the application of this model is usually limited to the case that crystal dimensions along both the *a* and *b* axes are made small so that the walls running through the crystals have small interface dimensions and can be easily aligned to a 1D wall array.

For large crystals, however, there may be some discrepancies and inconsistencies between the experiments and the above theories. First, internal stresses are usually constrained within these crystals on cooling down after growth, so that real domain configuration may be complicated. For instance, tapered domains terminating inside the crystals and even *b*-type twins (whose formation energy is very high) can be observed in these crystals due to the internal stresses. In these cases, the crystals cannot be considered as 1D structures. Second, planar walls running through a crystal of great dimensions along the *a* or *b* axis have large interfacial area, and consequently the energy of each wall is very large. This large wall energy makes it hard for the walls to form a 1D structure, or to obey the statistical mechanics strictly. Examples have been described in Ref. 6, where a special pattern of shear stress exerted on a NPP plate of 10 mm in the *a* dimension caused bubble domains and tapered domains in he crystal rather than moving the walls laterally.

Another point which should be emphasized is that in our model we have neglected the influence of elastic energy. In a homogeneous stress ε_5, the elastic energy induced by the stress can be separated from the Hamiltonian of Eq. (9). For other stresses, however, the interaction between the order parameter and the stress-induced elastic strains cannot be neglected.[14] For example, the coupling between the spontaneous strain e_5 and the normal elastic strain e_1, e_2, or e_3 can lead to significant variations of domain structures when the corresponding compression acts on the (100), (010), or (001) plane of NPP or $Nd_xLa_{1-x}P_5O_{14}$.[12] The detailed description of this coupling needs further development of the above theories.

In a word, the statistical model constructed in this paper reveals the intrinsic mechanisms of the switching process of domain arrays in NPP. Furthermore, domain arrays can occur in many ferroic crystals,[21,22] and the results obtained from this model may be quantitatively of generality for other continuous ferroelastic phase transitions as long as the wall energy decreases asymptotically to zero towards the Curie point T_c. For crystals whose transitions are of first order,[2] there is usually a cutoff of the order parameter around the transition temperature, which indicates that the wall energy associated with the parameter becomes zero discontinuously from below. So the dynamical properties of the domain arrays in these substances are seldom observed.

ACKNOWLEDGMENTS

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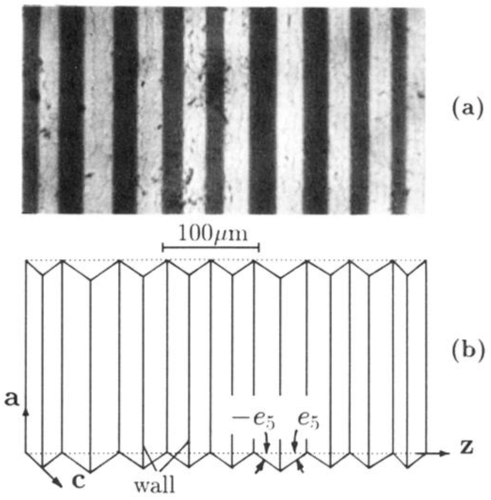

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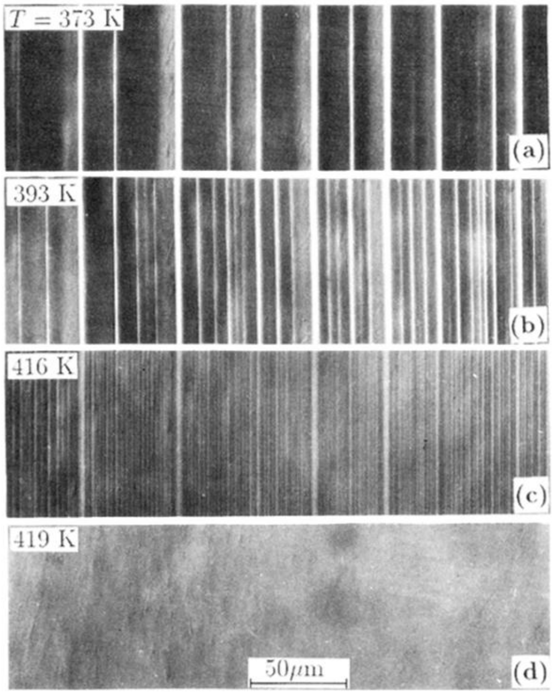

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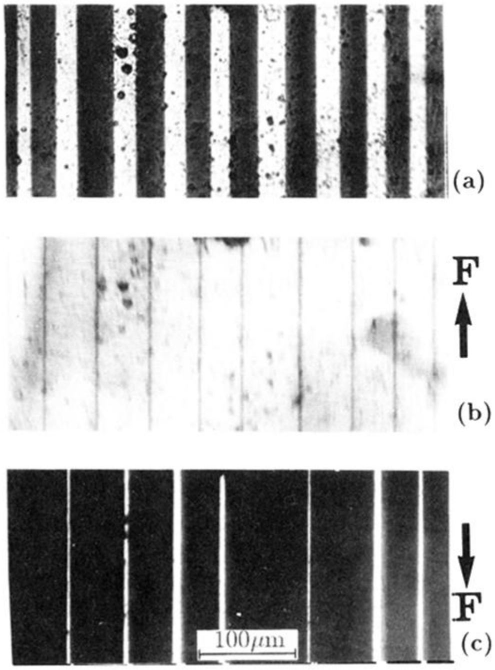

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