

Supercooled plastic crystals as frustrated elastic domains: Phenomenological theory for cyanoadamantane-family crystals

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A cubic crystal with orientationally disordered molecules, which mimics a plastic crystal of the cyanoadamantane family, under conditions of supercooling has been assumed to evolve into the metastable tetragonal phase as suggested by Ostwald's "law of stages." Representing small domains of local tetragonal structures by elastic dipoles, we have analyzed orientational relaxation of the grains embedded in an isotropic elastic medium. The elastic dipole density-density correlation function has been used to discuss a possible ordering of the domains. Implications of the model for elastic properties, diffuse scattering, and kinetics of the transformation of the supercooled plastic crystal have been discussed. The paper offers a contribution to the discussion on how glassy are the molecular crystals with orientational disorder.

INTRODUCTION

Molecular crystals are known for their rich polymorphism due to rotational and intramolecular degrees of freedom. Structures governed by the closest-packing principle result in the formation of a multim minima (free) energy surface. The stability or metastability of the structures is decided then by kinetics of corresponding nonequilibrium transitions. A supercooled stable structure may result in a metastable state, which is not necessarily an ordered one. Orientationally disordered (plastic) molecular crystals have been found to be particularly sensitive for such a transformation and they form solids with frozen molecular orientations, after quenching. The state is glasslike, and the solids are called "glassy crystals."¹ Among them, ethanol² and cyanoadamantane and its mixed crystals (cyanoadamantane family)³ have been found to be model systems. The main advantage of studying the glassy state behavior in plastic crystals is that, contrary to conventional glasses, the systems keep translational symmetry. On the other hand, this causes similarity between the orientationally disordered state and a glassy state to such an extent that the question, how glassy are plastic crystals,⁴ has to be addressed. In any case, often perfect single crystals of the orientationally disordered phases allows for detailed structural and kinetic studies, which give us an insight into the metastability of molecular systems, the important problem within the molecular materials.

The glassy crystals of the cyanoadamantane family have been objects of extensive studies for many years. Although significant progress has been achieved in understanding the transformations,⁵ a detailed picture of molecular and mesoscopic structures of the glassy state is still missing. The glassy phase is obtained when the rotationally disordered cubic phase is supercooled after deep quenching, close to a glass transition temperature (T_g), Fig. 1. The crystal keeps its cubic symmetry, but local structures are different; the system is evidently in a metastable state. Structural data are difficult to interpret consistently, although there are some signatures indicating that in a quenched sample there is an ordering process going on. It is not, however, an ordering according to

the pattern of the stable, low-temperature monoclinic phase. The scattering data seems to indicate a local tetragonal structure.^{5,6} In the process of an ordering of the supercooled, metastable phase, a growth of superstructure peaks at the X boundary point of the Brillouin zone indicates a slow ordering of the molecules in an antiferroelectric pattern. Correlation length for the ordering has been estimated to be about two lattice distances. In addition, some signatures of an ordering have been observed at the zone center Γ points. With time, there is an increase in diffuse components together with a decrease of the Bragg peaks.^{5,6} From the experiments, it has been concluded that the parallel evolution of Bragg peaks at the Γ points and superstructure peaks at X points have a common origin and that an ordering which appears below T_g develops in coherence with the parent, plastic phase.

How one can imagine a structure in the supercooled plastic phase? The simplest physical picture which appears from the observations suggest an ordering process at two levels. First, at a molecular level, the steric hindrance and dipolar interaction prefer to form antiferroelectric, local order. Such an order causes tetragonal distortion to the cubic lattice. Indeed, the experiments performed on the quenched crystals,⁵⁻⁷ could be best interpreted in terms of a local tetragonal structure. As it has to evolve from a deeply quenched orientationally disordered state, the antiferroelectric order appears at rather short distances and small tetragonal domains are formed. (There are some indications that the domains may have an orthorhombic structure,⁸ but this is a small distortion and we shall assume them as tetragonal.) They are oriented along the cube main axes, orientations preferred by the molecules in the disordered phase. A growth of a domain requires large reorientations of molecules and for the reason of steric hindrance none of the domains can grow at the expense of the others and a monodomain phase of tetragonal symmetry cannot be formed. It is postulated that there exists a locally preferred tetragonal structure that cannot be extended throughout space. This is a kind of frustration that leads to the "frustration-limited domain" formation, analogous to the situation in supercooled molecular

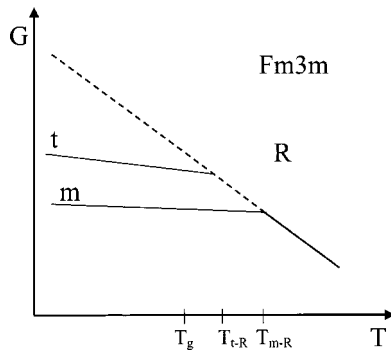


FIG. 1. Commonly used, schematic diagram (free enthalpy and temperature) of thermodynamical stabilities of plastic (R), monoclinic (m), and tetragonal (t) phases for cyanoadamantane family crystals. T_g indicates a transition into the glassy state.

liquids.⁹ As a result, the state of the supercooled plastic crystal of the cyanoadamantane family, at least at the beginning of the annealing process, consists of very small tetragonal domains with antiferroelectric local order. The time evolution of such a state towards a more stable structure proceeds as a (limited) growth of domains, seen as antiferroelectric ordering (monitored by the superlattice reflections) and ordering of the domains (monitored by the diffuse scattering at the Γ -points Bragg peaks).⁶ Thus, at a mesoscopic scale one may see the supercooled plastic crystal as a powder of frustrated tetragonal domains. Recently, some insight into a molecular structure of possible metastable states has been obtained;⁸ here we shall address the problem of ordering at the mesoscopic level.

At a molecular level, in the orientationally disordered, high-temperature cubic phase, a molecule is in one of six ‘‘pocket states.’’ Neglecting an orientational distribution, a molecule can be represented as a superposition of six electric dipoles, oriented along the cube axes. In the quenched, supercooled state, the dipoles tend to form small regions with antiferroelectric order and local tetragonal symmetry. Such regions cause stress to the host cubic lattice, which we shall consider as a main effect. Dipolar electrostatic interaction between the domains will be neglected. Thus, at the mesoscopic scale, a grain is represented as a superposition of three elastic dipoles, representing three tetragonal domains oriented along the main axes of the cube, x , y , and z . The domains interact via the elastic field of the host crystal. The frustration in the system is seen as a competition between short-range antiferroelectric coupling and long-range elastic interaction between the domains. We model the supercooled crystal as an elastic medium with embedded tetragonal ‘‘defects,’’ representing the domains. It has to be stressed that the notion of isolating these defects at the microscopic level in a real system is, in general, not well defined. One may ask what is the defect and what is the medium? It is especially important for coherently embedded defects. Thus, the model we want to develop can only be used in a phenomenological approach. We want to find the energetics and spatial correlation of the domains, expecting that it might help to understand a mesoscopic structure and ordering in the supercooled crystal, also that it might be related to the diffuse scattering observed around the Bragg peaks close to a transition into the glassy phase.^{5,6} An intuitive picture that the glassy state

of the cyanoadamantane family can be treated as a composition of different domains,¹⁰ and that elastic effects are important,⁵ have already been suggested. Here we shall bring this intuition into a model.

FORCE DISTRIBUTION AROUND A FROZEN MOLECULE; ELASTIC DIPOLES

We are concerned with a crystal of the cyanoadamantane family in the vicinity of the glass transition temperature. It is a cubic crystal, supercooled below the temperature of the transformation cubic tetragonal (see Fig. 1). The crystal is in a highly metastable state and evolves, as the experiments show,⁵ not towards its most stable structure, the monoclinic one, but rather to the tetragonal (called phase IV in Ref. 5) phase. We believe that this is merely a kinetic effect resulting from a competition of transformation rates. Guided by this assumption, we assume that an evolution of supercooled plastic crystals, quenched near the glass transition temperature, proceeds via a formation of (slightly) lower-symmetry local structures, tetragonal domains. A change into the thermodynamically stable monoclinic phase requires much more drastic structural rearrangement and this is, we believe, the reason for the apparent stability inversion.⁷ Thus, in the simplest model approach, we shall assume that the supercooled cubic crystal contains three types of tetragonal domains.

Since the main effect of formation of tetragonal domains in the cubic crystal, Fig. 2, is the local stress, we shall represent the domains by three ($\alpha = x, y, z$) elastic dipoles, oriented along the cube main axes (x, y, z) and given by tensors

$$\mathbf{P}^\alpha = P_s \mathbf{1} + P_0 \mathbf{D}^\alpha. \quad (1)$$

$P_s = (2B + A)/3$ is the isotropic, spherical part which plays a role of local pressure, and $P_0 = (A - B)/3$ is the anisotropic, deviatoric part with deviators $\mathbf{D}^\alpha = \{D_{11}^\alpha\} = \{2, -1, -1\}$. The elastic dipoles, representing diagonal stresses, can be considered as three-dimensional vectors $\mathbf{P}^\alpha = [P_{11}, P_{22}, P_{33}]$, and it might be convenient to treat deviatoric tensors as vectors.

There can be a more microscopic picture behind the elastic dipoles which represent the tetragonal domains. Let us imagine the formation of a local stress in the cubic crystal of the cyanoadamantane family. Deep undercooling of the orientationally disordered phase results in the freezing of a molecule in one of six ‘‘pocket states,’’ located along the main axes of the cube, Fig. 2(a). The freezing causes extra forces, $\mathbf{V}(\mathbf{R})$, acting on the surrounding molecules located at sites \mathbf{R} , apart from the frozen molecule. Assuming such a picture [Fig. 2(b)] we calculate the forces exerted by the nearest neighbors. For example, for the frozen orientation along z axis, the forces acting on the neighbors located in (001) plane are different from those acting on the neighbors above and below the plane. Moreover, there is an asymmetry in the forces acting above and below the plane due to the dipolar nature of the cyano(chloro)adamantane molecule. This causes a net excess force acting on the frozen molecule and is compensated by a displacement (assumed small) along the axis of the frozen orientation.

The distribution of forces around a frozen molecule is conveniently represented by force multipoles.¹¹ For a molecule in orientation α , the first nonzero multipole is the elastic dipole, defined as

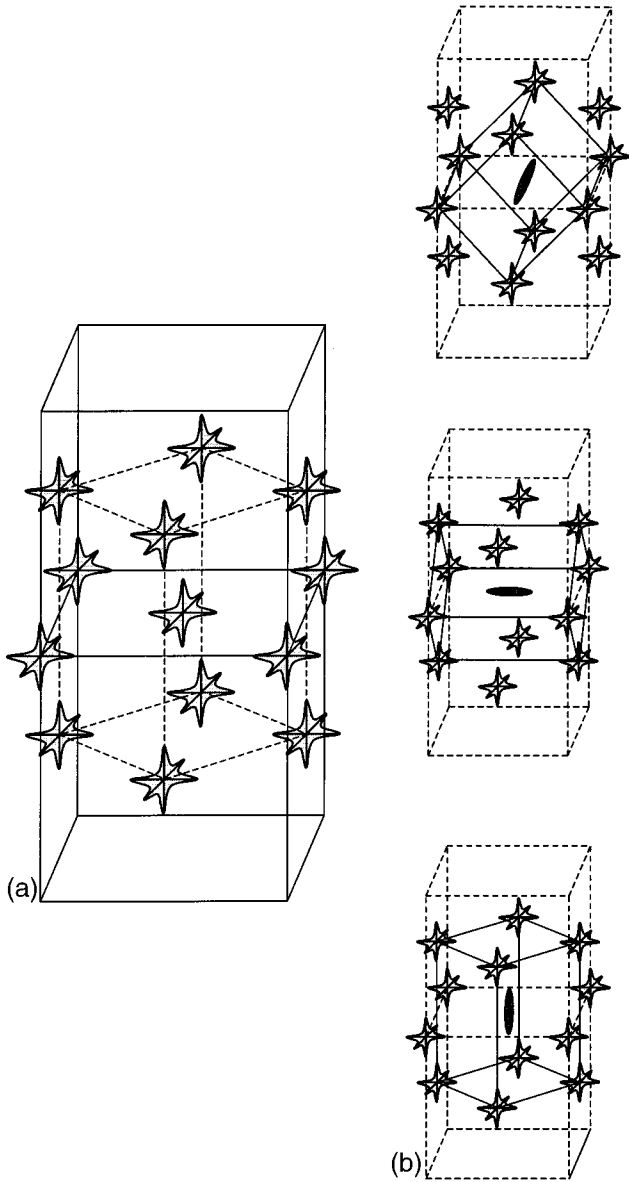


FIG. 2. (a) Illustration of the plastic crystal of cubic $Fm\bar{3}m$ symmetry with orientationally disordered molecules represented as six “pocket states.” Broken lines indicate a cell that becomes a unit cell in the tetragonal phase. (b) Visualization of three elastic dipoles, as molecules with frozen orientations along x , y , and z . For the stress representation caused by the fixed orientation, there is no distinction between opposite orientations along an axis. Tetragonal symmetry of the local stresses is indicated by the solid lines of a unit cell.

$$P_{ij}^{\alpha} = (1/2v) \sum_{\mathbf{R}} [V_i^{\alpha}(\mathbf{R})R_j + V_j^{\alpha}(\mathbf{R})R_i], \quad (2)$$

where v is the unit-cell volume and the summation is, in principle, over all neighbors that experience the extra forces. The elastic dipole representation of the force distribution is a convenient way to specify a local stress. In more detailed calculations, however, one should use the forces to characterize the frozen molecule or a grain of frozen molecules. It is convenient to express the excess forces by the Fourier transform,

$$\mathbf{V}^{\alpha}(\mathbf{q}) = N^{-1} \sum_{\mathbf{R}} \mathbf{V}^{\alpha}(\mathbf{R}) \exp(i\mathbf{q}\mathbf{R}). \quad (3)$$

When combined with Eq. (2) the forces can be expressed in terms of the elastic dipoles. For the molecule frozen in orientation $\alpha = z$ [Fig. 2(b)], taking into account only nearest neighbors, the forces are

$$V_1^z(\mathbf{q}) = 2Ba^2i \sin \varphi_x \cos \varphi_y, \quad (4a)$$

$$V_2^z(\mathbf{q}) = 2Ba^2i \sin \varphi_y \cos \varphi_x, \quad (4b)$$

$$V_3^z(\mathbf{q}) = Aa^2i \sin \varphi_z (\cos \varphi_x + \cos \varphi_y), \quad (4c)$$

where the angles $\varphi_{\alpha} = 1/2q_{\alpha}a$ are expressed in terms of the wave-vector components q_{α} , and the lattice constant for the $Fm\bar{3}m$ structure a . Parameters A and B specify the elastic dipole strength, Eq. (1). The force components for other orientations of a frozen molecule can be obtained from the above formula by appropriate permutation of the axes. In the long-wavelength (elastic) limit, $\mathbf{q} \rightarrow 0$, we find

$$V_i^z(\mathbf{q} \rightarrow 0) = iv P_{ii}^z q_i, \quad (5)$$

and this (continuum) approximation will be used in the paper. In the next step, we shall analyze a distribution of the centers of local stresses, considered as tetragonal domains. There is no clear distinction between a small domain and a frozen molecule, as there is complete coherency between the tetragonal defects and the matrix. Thus we shall use the terms “domain” and “local stress center” as synonyms, to indicate just a center of elastic interaction.

LOCAL EQUILIBRIUM AND DENSITY FLUCTUATION OF ELASTIC DIPOLES

Density of the domains at point \mathbf{x} in the system is denoted as $\rho_0(\mathbf{x})$. Here we use the symbol \mathbf{x} to locate a center of a local stress and in case of a frozen molecule this will be equivalent to \mathbf{R} , while for (slightly) larger domains it will indicate the location of a center of a tetragonal grain. The crystal we are considering as a powder of domains is in a metastable state (nonergodic), therefore we assume a local thermodynamic equilibrium. Density of domains of type α is given as

$$\rho_{\alpha}(\mathbf{x}) = \rho_0(\mathbf{x}) \left\{ \exp[-\beta E_{\alpha}(\mathbf{x})] / \sum_{\alpha} \exp[-\beta E_{\alpha}(\mathbf{x})] \right\}, \quad (6)$$

where $\beta = 1/kT$. $E_{\alpha}(\mathbf{x})$ is the energy of interaction of the domain in orientation α with the surrounding field formed by a distribution of domains. The essence of our model is that the energy is assumed to be purely elastic and determined by the coupling of the excess force to a displacement \mathbf{u} ,

$$E_{\alpha}(\mathbf{x}) = -\mathbf{V}^{\alpha}(\mathbf{x})\mathbf{u}(\mathbf{x}) = -V_i^{\alpha}(\mathbf{x})u_i(\mathbf{x}), \quad (7)$$

and summation over repeated indices is assumed through the paper. The displacement at the site is partitioned into a homogeneous part, expressed in terms of the strain tensor ε and inhomogeneous part $\mathbf{w}(\mathbf{x})$,

$$u_i(\mathbf{x}) = \varepsilon_{ij}x_j + w_i(\mathbf{x}). \quad (8)$$

The inhomogeneous part is caused by the elastic coupling $G_{ij}(\mathbf{x}, \mathbf{x}')$ between stress centers,

$$W_i(\mathbf{x}) = \sum_{\mathbf{x}'} G_{ij}(\mathbf{x}, \mathbf{x}') v_j(\mathbf{x}'), \quad (9)$$

where

$$v_j(\mathbf{x}') = \sum_{\alpha} V_i^{\alpha}(\mathbf{x}') [\rho_{\alpha}(\mathbf{x}') - \rho_0(\mathbf{x}')/3] \quad (10)$$

is the density of the excess forces at site \mathbf{x}' . The elastic coupling, which in terms of elementary excitations is a virtual phonon exchange, will bring a correlation between the local stresses and cause domains density fluctuation.

To proceed with the analysis, let us assume, that the excess forces around a tetragonal “defect” are well represented by the elastic dipoles, local stress tensors, as specified above. Within this approximation, the elastic energy gain experienced by the domain located at \mathbf{x} is

$$E_{\alpha}(\mathbf{x}) = -\mathbf{P}^{\alpha} \boldsymbol{\varepsilon}(\mathbf{x}) = -P_{ij}^{\alpha} \varepsilon_{ij}(\mathbf{x}), \quad (11)$$

and for simplicity, the elastic dipole has been assumed to be independent on a site. This constrain is not essential for the description. $\boldsymbol{\varepsilon}(\mathbf{x})$ is the effective strain tensor acting at the site \mathbf{x} . It is, in general, a sum of macroscopic uniform strain, $\boldsymbol{\varepsilon}$, and the local, inhomogeneous strain due to surrounding elastic dipoles. Thus

$$\varepsilon_{ij}(\mathbf{x}) = \varepsilon_{ij} + \sum_{\mathbf{x}' \neq \mathbf{x}} K_{ijlm}(\mathbf{x}, \mathbf{x}') p_{lm}(\mathbf{x}'). \quad (12)$$

The local strain is expressed by the elastic strain field, $K_{ijlm}(\mathbf{x}, \mathbf{x}')$, and the density of elastic dipoles at site \mathbf{x}' , $p_{lm}(\mathbf{x}')$,

$$p_{lm}(\mathbf{x}') = \sum_{\alpha} \delta\rho_{\alpha}(\mathbf{x}') P_{lm}^{\alpha}. \quad (13)$$

The fluctuation in the elastic dipole density,

$$\delta\rho_{\alpha}(\mathbf{x}) = \rho_{\alpha}(\mathbf{x}) - \rho_0(\mathbf{x})/3, \quad (14)$$

or equivalently, the density of elastic dipoles, Eq. (13), is the key parameter. It determines local order and may serve as the *local order parameter*. Let us observe that in an orientationally disordered state, $\delta\rho_{\alpha}(\mathbf{x}) = 0$, at every site, while in the state with a local order, $\delta\rho_{\alpha}(\mathbf{x}) \neq 0$. The local order indicates a random freezing of the elastic dipoles, characteristic for the glassy state of supercooled plastic crystal. As follows from Eq. (13), such random freezing gives rise to a static local stress, described by the elastic dipole density. The density fluctuation is, therefore, a proper parameter to characterize the glassy state. Indeed, it is related to the three-states Potts model variable, used for orientational glasses,¹² $s_{\alpha}(\mathbf{x}) = n_{\alpha}(\mathbf{x}) - 1/3$, where $n_{\alpha}(\mathbf{x})$ is 1 if the site is occupied by the domain in orientation α . Thus, the equivalence, $\delta\rho_{\alpha}(\mathbf{x}) = \langle s_{\alpha}(\mathbf{x}) \rangle$, is evident.

From the local equilibrium condition, Eq. (6), with the assumption that the elastic energy is smaller than the thermal energy, we find the density fluctuation

$$\delta\rho_{\alpha}(\mathbf{x}) = -\beta\rho_0(\mathbf{x})/3 \left[E_{\alpha}(\mathbf{x}) - \frac{1}{3} \sum_{\alpha} E_{\alpha}(\mathbf{x}) \right]. \quad (15)$$

It is an interpretation of the local order parameter in terms of energy competition. On introducing Eq. (11) into (15) one obtains an elastic dipole density fluctuation as a response to a homogeneous, macroscopic strain,

$$\begin{aligned} \delta\rho_{\alpha}(\mathbf{x}) &= \beta\rho_0(\mathbf{x})/3 \left[P_{ij}^{\alpha} - \frac{1}{3} \sum_{\alpha} P_{ij}^{\alpha} \right] \varepsilon_{ij}(\mathbf{x}) \\ &= \beta\rho_0(\mathbf{x})/3 [P_{ij}^{\alpha}(\text{dev})] \varepsilon_{ij}(\mathbf{x}), \end{aligned} \quad (16)$$

where $P_{ij}^{\alpha}(\text{dev}) = [P_{ij}^{\alpha} - \frac{1}{3} \sum_{\alpha} P_{ij}^{\alpha}]$. In case of the *local* thermodynamic equilibrium, only the deviatoric part of the elastic dipoles, $P_{ij}^{\alpha}(\text{dev})$, causes the density fluctuation. This is known as orientational elastic relaxation.¹³ It is important in the context of supercooled plastic crystal, treated as a powder of domains, because the crystal is a nonergodic system. Thus, local stresses which appear at a glassy state of plastic crystals may cause an orientational relaxation rather than diffusional elastic relaxation.¹⁴ The orientational relaxation is a source of *intrinsic frustration* and may be responsible for the kinetic aspect of a formation of the glassy crystal.

FLUCTUATION DENSITY CORRELATION

The density fluctuation expressed in Eq. (16) shows a self-consistent dependence via the local strain field, coupled to the elastic dipole density, Eqs. (12) and (13). For this inter-relation it is important to specify the elastic strain field, the coupling, $K_{ijlm}(\mathbf{x}, \mathbf{x}')$. As it follows from the elasticity theory,¹¹ the coupling is conveniently expressed as the Fourier transformation of corresponding elastic Green's function, $G_{ijlm}(\mathbf{q})$. In order to take into account correlation between sites and exclude self-deformation of a site, $K_{ijlm}(\mathbf{x} = \mathbf{x}') = 0$, the transformation is formulated as follows:¹⁵

$$\begin{aligned} K_{ijlm}(\mathbf{x}, \mathbf{x}') &= (1/N) \sum_{\mathbf{q}} [G_{ijlm}(\mathbf{q}) - \langle G_{ijlm}(\mathbf{q}) \rangle_{\mathbf{q}}] \\ &\quad \times \exp[i\mathbf{q}(\mathbf{x} - \mathbf{x}')]. \end{aligned} \quad (17)$$

The second term in the square brackets is the average over the wave-vector space and assures that self-deformation is excluded from the elastic coupling. For an isotropic medium, the elastic Green's function is known analytically and the coupling constants can be calculated.¹⁶

Let us denote

$$J_{\alpha\beta}(\mathbf{x}, \mathbf{x}') = P_0^2 D_{ij}^{\alpha} K_{ijlm}(\mathbf{x}, \mathbf{x}') D_{lm}^{\beta} \quad (18)$$

as the elastic energy due to interaction of deviatoric parts of the elastic dipoles in orientations α and β . In terms of the interaction, Eq. (16) can be rewritten as

$$\begin{aligned} \delta\rho_{\alpha}(\mathbf{x}) &= \beta[\rho_0(\mathbf{x})/3] J_{\alpha\beta}(\mathbf{x}, \mathbf{x}') \delta\rho_{\beta}(\mathbf{x}') \\ &\quad + \beta[\rho_0(\mathbf{x})/3] P_0 D_{ij}^{\alpha} \varepsilon_{ij}, \end{aligned} \quad (19)$$

and for the density fluctuation as a response to macroscopic uniform strain, one gets

$$\delta\rho_\alpha(\mathbf{x}) = \beta[\rho_0(\mathbf{x})/3] \left\{ \sum_{x'} [\mathbf{1} - \beta\rho_0(\mathbf{x})/3\mathbf{J}]^{-1}(\mathbf{x}, \mathbf{x}') \right\}_{\alpha\beta} \times P_0 D_{ij}^\beta \varepsilon_{ij}. \quad (20)$$

This is an important relation as it shows that the local elastic dipole density fluctuation is generated by a uniform strain, as appears in a crystal due to a thermal stress, for example. The effect may have some significance in a strongly nonequilibrium system of the supercooled plastic crystal and can result in a different distribution of the elastic domains, depending on how the phase has been prepared (a thermal history of a sample). Indeed, for the cyanoadamantane family it has been observed that thermodynamical stability of the phase with tetragonal domains was strongly dependent on the conditions of annealing.¹⁷

To get a better insight into the correlation between elastic dipoles, we have to solve the self-consistent Eq. (19). Here, we shall take advantage, mentioned in the Introduction, of considering the plastic crystal, which keeps translational symmetry in the supercooled, glassy state. Now, Eq. (19) is rewritten as

$$\delta\rho_\alpha(\mathbf{q}) = \beta[\rho_0/3] J_{\alpha\beta}(\mathbf{q}) \delta\rho_\beta(-\mathbf{q}) + \beta[\rho_0/3] P_0 D_{ij}^\alpha \varepsilon_{ij}, \quad (21)$$

and the wave-vector- (\mathbf{q}) dependent density fluctuation, as the response to uniform strain is

$$\delta\rho_\alpha(\mathbf{q}) = \beta[\rho_0/3] \{ \mathbf{1} - [\beta\rho_0/3] \mathbf{J}(\mathbf{q}) \}_{\alpha\beta}^{-1} P_0 D_{ij}^\beta \varepsilon_{ij}. \quad (22)$$

The \mathbf{q} dependence of the average density ρ_0 has been neglected. The inverse matrix in Eq. (22) plays a role of elastic screening

$$\vartheta(\mathbf{q}) = \{ \mathbf{1} - [\beta\rho_0/3] \mathbf{J}(\mathbf{q}) \}^{-1}, \quad (23)$$

and shows how the uniform strain field is screened by the elastic coupling between the domains. Eigenvalues of the screening matrix $\vartheta(\mathbf{q})$ are the energies of density fluctuation waves, collective modes, which are the elementary excitations of the elastic field. They may be seen as collective analogs of the localized excitations in orientational glasses,¹⁸ also called boson peaks. The matrix has to reflect the symmetry of the system, cubic in the case of the cyanoadamantane family.

The response function,

$$\chi_{\alpha\beta}(\mathbf{q}) = \beta[\rho_0/3] \{ \mathbf{1} - [\beta\rho_0/3] \mathbf{J}(\mathbf{q}) \}_{\alpha\beta}^{-1} \quad (24)$$

is the density fluctuation correlation function. The system becomes unstable against the formation of a density fluctuation wave, when the energy of a fluctuation wave becomes zero, e.g., for

$$\det|\vartheta(\mathbf{q})| = 0. \quad (25)$$

In the limit, $\mathbf{q} \rightarrow 0$, the instability corresponds to a formation of one macroscopic domain, a tetragonal phase, in the process of a continuous, ferroelastic phase transition. However, as follows from the above considerations, local stress densities are created before the generalized susceptibility ex-

pressed in Eq. (24) blows up; therefore, a transition to a glassy crystal (T_g) is expected to appear before a hypothetical ferroelastic ordering.

The density fluctuation correlation, determined by the susceptibility, Eq. (24), shows the \mathbf{q} dependence via the elastic interaction term $\mathbf{J}(\mathbf{q})$. In the continuum limit, $\mathbf{q} \rightarrow 0$, the interaction between tetragonal domains α and β , embedded in an isotropic elastic medium, has the following form:

$$J_{\alpha\beta}(\mathbf{q} \rightarrow 0) = (P_0^2/c_{44}) \left[\sum_i D_i^\alpha n_i^2 D_i^\beta - 3\{(c_{12} + c_{44})/c_{11}\} \times Y_{2,0}(n_\alpha) Y_{2,0}(n_\beta) \right] - E_{\text{self}}, \quad (26)$$

where $Y_{2,0}(n_\alpha) = (3n_\alpha^2 - 1)$, and the unit vector $\mathbf{n} = \mathbf{q}/q$ has been used to specify a direction of the wave vector. The elastic constants c_{ijklm} of the medium are written in Voigt's notation. The self-deformation term has been calculated for an elastically isotropic medium with embedded tetragonal defects,¹⁶

$$E_{\text{self}} = 3P_0^2/2c_{44}[2/5 + 4c_{44}/15c_{11}]. \quad (27)$$

Equation (26) shows that the elastic interaction in the limit $\mathbf{q} \rightarrow 0$ is not well defined, analogously to electric dipolar interaction. The matrix $J_{\alpha\beta}(\mathbf{q} \rightarrow 0)$ has different values depending on the direction from which one approaches the $\mathbf{q} = 0$ point. This means that when a ferroelastic instability temperature is estimated from the condition, Eq. (25), it will depend on the shape of a sample. With the help of Eq. (26) this dependence can be found.

In the continuum limit, ($\mathbf{q} \rightarrow 0$), the density fluctuation correlation function does not depend on a value of the wave vector, only on its direction. In order to get a spatial correlation for the density fluctuations we need an explicit \mathbf{q} dependence of the susceptibility, Eq. (24). This requires the elastic interaction between domains to be expressed by Fourier transforms of the excess forces, specified in Eq. (4),

$$J_{\alpha\beta}(\mathbf{q}) = V_i^\alpha(\mathbf{q}) G_{ij}(\mathbf{q}) V_j^\beta(-\mathbf{q}) - E_{\text{self}}. \quad (28)$$

The coupling of the excess forces is, however, still kept within the continuum approximation and the elastic Green's function is

$$G_{ij}(\mathbf{q}) = (1/q^2) \Omega_{ij}(\mathbf{n}). \quad (29)$$

Assuming, as before, that the cubic crystal in an orientationally disordered state can be approximated by an isotropic elastic medium, the matrix $\Omega_{ij}(\mathbf{n})$ is^{15,16}

$$\Omega_{ij}(\mathbf{n}) = (1/c_{44}) [\delta_{ij} - \{(c_{12} + c_{44})/c_{11}\} n_i n_j]. \quad (30)$$

On introducing Eq. (28) into Eq. (24), an explicit \mathbf{q} dependence of the density fluctuation correlation can be calculated. If the elastic interaction given by Eq. (28) has its minimum value at wave vector $\mathbf{q} = \mathbf{q}_c \neq 0$, then from the instability condition, Eq. (25), one finds the critical temperature for a "spinodal decomposition," e.g., the temperature below which the tetragonal domains are formed in a pattern of a static density fluctuation wave with periodicity given by \mathbf{q}_c .

The instability condition, Eq. (25), specifies a surface in the reciprocal space, which separates the disordered from ordered phases. The surface is essentially determined by the elastic interaction $\mathbf{J}(\mathbf{q})$.

(HYPOTHETICAL) FERROELASTICITY OF THE SUPERCOOLED PLASTIC CRYSTAL

To discuss the possible ferroelastic behavior of the supercooled crystal we shall analyze the instability condition, Eq. (25), at the Brillouin-zone center, $\mathbf{q}=0$. As follows from the elasticity theory,^{11,16} the elastic Green's function for the Γ point is just the compliance tensor \mathbf{S} . The elastic screening matrix is

$$\vartheta(\mathbf{0}) = \{\mathbf{1} - [\beta\rho_0/3]\mathbf{J}(\mathbf{0})\}^{-1}, \quad (31)$$

where the elastic energy for the coupling of domains is given as

$$J_{\alpha\beta}(\mathbf{0}) = 1/3[3P_0^2/2c_{44} - E_{\text{self}}]D_i^\alpha D_i^\beta. \quad (32)$$

The energy in the square brackets is the barrier height for reorientation of a domain. Equation (32) indicates that orthogonal orientations of neighboring domains are energetically favored. Such an arrangement, however, is a source of frustration in the three-dimensional cubic lattice.¹⁸ This might be an important intrinsic frustration in glassy crystals of the cyanoadamantane family.

As follows from the instability condition, the density fluctuation correlation function becomes infinite at the temperature

$$kT_c = \rho_0/3[3P_0^2/2c_{44} - E_{\text{self}}], \quad (33)$$

which is the critical temperature for (hypothetical) ferroelastic transition—an ordering of domains. One may estimate a value of the elastic dipole, assuming that the (hypothetical) ferroelastic transition temperature for the cyanoadamantane family is below 100 K. Taking elastic constants estimated for the glassy crystal (see the Appendix), the deviatoric part of the elastic dipoles is expected in the range, $P_0 \approx 10^{-1} \div 10^{-2}$ GPa.

An important consequence of the ferroelastic ordering of domains is a renormalization of the elastic properties of the system. Let \mathbf{S}^0 denote the elastic compliance tensor of the orientationally disordered crystal and σ a macroscopic stress. For the orientational stress relaxation, total strain experienced by the macroscopic system is the sum of the elastic ($\mathbf{S}^0\sigma$) and plastic strains (the density of elastic dipoles \mathbf{p}). Written in the tensor notation, we have

$$\varepsilon = \mathbf{S}^0[\sigma + \mathbf{p}], \quad (34)$$

where the elastic dipole density calculated from Eqs. (13), (22), and (24) is

$$\mathbf{p} = P_0^2 \mathbf{D}^\alpha \chi_{\alpha\beta} \mathbf{D}^\beta \mathbf{S}^0 \sigma. \quad (35)$$

For the total strain one gets

$$\varepsilon = \mathbf{S}^0[\mathbf{1} + \mathbf{D}^\alpha \chi_{\alpha\beta} \mathbf{D}^\beta \mathbf{S}^0] \sigma, \quad (36)$$

and the renormalized compliance tensor can be identified

$$\mathbf{S} = \mathbf{S}^0 + (\rho_0/3)P_0^2 \sum_{\alpha\beta} (\mathbf{S}^0 \mathbf{D}^\alpha) \chi_{\alpha\beta}(\mathbf{0}) (\mathbf{S}^0 \mathbf{D}^\beta). \quad (37)$$

The macroscopic, cubic symmetry of the supercooled crystal gives renormalization of two elastic compliance components (in the Voigt's notation),

$$S_{11} = S_{11}^0 + 2(\rho_0/3)P_0^2(S_{11}^0 - S_{12}^0)^2 \chi, \quad (38)$$

$$S_{12} = S_{12}^0 - (\rho_0/3)P_0^2(S_{11}^0 - S_{12}^0)^2 \chi, \quad (39)$$

where

$$\chi^{-1} = kT - \rho_0/3[3P_0^2(S_{11}^0 - S_{12}^0)^2 - E_{\text{self}}]. \quad (40)$$

The important consequence of the orientational elastic relaxation is that it does not change the compressibility modulus of the system, $\Delta = (S_{11} + 2S_{12})$. For dynamical experiments, one has to replace the static susceptibility by its frequency dependence, assuming a relaxator-type process, $\chi^{-1} \rightarrow \chi^{-1}(1 + i\omega\tau)^{-1}$, with a possible distribution of the relaxation times. For the orientational relaxation, the characteristic time is related to a barrier height for reorientation of a tetragonal domain.

Relations (38) and (39) indicates the softening of the c_{11} elastic constant and the hardening of c_{12} with decreasing temperature. It is seen that the elastic interaction, modified by self-deformation energy, which takes into account the correlation between domains, gives a Curie-Weiss-type temperature dependence for the elastic compliance components. We may expect, therefore, that for the supercooled plastic crystal of the cyanoadamantane family, there are changes in thermoelastic properties, according to the assumed physical picture of the system. Within the picture, the glassy crystal is formed by undercooling, when the elastic interaction between domains is weak, smaller than the thermal energy, and unable to order the domains. However, the random interaction between the domains is important. The randomness is the effect of frustration caused by distributing tetragonal domains within global cubic structure. When the lattice becomes softer, the deformations become larger; therefore, the random elastic coupling between the domains increases as the lattice softens. This increasing random elastic coupling leads to the stabilization of the glassy crystal, before it becomes unstable and elastically ordered. Therefore, the following physical picture of transformations in the supercooled plastic crystal is expected. When the cubic orientationally disordered crystal is undercooled, the short-range coupling between molecules tends to form triple-degenerate tetragonal defects which act as local stress centers. For such a system with long-range interaction, a strongly discontinuous phase transition is expected.¹² When a sample is cooled down below T_g , a glassy phase is formed as a result of the random elastic coupling. This appears well before (hypothetical) ferroelastic ordering of domains, which requires stronger elastic couplings.

IMPLICATION FOR THE DIFFUSE SCATTERING

According to the kinematic theory of x-ray scattering, the scattering intensity at point $\mathbf{Q} = \mathbf{q} + 2\pi\mathbf{H}$, where \mathbf{H} is a reciprocal-lattice vector, is given by¹⁹

$$I_{\text{dif}}(\mathbf{Q}) = \langle |\Delta\varphi(\mathbf{q})|^2 \rangle, \quad (41)$$

where $\Delta\varphi(\mathbf{q})$ is a fluctuation in the scattering amplitude at point \mathbf{q} . For the crystal composed of the tetragonal stress centers, this fluctuation is due to both the density fluctuation of domains $\delta\rho_\alpha(\mathbf{q})$ and inhomogeneous displacement $\mathbf{w}(\mathbf{q})$ produced by the local stress. The displacement has been already calculated and from Eqs. (9) and (10) one finds

$$\mathbf{w}(\mathbf{q}) = \mathbf{G}(\mathbf{q}) \sum_{\alpha} \mathbf{V}^{\alpha}(\mathbf{q}) \delta\rho_{\alpha}(\mathbf{q}). \quad (42)$$

Assuming the inhomogeneous displacements are small, the scattered amplitude fluctuation is

$$\Delta\varphi(\mathbf{q}) = \sum_{\alpha} [\Delta f_{\alpha} + if\mathbf{Q}\mathbf{G}(\mathbf{q})\mathbf{V}^{\alpha}(\mathbf{q})] \delta\rho_{\alpha}(\mathbf{q}). \quad (43)$$

$\Delta f_{\alpha} = f_{\alpha} - f_0$ is the difference between the scattering factors for different tetragonal domains and the reference, disordered crystal; f is the average scattering factor. When Eq. (43) is introduced into Eq. (41), the intensity of diffuse scattering is conveniently expressed in terms of the density fluctuation correlation function,

$$I_{\text{dif}}(\mathbf{Q}) = \beta^{-1} \chi_{\alpha\beta}(\mathbf{q}) F_{\alpha}(\mathbf{q}) F_{\beta}(-\mathbf{q}), \quad (44)$$

where

$$F_{\alpha}(\mathbf{q}) = [\Delta f_{\alpha} + f\mathbf{Q}\mathbf{G}(\mathbf{q})\mathbf{V}^{\alpha}(\mathbf{q})]. \quad (45)$$

All quantities needed to calculate the scattering intensity are known and have been written explicitly for the model. Moreover, one may choose between the continuum limit, valid for small \mathbf{q} vectors, and an approximation valid for larger wave vectors. In the latter case we use Fourier transforms of the excess forces as given by Eqs. (4) and for the density fluctuation susceptibility we use Eq. (24) with the elastic energy given by Eq. (28). The elastic Green's function is still, however, in the limit of $\mathbf{q} \rightarrow 0$. To go beyond this limitation, we need to know explicitly a dynamical matrix for the system.

In the context of diffuse scattering, it is convenient to use the continuum approximation, the limit $\mathbf{q} \rightarrow 0$. Within the approximation, the excess forces are expressed as in Eq. (5), and then scattering intensity is given explicitly in terms of elastic dipoles

$$I_{\text{dif}}(\mathbf{Q}) = \beta^{-1} \chi_{\alpha\beta}(\mathbf{q}) [\Delta f_{\alpha} + f\mathbf{Q}\mathbf{G}(\mathbf{q})\mathbf{P}^{\alpha}\mathbf{q}] \times [\Delta f_{\beta} + f\mathbf{Q}\mathbf{G}(\mathbf{q})\mathbf{P}^{\beta}\mathbf{q}], \quad (46)$$

and written in terms of components

$$I_{\text{dif}}(\mathbf{Q}) = \beta^{-1} \chi_{\alpha\beta}(\mathbf{q}) [\Delta f_{\alpha} + f q^{-1} Q_i \Omega_{ij}(\mathbf{n}) P_{jj}^{\alpha} n_j] \times [\Delta f_{\beta} + f q^{-1} Q_i \Omega_{ij}(\mathbf{n}) P_{jj}^{\beta} n_j]. \quad (47)$$

Equation (29) has been used to express the Green's function in terms of a direction of the wave vector, $\mathbf{n} = \mathbf{q}/q$. For the model considered, only diagonal elements of the elastic dipole tensor are nonzero.

For an analysis of the diffuse scattering it is convenient to express the intensity as a sum of three terms

$$I_{\text{density}}(\mathbf{Q}) = \beta^{-1} \chi_{\alpha\beta}(\mathbf{q}) [\Delta f_{\alpha} \Delta f_{\beta}], \quad (48)$$

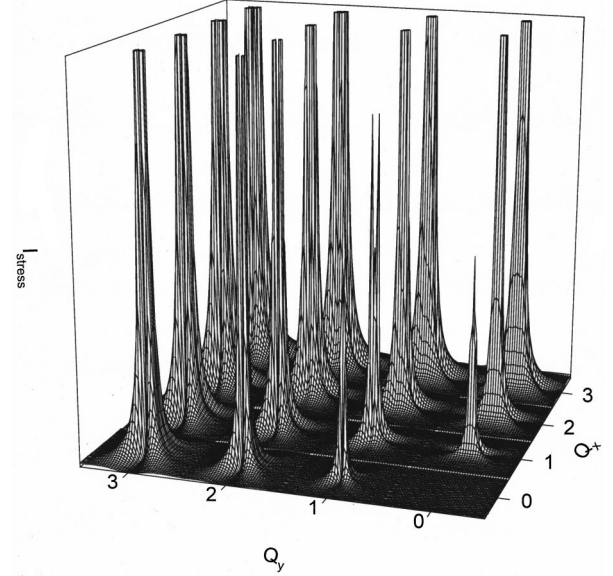


FIG. 3. The contribution to diffuse scattering due to local stresses, $I_{\text{stress}}(Q_x, Q_y)$, calculated according to Eq. (49). The elastic constants used in calculations are as given in the Appendix and elastic dipoles representing the local stresses are given by Eq. (1) with parameters $A = 0.1$ GPa and $B = 0.2$ GPa.

$$I_{\text{stress}}(\mathbf{Q}) = \beta^{-1} \chi_{\alpha\beta}(\mathbf{q}) f^2 q^{-2} [Q_i \Omega_{ij}(\mathbf{n}) P_{jj}^{\alpha} n_j] \times [Q_i \Omega_{ij}(\mathbf{n}) P_{jj}^{\beta} n_j], \quad (49)$$

$$I_{\text{asym}}(\mathbf{Q}) = \beta^{-1} \chi_{\alpha\beta}(\mathbf{q}) 2 f \Delta f_{\alpha} q^{-1} [Q_i \Omega_{ij}(\mathbf{n}) P_{jj}^{\beta} n_j]. \quad (50)$$

The term in Eq. (48) gives information about local orientational order. For a disordered system it is reduced to so-called Laue scattering. The contribution given by Eq. (49) is due to local stresses produced by orientationally frozen molecules, e.g., it is a direct effect of the transformation and formation of a new phase. In our model it is a formation of tetragonal ‘‘defects’’ as the coherent nucleus of a tetragonal phase. This intensity is proportional to the square of the elastic dipoles and Fig. 3 presents the contribution $I_{\text{stress}}(Q_x, Q_y)$ calculated according to Eq. (49) with parameters representative of the cyanoadamantane family crystals. Finally, the intensity expressed by Eq. (50) is due to coupling between the orientational order and the local stress and causes an asymmetry of the diffuse scattering around a node of reciprocal space. How strong the asymmetry is depends not only on the strength of the elastic dipole but also on the difference in scattering factors, Δf_{α} . In other words, it depends how different in the scattering ability is a new phase with respect to the matrix. In a limiting case, when this difference is negligible, the diffuse scattering intensity is given by Eq. (49). On the other hand, if the asymmetric contribution is not negligible, it becomes more important than the one due to deformations, because the asymmetric contribution depends on the elastic dipole in the first power, while the deformation contribution depends on the square of the local stress.

KINETIC ASPECT

For every metastable system it is important that a response to a perturbation is a nonequilibrium one. The super-

cooled plastic crystal is considered as responding to a thermal stress applied to the system in a process of annealing. This response is assumed to be due to the orientational relaxation of the frustrated elastic domains. Thus, it is important to ask what is a time evolution of the elastic domains and how the response is influenced by the relaxation process. The elastic dipole density fluctuation for the tetragonal domains, which will be reached at thermodynamical equilibrium, is denoted as

$$\delta\rho_\alpha(\mathbf{q},\infty)=\chi_T(\mathbf{q})P_0D_i^\alpha\varepsilon_{ii}, \quad (51)$$

where $\chi_T(\mathbf{q})$ is the transverse eigenvalue of the susceptibility, Eq. (24). The time evolution of the elastic dipole density fluctuation is assumed to follow the first-order kinetics,

$$\delta\rho_\alpha(\mathbf{q},t)=\delta\rho_\alpha(\mathbf{q},\infty)[1-\exp(-t/\tau_q)], \quad (52)$$

where τ_q is a relaxation time for a process of ordering of the elastic domains according to a pattern of density waves characterized by the wave vector \mathbf{q} . In a general case one may have a distribution of the relaxation times, while in a situation that the ordering process follows a particular pattern (for example a ferroelastic one) the process is characterized by one relaxation time. The kinetics of the ordering of the elastic domains might be quite complicated, indeed.

On measuring an elastic response directly one can probe a kinetics of the ferroelastic ordering ($\mathbf{q}=0$) from a time evolution of the renormalized elastic compliance tensor,

$$\mathbf{S}(t)=\mathbf{S}^0[\mathbf{1}+\mathbf{D}^\alpha\chi_{\alpha\beta}\mathbf{D}^\beta\mathbf{S}^0][1-\exp(-t/\tau_0)]. \quad (53)$$

As follows from the model, which has assumed the *local* thermodynamic equilibrium, the orientational elastic relaxation does not change the compressibility modulus of the system [see Eq. (40)]. Thus, measurements of the time evolution of a unit-cell volume or cell parameters do not probe a dynamics of the orientational relaxation. However, they do probe diffusional relaxation which takes place in a system when a global thermodynamical equilibrium is assumed. The isothermal relaxation of a lattice parameter of a supercooled cyanoadamantane crystal, on aging at 160 K, has been studied.⁷ Following our model, but assuming global equilibrium, the lattice parameter change is

$$\Delta a(t)/a_0=\rho_0(t)(S_{11}+S_{12})P_s, \quad (54)$$

where $P_s=A+2B$ is the isotropic part of the elastic dipole, Eq. (1), and a_0 is the lattice parameter at the reference state, $t=0$. A time evolution of the changes are then due to a dynamics of growing of the elastic domains, which may be assumed in simplest form,

$$\rho_0(t)=\rho_0(\infty)[1-\exp(-t/\tau)]. \quad (55)$$

It is interesting to notice that the experiments performed for the cyanoadamantane crystals have shown to fit the above time evolution with a relaxation time of the order 50 h.⁷

Much more often, the x-ray scattering intensity is used to probe the kinetics of ordering, as is in the case of cyanoadamantane family crystals.⁵ For this purpose, the scattering amplitude fluctuation in Eq. (40) is replaced by its time-dependent version,

$$\begin{aligned} \Delta\varphi(\mathbf{q},t)=\sum_{\alpha}[\Delta f_{\alpha}+if\mathbf{Q}\mathbf{G}(\mathbf{q})\mathbf{V}^{\alpha}(\mathbf{q})]\delta\rho_{\alpha}(\mathbf{q},\infty) \\ \times[1-\exp(-t/\tau_q)], \end{aligned} \quad (56)$$

and the time evolution of the diffuse scattering due to reorientation of elastic domains is expressed as

$$I_{\text{dif}}(\mathbf{Q},t)=\langle|\Delta\varphi(\mathbf{q},t)|^2\rangle. \quad (57)$$

Numerous studies of transformation kinetics of the supercooled cyanoadamantane family crystals using diffraction methods were summarized in Refs. 5 and 6. They were concentrated, however, on a time evolution of superstructure peaks, which have been assumed to change parallelly to diffuse scattering around the Bragg peaks. What became clear from the studies was that the evolution of the supercooled plastic crystal after a deep quench, towards metastable (tetragonal) phase, follows a kinetics which depends on the superstructure peak taken as a probe. The time evolution of peak intensities for (121) reflection follows the stretch exponential law, while for (300) reflection it follows simple exponential dependence,²⁰ as predicted in the simple model. The observations suggest that the model does reflect some of essential features of the transformations but has to be improved for more quantitative comparison with experiment.

CONCLUDING REMARKS

In an attempt to find a physical picture of transformations which take place in supercooled plastic crystals after deep quenching, we have been guided by the empirical rule, known as Ostwald's law of stages. Taking the crystals of the cyanoadamantane family as a model system, we have been considering a cubic crystal with orientationally disordered molecules as evolving under conditions of supercooling not into the most stable (and ordered) phase (monoclinic) but rather into a metastable phase of tetragonal symmetry, easier to reach kinetically. This has suggested the supercooled crystal as a mixture of coherent (small) domains with tetragonal local structure, which introduces stress to the global cubic lattice. The domains were characterized by elastic dipoles, centers for long-range elastic interaction, which introduces frustration to the system. Elastic dipoles are frustrated in the cubic lattice and form an orientationally disordered state with random interaction, which can mimic a glassy state of deeply quenched plastic crystals. We have analyzed the orientational relaxation of the elastic dipoles embedded in an isotropic elastic medium, and calculated the elastic dipole density fluctuation as a local order parameter. The density-density correlation function has been used to discuss a possible ordering of the tetragonal domains as a hypothetical ferroelastic transition into the tetragonal phase. Implications of the model for elastic properties and diffuse scattering have been analyzed, also in the context of kinetic experiments. It was suggested that experiments on time evolution of elastic constants, which are renormalized by the orientational relaxation of domains, can provide a direct measure of the kinetics. As for the scattering experiments, numerous measurements of kinetics might be correlated with the model quantitatively, even to the extent that local stresses can be estimated and this will be an extension of the project.

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APPENDIX

Here we give the elastic constants, estimated from dispersion curves for glassy crystals at 100 K:²¹ $c_{11}=0.54$ GPa = 5.4×10^9 dyna cm⁻², $c_{44}=8.7 \times 10^{-2}$ GPa = 8.7×10^8 dyna cm⁻², $c_{12}=0.37$ GPa = 3.7×10^9 dyna cm⁻² (assuming isotropic elastic medium).

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