

Dynamics of a quadrupolar glass

C. Bostoen and K. H. Michel

Department of Physics, University of Antwerp (UIA), 2610 Wilrijk, Belgium

(Received 5 February 1990; revised manuscript received 21 May 1990)

Substitutional disorder in an orientationally disordered crystal generates static random strain fields. Strains cause scattering of orientational and displacive waves. The resulting friction processes may lead to structural arrest (nonergodic instability) at a threshold temperature T_f . The slow dynamics associated with structural arrest is studied. The scattering law exhibits a dynamic central peak. The influence of microscopic relaxation processes on the dynamics of structural arrest is investigated. Phonon resonances and ultrasonic attenuation are calculated. A comparison with experiments in $\text{K}(\text{CN})_x\text{Br}_{1-x}$ ranging from high- to low-frequency methods is made.

I. INTRODUCTION

Conventional glasses can be regarded as frozen liquids where positional long-range order (LRO) of atomic nuclei is absent.¹ Generalizing this concept, one considers crystals, where other than positional degrees of freedom are frozen without LRO, as glasses. Examples are (magnetic) spin glasses,² orientational glasses, etc. Notice that in the latter categories, in contradistinction to conventional glasses, substitutional atomic disorder is necessary for obtaining the glass state. We will consider in particular $\text{K}(\text{CN})_x\text{Br}_{1-x}$ as a model system, where the CN ion is the orientational component.^{3,4}

Substitutional disorder generates static random strain fields.⁵⁻⁸ The effect of the random fields is twofold. Firstly, a linear coupling to the orientational order parameter leads to a continuous orientational freezing process, while the structural phase transition with LRO is suppressed.⁹⁻¹² Secondly, the lattice strains provide a scattering mechanism for orientational and displacive waves.¹³ The scattering can lead to structural arrest, also called nonergodic instability or dynamic glass transition.

The method for treating this type of problem was originally developed by Götze for the description of the Anderson localization due to electron-impurity scattering.¹⁴ An extension to the more complicated case of binary collisions has led to the mode-coupling theory of the conventional glass transition.^{15,16} In the presence of static strain fields, the scattering processes are more simple, and the structure of the theory has analogies with the electronic problem.

Previously,^{13,17} we have studied the problem of structural arrest in the zero-frequency limit, in particular the temperature and wave-vector dependence of the glass order parameter. In the present paper, we will study dynamic correlations at low frequencies, thereby obtaining information about the relaxation phenomena which accompany orientational and displacive arrest. This problem is of great experimental and theoretical importance. It has been realized for some time^{18,19} that the tempera-

ture behavior of the transverse-acoustic (TA) phonons depends on the measuring frequency of the experimental method. It is obvious that microscopic relaxation processes are relevant to account for dispersion effects. However, these relaxation processes are in no way able to describe the anomalous damping phenomena, which rise strongly near the temperature where the TA phonons have a minimum.^{20,21} Recent low-frequency shear torque experiments suggest that the anomalous damping (primary loss) is intimately related to structural arrest.²² A unified theoretical formulation has to take into account the low-frequency phenomena near structural arrest as well as the relatively fast microscopic relaxation processes.

The content of the paper is as follows. In Sec. II we give a short overview of the model which, in addition to translation-rotation (TR) coupling terms, includes random strain fields and anharmonic scattering terms. Next (Sec. III) we discuss the glass transition as the zero-frequency limit of a dynamic theory. In particular, the transition temperature T_f is studied as a function of CN concentration x and random-field strength h . In Sec. IV we study the slow dynamics associated with structural arrest. The scattering law exhibits a dynamic central peak. The influence of microscopic relaxation processes is studied in Sec. V. The transverse-acoustic phonons depend on frequency of the experimental method. At low frequency, the shear modes remain soft for $T < T_f$. The ultrasonic attenuation α is calculated. Finally (Sec. VI) we discuss our results in comparison with experiments.

II. MODEL

A detailed description of the model Hamiltonian has been given in Refs. 11 and 13. We therefore restrict ourselves here in recalling essential concepts. We consider a crystal $M(\text{CN})_xX_{1-x}$, where M is an alkali metal and X^+ a halogen ion in the high-temperature cubic phase. The CN^- ions have dynamic orientational disorder, described by quadrupolar orientational coordinates $Y_\alpha(\mathbf{n})$, $\alpha = 1-3$,

of symmetry T_{2g} and at lattice site \mathbf{n} . Substitutional disorder is taken into account by the occupation variable $\sigma(\mathbf{n})$ with value $+1$ for a CN^- ion and value 0 for a halogen X^+ . We therefore write in Fourier space

$$Y_\alpha(\mathbf{q}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \sigma(\mathbf{n}) Y_\alpha(\mathbf{n}) \exp[-i\mathbf{q} \cdot \mathbf{X}(\mathbf{n})], \quad (2.1)$$

where N is the number of unit cells, $\mathbf{X}(\mathbf{n})$ is the rigid lattice position, and \mathbf{q} is the wave vector. As dispersive coordinates we consider acoustic lattice displacement $s_i(\mathbf{q})$, $i=1-3$. Of primary importance for the description of ferroelastic phenomena is the rotation-translation coupling²³

$$V^{RT} = \sum_{\mathbf{q}} v_{ai}(\mathbf{q}) Y_\alpha^\dagger(\mathbf{q}) s_i(\mathbf{q}). \quad (2.2)$$

The TR coupling leads to an effective lattice mediated interaction between orientational quadrupoles. The interaction matrix reads

$$C(\mathbf{q}) = v(\mathbf{q}) M^{-1}(\mathbf{q}) v^\dagger(\mathbf{q}). \quad (2.3)$$

Here $M(\mathbf{q})$ is the bare acoustic dynamical matrix.

Substitutional impurities produce random strain (RS) fields $s_i^e(\mathbf{q}, \{\sigma\})$ which couple linearly to the remaining quadrupoles:⁵

$$V^{RS} = \sum_{\mathbf{q}} Y_\alpha^\dagger(\mathbf{q}) h_\alpha(\mathbf{q}, \{\sigma\}), \quad (2.4)$$

where

$$h_\alpha(\mathbf{q}, \{\sigma\}) = v_{ai}(\mathbf{q}) s_i^e(\mathbf{q}, \{\sigma\}). \quad (2.5)$$

h_α is a random field with a Gaussian distribution. Denoting the configurational average by an overbar, we have $\overline{h_\alpha} = 0$ and

$$\overline{h_\alpha^\dagger(\mathbf{q}, \{\sigma\}) h_\beta(\mathbf{k}, \{\sigma\})} = x(1-x) h^2 \delta_{\alpha\beta} \delta_{\mathbf{k}\mathbf{q}}. \quad (2.6)$$

The quantity h^2 is calculated numerically,¹⁷ δ stands for the Kronecker symbol, and x is the CN^- concentration.

The coupling V^{RS} affects all thermodynamic quantities. In particular, the collective static orientational susceptibility is given by⁵

$$\chi(\mathbf{q}) = [1 - \chi^0 L(\mathbf{q})]^{-1} \chi^0. \quad (2.7)$$

Here all quantities are 3×3 matrices. The total interaction is given by

$$L(\mathbf{q}) = C(\mathbf{q}) - 1C^s - J(\mathbf{q}), \quad (2.8)$$

where $C^s = (1/N) \sum_{\mathbf{q}} C(\mathbf{q})$ is the self-interaction and $J(\mathbf{q})$ the direct electric-quadrupole interaction.²⁴ The single-particle susceptibility χ^0 at temperature T reads

$$\chi^0 = x(y/T) [1 - x(1-x)\xi(h^2/T^2)]. \quad (2.9)$$

Here y and ξ are single-particle thermal averages. The orientational susceptibility $\chi(\mathbf{q})$ is related to the inverse of the displacement-displacement susceptibility by²³

$$D(\mathbf{q}) = M(\mathbf{q}) [1 - M^{-1}(\mathbf{q}) v^\dagger(\mathbf{q}) \chi(\mathbf{q}) v(\mathbf{q})]^{-1}. \quad (2.10)$$

This quantity corresponds to the restoring forces and is proportional to the elastic constants. A second-order

phase transition leads to a divergence of $\chi(\mathbf{q})$ at a transition temperature T_c given by

$$\chi^0(T_c) \delta = 1, \quad (2.11)$$

where δ is the largest eigenvalue of $L(\mathbf{q})$ at $\mathbf{q} = \mathbf{q}_0$.

The static strain fields s^e not only lead to the coupling V^{RS} but also generate scattering processes of orientational and acoustic waves:¹³

$$V^{RTS} = \frac{1}{\sqrt{N}} \sum_{\mathbf{p}, \mathbf{q}, \mathbf{k}} w \begin{pmatrix} \alpha & i & j \\ \mathbf{p} & \mathbf{q} & \mathbf{k} \end{pmatrix} Y_\alpha(\mathbf{p}) s_i(\mathbf{q}) s_j^e(\mathbf{k}). \quad (2.12)$$

III. GLASS TRANSITION

Dynamic phenomena are described in terms of Kubo's relaxation functions²⁵ $\Phi^{ss}(z)$ and $\Phi^{YY}(z)$ for displacements and rotations, respectively. Using the Zwanzig-Mori projection-operator technique,²⁶ we have derived dynamic equations for the relaxation functions. For the displacements we obtain²⁷ ($z = \omega + i0$, ω is the frequency)

$$[1z^2 - D + z\Pi(z) - z\sigma(z)] \Phi^{ss}(z) = [1z + \Pi(z) - \sigma(z)] D^{-1}. \quad (3.1)$$

The matrices D , Π , σ , and Φ depend on the wave vector \mathbf{q} . Here D represents the restoring forces (2.10). The memory kernel $\Pi(z)$ is calculated by using mode-coupling technique, first introduced²⁸ for the study of low-frequency phenomena at second-order phase transition. In the present problem, the scattering mechanism V^{RTS} , Eq. (2.12), is particularly simple and we obtain

$$\Pi_{ij}(\mathbf{q}, z) = -\frac{1}{N} \sum_{\mathbf{p}} U \begin{pmatrix} \alpha\beta & ij \\ \mathbf{p} & \mathbf{q} \end{pmatrix} \Phi_{\alpha\beta}^{YY}(\mathbf{p}, z), \quad (3.2)$$

with

$$U \begin{pmatrix} \alpha\beta & ij \\ \mathbf{p} & \mathbf{q} \end{pmatrix} = x(1-x) \sum_{\mathbf{k}} w \begin{pmatrix} \alpha & i & i' \\ \mathbf{p} & \mathbf{q} & \mathbf{k} \end{pmatrix} w \begin{pmatrix} \beta & j & j' \\ \mathbf{p} & \mathbf{q} & \mathbf{k} \end{pmatrix} \times A_i(\mathbf{k}) A_j(\mathbf{k}), \quad (3.3)$$

where $A_i(\mathbf{k})$ is the amplitude⁵ of the strain field $s_i^e(\mathbf{k})$. The memory kernel σ is due to RT coupling and reads

$$\sigma(\mathbf{q}, z) = \beta^\dagger(\mathbf{q}) X \times \{1z - [1z + \Lambda(\mathbf{q}, z) + i\gamma]^{-1} \langle \omega^2 \rangle_0\}^{-1} \beta(\mathbf{q}), \quad (3.4)$$

with

$$\beta^\dagger = v^\dagger X^{-1}, \quad (3.5)$$

where X^{-1} is a noncritical single-particle orientational susceptibility and $\langle \omega^2 \rangle_0 = (\mathcal{L}Y, \mathcal{L}Y)X$ is the corresponding second moment. \mathcal{L} is the Liouville operator. The quantity γ is a frequency-independent transport coefficient which accounts for fast relaxation processes. The memory kernel Λ is obtained as¹³

$$\Lambda_{\alpha\beta}(\mathbf{q}, z) = -(\mathcal{L}Y_\alpha, \mathcal{L}Y_\gamma) \frac{1}{N} \sum_{\mathbf{p}} U \begin{bmatrix} \gamma\beta & ij \\ \mathbf{q} & \mathbf{p} \end{bmatrix} \Phi_{ij}^{ss}(\mathbf{p}, z). \quad (3.6)$$

We notice that equations similar to (3.1)–(3.6) can be derived for the rotational relaxation function $\Phi^{YY}(z)$.^{13,17} In the zero-frequency limit, the equations of Φ^{ss} and Φ^{YY} lead to glass order parameters that are proportional to each other.¹³ In order to keep the formulation transparent, we will restrict ourselves essentially to a discussion of Eq. (3.1).

An arrested structure leads to a time-persistent (nonergodic) part in the correlation function

$$\lim_{t \rightarrow \infty} \langle X^\dagger(\mathbf{q}, t) X(\mathbf{q}, 0) \rangle \equiv \Psi^{XX}(\mathbf{q}), \quad (3.7a)$$

or equivalently to a $(1/z)$ singularity in the relaxation function¹⁴

$$\Phi^{XX}(\mathbf{q}, z) = \frac{f^{XX}(\mathbf{q})}{z} + \tilde{\Phi}^{XX}(\mathbf{q}, z), \quad (3.7b)$$

where

$$f^{XX}(\mathbf{q}) = \Psi^{XX}(\mathbf{q})/T. \quad (3.8)$$

In particular we consider $X=s$ or $X=Y$, which correspond to the time-persistent displacive and orientational correlations f^{ss} and f^{YY} , respectively. The memory kernels (3.2) and (3.6) then also are written in the form (3.7b)

$$\Pi(\mathbf{q}, z) = -\frac{1}{z} \rho(\mathbf{q}) + \tilde{\Pi}(\mathbf{q}, z), \quad (3.9a)$$

$$\Lambda(\mathbf{q}, z) = -\frac{1}{z} \nu(\mathbf{q}) + \tilde{\Lambda}(\mathbf{q}, z), \quad (3.9b)$$

where

$$\rho_{ij}(\mathbf{q}) = \frac{1}{N} \sum_{\mathbf{p}} U \begin{bmatrix} \alpha\beta & ij \\ \mathbf{p} & \mathbf{q} \end{bmatrix} f_{\alpha\beta}^{YY}(\mathbf{p}), \quad (3.10a)$$

$$\nu_{\alpha\beta}(\mathbf{q}) = (\mathcal{L}Y_\alpha, \mathcal{L}Y_\gamma) \frac{1}{N} \sum_{\mathbf{p}} U \begin{bmatrix} \gamma\beta & ij \\ \mathbf{q} & \mathbf{p} \end{bmatrix} f_{ij}^{ss}(\mathbf{p}). \quad (3.10b)$$

One can show that¹³

$$f^{YY}(\mathbf{q}) = \beta(\mathbf{q}) f^{ss}(\mathbf{q}) \beta^\dagger(\mathbf{q}), \quad (3.11)$$

where β is given by Eq. (3.5). Relation (3.11) indicates that freezing or orientational and displacive correlations occur concomitantly. This fact was already assumed in Ref. 4 in order to interpret neutron-scattering experiments.³

Using Eqs. (3.7b)–(3.11) we collect the most singular (in $1/z$) terms in Eq. (3.1) and arrive at a closed integral equation for the nonergodic part $f^{ss}(\mathbf{q})$. In terms of the normalized glass order parameter

$$\phi(\mathbf{q}) \equiv D(\mathbf{q}) f^{ss}(\mathbf{q}), \quad (3.12)$$

we obtain

$$\phi(\mathbf{q}) [1 - \phi(\mathbf{q})]^{-1} = \frac{1}{N} \sum_{\mathbf{p}} K(\mathbf{q}, \mathbf{p}) \phi(\mathbf{p}), \quad (3.13)$$

where

$$K(\mathbf{q}, \mathbf{p}) = D^{-1}(\mathbf{q}) [\beta^\dagger(\mathbf{q}) U(\mathbf{q}, \mathbf{p}) \beta(\mathbf{q}) + \beta^\dagger(\mathbf{p}) U(\mathbf{p}, \mathbf{q}) \beta(\mathbf{p})] D^{-1}(\mathbf{p}). \quad (3.14)$$

A solution $\phi(\mathbf{q}) > 0$ is obtained if the kernel K is of order unity. The threshold condition, also called nonergodic instability, is attained if the restoring forces D are sufficiently small. Equivalently, see Eq. (2.10), the susceptibility $\chi(\mathbf{q})$ has to be large. The last condition is realized close to a second-order phase transition. The nonergodic instability then occurs at a temperature $T_f > T_c$. Starting from value zero at T_f , the glass order parameter $\phi(\mathbf{q})$ increases continuously with decreasing T . This type of glass transition is called type *A*, while the conventional liquid-glass transition, characterized by a discontinuity of the order parameter at T_f , is called type *B*.²⁹ The freezing process leads to a depletion of thermal fluctuations. The collective orientational susceptibility now reads

$$\chi(\mathbf{q}) = [1 - \tilde{\chi}^0(\mathbf{q}) L(\mathbf{q})]^{-1} \tilde{\chi}^0(\mathbf{q}), \quad (3.15a)$$

where

$$\tilde{\chi}^0(\mathbf{q}) = [1 - \phi(\mathbf{q})] \chi^0(\mathbf{q}), \quad (3.15b)$$

with χ^0 given by Eq. (2.9).

In Ref. 17 we have solved numerically the coupled system of equations (3.13) and (3.15a), with potential parameters corresponding to $\text{K}(\text{CN})_x \text{Br}_{1-x}$. More recent and extended calculations have essentially confirmed our previous results. We have gained additional insight in the phase diagram. Whether a nonergodic instability occurs or not depends on the strength of the random field, in comparison with the strength of the interaction. This ratio increases with decreasing x and therefore the threshold condition is not reached for low values of x . Our numerical results for $T_f(x, h)$ are summarized in Table I. For details of the numerical method, see Ref. 17.

TABLE I. Temperature T_f as function of CN concentration x and random-field strength h . Dashes correspond to absence of nonergodic instability.

x/h	100	150	200	250	300
0.3	$T_f = 54.4$	50.5	–	–	–
0.4	73.7	70.9	–	–	–
0.5	93.1	90.9	87.3	81.3	–

IV. SLOW DYNAMICS

We want to study the displacement relaxation function $\Phi^{ss}(z)$ in the low-frequency regime for T close to T_f . Equations (3.1) and (3.4) reduce to

$$[-D + z\Pi(z) - z\sigma(z)]\Phi^{ss}(z) = [\Pi(z) - \sigma(z)]D^{-1} \quad (4.1a)$$

and

$$\sigma(z) = -\beta^\dagger X \frac{[\Lambda(z) + i\gamma]}{\langle \omega^2 \rangle_0} \beta, \quad (4.1b)$$

respectively. Here Π and Λ are given by Eqs. (3.2) and (3.6), respectively. We assume that z is sufficiently small such that

$$\frac{z\beta^\dagger\gamma\beta}{(\mathcal{L}Y, \mathcal{L}Y)} < D. \quad (4.2)$$

Defining the normalized relaxation function

$$F(\mathbf{q}, z) = D(\mathbf{q})\Phi^{ss}(\mathbf{q}, z), \quad (4.3)$$

and using relation (4.2), we get from Eqs. (4.1a) and (4.1b)

$$\begin{aligned} [F(\mathbf{q}, z) + i\eta(\mathbf{q})D^{-1}(\mathbf{q})][1 - zF(\mathbf{q}, z)]^{-1} \\ = \frac{1}{N} \sum_{\mathbf{p}} K(\mathbf{q}, \mathbf{p})F(\mathbf{p}, z), \end{aligned} \quad (4.4)$$

where K is given by Eq. (3.14) and where

$$\eta(\mathbf{q}) = \frac{\beta^\dagger(\mathbf{q})\gamma\beta(\mathbf{q})}{(\mathcal{L}Y, \mathcal{L}Y)}. \quad (4.5)$$

At $T = T_f$ and for small z we assume that $F = z^{-n}$, with $0 < n < 1$. We will show that this assumption is self-consistent with Eq. (4.4). In leading order of small frequencies, we neglect the terms ηD^{-1} and zF in Eq. (4.4), thereby obtaining

$$F(\mathbf{q}, z) = \frac{1}{N} \sum_{\mathbf{p}} K_f(\mathbf{q}, \mathbf{p})F(\mathbf{p}, z). \quad (4.6)$$

The subscript f indicates that K is taken at $T = T_f$. Replacing the right-hand side of Eq. (4.4) by $F(\mathbf{q}, z)$, we obtain

$$F_f(\mathbf{q}, z) = \left[-\frac{i}{z} \eta(\mathbf{q})D_f^{-1}(\mathbf{q}) \right]^{1/2}. \quad (4.7)$$

Here D_f stands for D at $T = T_f$. The $z^{-1/2}$ dependence of the relaxation function $F(z)$ is characteristic for the simple glass transition described in Sec. III. It is also familiar from spin-glass theory.³⁰⁻³² For a comparative discussion, see Ref. 32.

For $T \neq T_f$, the kernel K in Eq. (4.6) becomes different from K_f . We therefore write

$$(1 + \epsilon)F(\mathbf{q}, z) = \frac{1}{N} \sum_{\mathbf{p}} K(\mathbf{q}, \mathbf{p})F(\mathbf{p}, z), \quad (4.8)$$

where ϵ has to be determined. For $T > T_f$, the factor $D^{-1}(\mathbf{q})$ in expression (3.14) leads to the dominant T dependence, and writing

$$D^{-1} \cong D_f^{-1} [1 - (D - D_f)D_f^{-1}], \quad (4.9)$$

we identify

$$\epsilon = [D_f - D(T)]D_f^{-1}, \quad (4.10a)$$

where $D(T) > D_f$ and hence $\epsilon < 0$. For $T < T_f$, we infer by comparison with Eq. (3.13) that

$$\epsilon = \phi(\mathbf{q}), \quad (4.10b)$$

where $\epsilon > 0$.

Using Eq. (4.8) instead of (4.6), we rewrite Eq. (4.4) as

$$zF^2 - \epsilon F + i\eta D_f^{-1} = 0. \quad (4.11)$$

We recall that ϵ , D , η , and F depend on \mathbf{q} . Depending on whether $T > T_f$ or $T < T_f$, we take expressions (4.10a) or (4.10b) for ϵ , respectively, while $\epsilon = 0$ at $T = T_f$. The solution of Eq. (4.11) is given by

$$F(z) = \frac{\epsilon}{2z} + \frac{(\epsilon^4 + 16z^2\eta^2 D_f^{-2})^{1/4}}{2z} \exp[-i\theta(z)], \quad (4.12a)$$

with

$$\theta(z) = \frac{1}{2} \arctan \left[\frac{4z\eta D_f^{-1}}{\epsilon^2} \right]. \quad (4.12b)$$

Using $z = \omega + i0$ and defining

$$\omega_\epsilon = \frac{\epsilon^2 D_f}{4\eta}, \quad (4.13)$$

we obtain for the real and imaginary parts of $F(z)$

$$F'(\omega) = \mathbf{P} \frac{1}{2\omega} \left[\epsilon + \frac{|\epsilon|}{\sqrt{\omega_\epsilon}} (\omega_\epsilon^2 + \omega^2)^{1/4} \cos \left[\frac{\theta}{2} \right] \right], \quad (4.14a)$$

$$\begin{aligned} F''(\omega) = - \left[\frac{\epsilon + |\epsilon|}{2} \right] \pi \delta(\omega) \\ - \mathbf{P} \left[\frac{|\epsilon|}{2\omega\sqrt{\omega_\epsilon}} (\omega_\epsilon^2 + \omega^2)^{1/4} \sin \left[\frac{\theta}{2} \right] \right], \end{aligned} \quad (4.14b)$$

where \mathbf{P} denotes the principal part and where $\theta = (\frac{1}{2})\arctan(\omega/\omega_\epsilon)$. At T_f , we get

$$F''_f(\omega) = - \left[\frac{\eta D_f^{-1}}{2|\omega|} \right]^{1/2}, \quad (4.15)$$

in agreement with expression (4.7). At low frequencies, such that $\omega < k_B T$, the dynamic scattering law reads

$$S(\mathbf{q}, \omega) = -T\Phi''(\mathbf{q}, \omega). \quad (4.16)$$

Using definition (4.3), we have $\Phi''(\omega) = D^{-1}F''(\omega)$. Con-

sidering expression (4.14b) for $F''(\omega)$ for T close to T_f such that $\omega_\epsilon < \omega$, we finally obtain

$$S(\mathbf{q}, \omega) = TD^{-1}(q) \left[\left[\frac{|\epsilon| + \epsilon}{2} \right] \pi \delta(\omega) - \left[1 - \frac{\omega_\epsilon}{2|\omega|} \right] F_f''(\omega) \right]. \quad (4.17)$$

The first term within square brackets is different from zero for $T < T_f$ where $\epsilon = \phi(\mathbf{q})$. It represents a static central-peak contribution of intensity

$$\Psi_n(\mathbf{q}) \equiv TD^{-1}(\mathbf{q})\phi(\mathbf{q}). \quad (4.18)$$

Starting from 0 at T_f , Ψ_n , due to nonergodicity, increases continuously with decreasing T . Ψ_n accounts for collective freezing processes and exhibits a characteristic q dependence.¹⁷ In addition, there is a further contribution Ψ_h , due to local freezing, to the central peak intensity. Ψ_h is a direct consequence of the coupling V^{RS} of random strain fields to the orientational order parameter. Its intensity is given by¹¹

$$\Psi_h^{YY} = x(y/T)^2 x(1-x)h^2. \quad (4.19)$$

The sum

$$\Psi^{YY}(\mathbf{q}) = \Psi_n^{YY}(\mathbf{q}) + \Psi_h^{YY} \quad (4.20)$$

is shown in Fig. 1. In presence of strong random fields, Ψ_h^{YY} is zero (see remark at the end of Sec. III), and the central peak intensity is solely due to local freezing processes. We believe that this situation occurs in $(\text{NaCN})_{1-x}(\text{KCN})_x$ with $x = 0.5$.³³

The second term within square brackets in Eq. (4.17) is proportional to $F_f''(\omega)$ and therefore leads to a quasielastic central peak, the intensity of which has a $\omega^{-1/2}$ singularity. Away from T_f , the quasielastic intensity decreases with increasing ω_ϵ and disappears for $\omega_\epsilon = 2\omega$. The decrease is asymmetric in T with respect to T_f , since ϵ is

given by expressions (4.10a) and (4.10b) for $T > T_f$ and $T < T_f$, respectively. Recent neutron^{34,35} and Brillouin³⁶ scattering data suggest the existence of a dynamic central peak in addition to the static component.

V. MICROSCOPIC RELAXATION

Here we want to study the T and ω dependence of the displacement-displacement response function, with particular emphasis on the phonon damping. Low-frequency shear response experiments²⁰ have shown anomalous elastic loss peaks to occur in $\text{K}(\text{CN})_x\text{Br}_{1-x}$. In a recent extension of these experiments,²² it has been found that additional relaxation processes influence the T dependence of the elastic constants c_{44} .

We start again from Eq. (3.1), where we consider the memory kernels $\Pi(z)$ and $\sigma(z)$ in the slow dynamics regime according to Sec. IV. Using Eqs. (3.2), (3.6), and (3.14), we find

$$\begin{aligned} \Pi(z) - \sigma(z) = & -D(\mathbf{q}) \frac{1}{N} \sum_{\mathbf{p}} K(\mathbf{q}, \mathbf{p}) F(\mathbf{p}, z) \\ & + \frac{i\beta^\dagger(\mathbf{q})X\beta(\mathbf{q})\gamma}{\langle \omega^2 \rangle_0}. \end{aligned} \quad (5.1)$$

The first term on the right-hand side is rewritten by means of Eqs. (4.9) and (4.8) with the result

$$-D(\mathbf{q}) \frac{1}{N} \sum_{\mathbf{p}} K(\mathbf{q}, \mathbf{p}) F(\mathbf{p}, z) = -D_f(\mathbf{q}) F(\mathbf{q}, z) \quad (5.2)$$

for $T > T_f$. Since $D \propto \chi^{-1}$ and since $\chi(\mathbf{q})$ for $\mathbf{q} \approx \mathbf{0}$ is almost constant for $T < T_f$, we adopt Eq. (5.2) also for $T < T_f$. The second term on the right-hand side of Eq. (5.1) accounts for single-particle orientational relaxation. In principle, γ is frequency dependent and identification with single-particle dynamics yields

$$\frac{\gamma}{\langle \omega^2 \rangle_0} \rightarrow (z + i\lambda)^{-1}, \quad (5.3)$$

where λ is a relaxation frequency. Taking into account Eqs. (5.2) and (5.3), we get for Eq. (5.1)

$$\Pi(z) - \sigma(z) = -D_f(\mathbf{q}) F(\mathbf{q}, z) + i\eta(\mathbf{q}, z), \quad (5.4a)$$

where

$$\eta(\mathbf{q}, z) = \frac{\Delta(\mathbf{q})}{z + i\lambda}, \quad (5.4b)$$

with $\Delta(\mathbf{q}) = \beta^\dagger(\mathbf{q})X\beta(\mathbf{q})$. In the following, we assume that the relaxation frequency λ is given by an Arrhenius-type expression

$$\lambda = \lambda_0 \exp(-A/T). \quad (5.5)$$

Here λ_0 is an attempt frequency and A is an activation energy. We notice that for $\lambda > z$, η reduces to expression (4.5). This situation, which corresponds to the fast relaxation case, breaks down at low T close to T_f .

Taking into account Eq. (5.4a) we rewrite (3.1) as

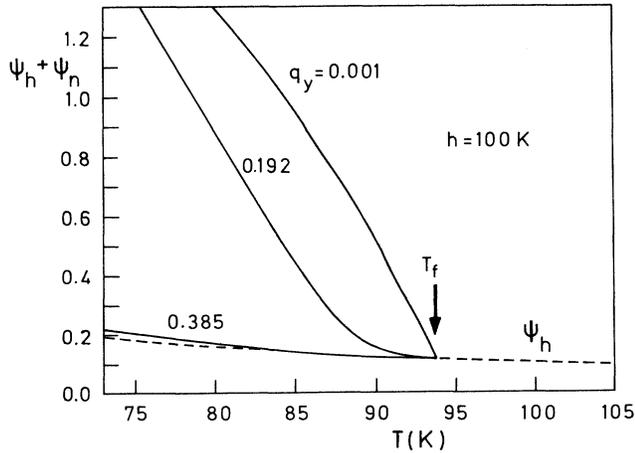


FIG. 1. Glass order parameter $\Psi^{YY}(\mathbf{q})$, Eq. (4.20), as function of temperature and wave vector, random field $h = 100$ K.

$$[\mathbb{1}z^2 - D - zD_f F(z) + iz\eta(z)]\Phi^{ss}(z) = [\mathbb{1}z - D_f F(z) + i\eta(z)]D^{-1}. \quad (5.6)$$

We consider the component Φ_{11}^{ss} with $\mathbf{q}=(0,q,0)$. The imaginary part of Φ reads

$$\Phi^{ss''}(\omega) = \frac{\Sigma''(\omega)}{[\omega^2 - D - \omega\Sigma'(\omega)]^2 + [\omega\Sigma''(\omega)]^2}, \quad (5.7)$$

where

$$\Sigma'(\omega) = D_f F'(\omega) + \frac{\omega\Delta}{\omega^2 + \lambda^2}, \quad (5.8a)$$

$$\Sigma''(\omega) = D_f F'' - \frac{\lambda\Delta}{\omega^2 + \lambda^2}, \quad (5.8b)$$

with F' and F'' given by expressions (4.14a) and (4.14b), respectively. Here it is understood that we consider the 1-1 component of matrices Δ , D , and F . In Fig. 2 we have plotted the scattering function $\Phi^{ss''}(\omega)$, given by Eq. (5.7), taking $\mathbf{q}=(0,q,0)$, $q=10^{-3}(\pi/a)$ with $a=3.26$ Å. In expressions (5.8a) and (5.8b) for Σ' and Σ'' , we take $\omega=\sqrt{D_{11}(q)}$. At $T_f=93.5$ K, we find a central peak, which is due to the slow relaxation processes, accounted for by the function $F''(\omega)$. The side peaks describe the phonon resonances. We have taken $\lambda_0=100$ THz, $A=300$ K, which gives $\lambda\approx 4$ THz near T_f . Obviously we are in the fast relaxation case; the features due to microscopic relaxation are flat and disappear in the background. We notice the asymmetry with respect to T_f in the T dependence of the central peak intensity. (See also comments at the end of Sec. IV.) The integrated intensity of the central peak increases strongly for $T \rightarrow T_f$, in qualitative agreement with Brillouin scattering experiments.²¹

In order to study the frequency and temperature dependence of the shear restoring forces, we have calculated the quantity

$$\bar{D}_{11}(\mathbf{q}, \omega) = [D_{11}(\mathbf{q}) + \omega\Sigma'_{11}(\mathbf{q}, \omega)]M_{11}^{-1}(\mathbf{q}) \quad (5.9)$$

for $\mathbf{q}=(0,q,0)$. We recall that $D_{11} \propto c_{44}q^2$. In Fig. 3 we show the transition from the regime $\omega < \lambda$ to $\omega > \lambda$. Obviously, the location of the minimum of D_{11} , or equivalently of the transverse-acoustic (TA) phonon ener-

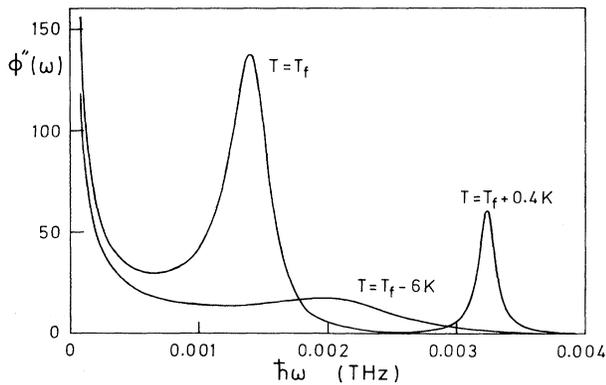


FIG. 2. Dynamic scattering law, Eq. (5.7)

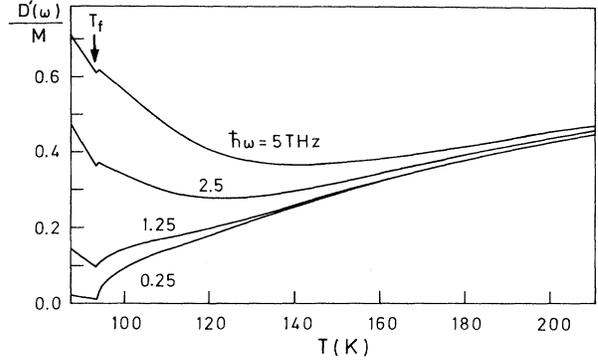


FIG. 3. Normalized squared phonon frequency $D'(\omega)/M$ as function of temperature close to T_f for various values of ω .

gy, which was originally discovered by neutron³⁷ and Brillouin³⁸ scattering, is shifted to higher values $T_m(\omega)$ for increasing energy transfer. Experimentally, this fact has been known for some time.^{18,19,39} However, a theory based solely on microscopic relaxation processes⁴⁰ could only account incompletely⁴ for the experimental situation. In particular, the occurrence of a static central peak, which is the signature of freezing, could not be understood. Furthermore, the anomalously strong damping of TA phonons is beyond the reach of a simple relaxation model.⁴¹

Recent low-frequency shear response experiments suggest that the primary loss phenomena and dispersion effects are due to different physical processes.²² We have therefore calculated the ultrasonic attenuation coefficient for acoustic shear modes

$$\alpha(\omega) = -\left(\frac{1}{2}\right)\mathbf{q}\omega^2\Sigma''(\mathbf{q}, \omega)[D'(\mathbf{q}, \omega)]^{-3/2}, \quad (5.10a)$$

with

$$D'(\mathbf{q}, \omega) = D(\mathbf{q}) + \omega\Sigma'(\mathbf{q}, \omega), \quad (5.10b)$$

where again we consider only 1-1 components and $\mathbf{q}=(0,q,0)$ and where $\omega=\sqrt{D_{11}(\mathbf{q})}$. Figures 4 and 5 refer to the cases $A=300$ and 900 K, which correspond to fast and slow microscopic relaxation, respectively. Notice that in both cases there is a strong increase of the

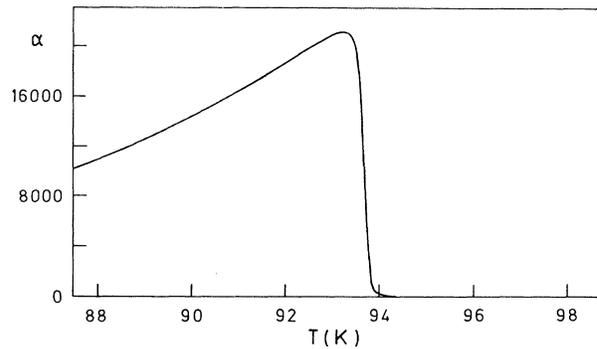


FIG. 4. Ultrasonic attenuation α , activation energy $A=300$ K.

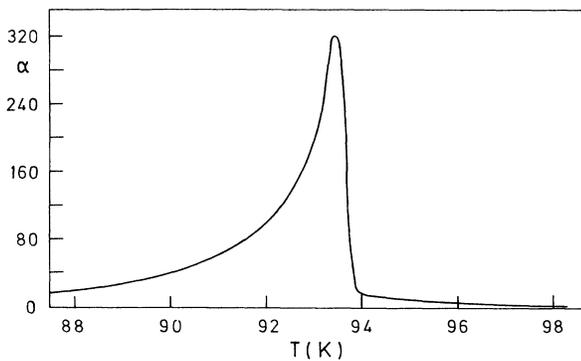


FIG. 5. Same as Fig. 4, $A = 900$ K.

attenuation at T_f . It is a consequence of the $\omega^{-1/2}$ singularity in $F''(\omega)$, Eq. (4.15), and therefore of the slow dynamics associated with structural arrest. Furthermore, we notice that the asymmetric T dependence with respect to the maximum of α near T_f reflects the corresponding asymmetric T behavior of $F''(\omega)$. (See remarks at the end of Sec. IV.) The asymmetric T dependence of the attenuation is in agreement with experiment.^{20,41} Finally, we show in Fig. 6 the attenuation α as function of the measuring frequency ω . We recall that the anomalous increase of the attenuation α is absent in KCN,⁴² where the ferroelastic phase transition is of first order.

VI. DISCUSSION

We have presented a theory where the transition to the orientational glass state in mixed crystals is essentially a dynamic phenomenon. As a particular example, we have in mind the quadrupole glass $\text{K}(\text{CN})_x\text{Br}_{1-x}$. We therefore confront our results with the experimental situation in that substance.

A direct signature of the glass state is the appearance of a static central peak in neutron scattering.³ The central peak has a characteristic temperature and wave-

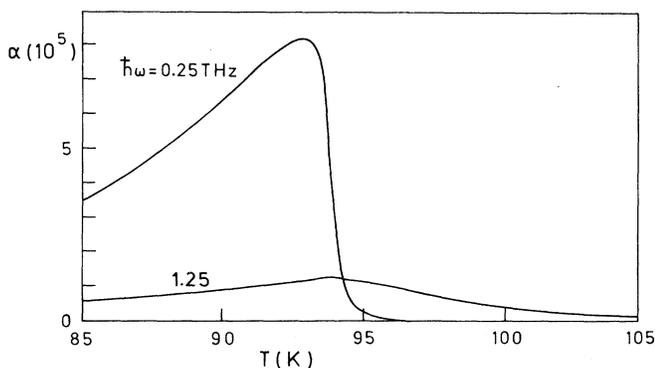


FIG. 6. Attenuation for high and low frequencies, $A = 300$ K.

vector dependence. We find [Eq. (4.20) and Fig. 1] that the central peak intensity is a sum of two contributions, a first one Ψ_h already present in the orientationally disordered phase and varying as T^{-2} . It is \mathbf{q} independent and accounts for local freezing. The second contribution $\Psi_n(\mathbf{q})$ is due to the nonergodic instability, and represents a collective freezing process. Its intensity is zero at T_f and then increases continuously with decreasing T . The total central peak intensity has therefore a steeper increase than a T^{-2} law for $T < T_f$. This fact had been pointed out previously⁴³ when the intensity Ψ_h was compared with the experimental situation in $\text{K}(\text{CN})_x\text{Br}_{1-x}$ for $x \approx 0.5$. From the \mathbf{q} dependence of $\Psi_n(\mathbf{q})$ in Fig. 1, we conclude that for $T < T_f$, correlated regions of dimensions q^{-1} and infinite lifetime start to build up. For a given T , regions of larger extension are blocked more easily than smaller regions. This fact is reminiscent of the situation at a second-order phase transition, where long-range correlations have a longer (finite) lifetime than short-range ones. The proximity of a second-order phase transition in the case $x \approx 0.50$ is also borne out by diffuse scattering intensities measured by neutron scattering³⁴ and by low-frequency shear response experiments^{20,22} in $\text{K}(\text{CN})_x\text{Br}_{1-x}$.

The low-frequency experiments are particularly instructive, since they allow the study of slow relaxation processes. The primary elastic loss peak in the $x = 0.50$ sample occurs at a temperature $T_f = 75$ K, where the elastic constant c_{44} reaches its minimum. The situation is in qualitative agreement with our theoretical results on the ultrasonic attenuation α (Figs. 4 and 5). The elastic loss peak is due to the slow dynamics associated with structural arrest [Eqs. (4.14a) and (4.14b)] and affects the memory kernel $\Pi(z)$ in Eq. (4.1a) for the displacement relaxation function $\Phi^{ss}(q, z)$. Notice that the asymmetric T dependence (with respect to T_f) of α is also in qualitative agreement with experiment.^{20,41}

It has been suggested that the primary elastic loss is due to dissipative motion of the walls of ferroelastic quasidomains. This physical picture does not contradict our theoretical formulation. Indeed, we can identify the domains with the correlated regions, described by $\Psi_n(\mathbf{q})$ in the glass state, and by the relaxation function $F(\mathbf{q}, z)$ (see Sec. IV) in the regime of slow dynamics.

The presence of microscopic relaxation effects is obvious from many experimental data.^{18,19} In particular, the T value where the elastic constant c_{44} is minimum depends on the measuring frequency of the experimental method. Our formulation (Sec. V) takes into account single-particle orientational relaxation. The results of Fig. 3 show that the position of the minimum shifts to higher- T value with increasing frequency. Concomitantly, the values of $D'(\omega)$ at low T are much lower for the low-frequency case than for the high-frequency case. Also, here our results agree with experiment,²² in particular, one sees that the low- T results of $D'(\omega)$ in the low-frequency case are much lower than the corresponding high- T results. The low-frequency results demonstrate that the crystal remains soft to a large extent below T_f .

The essential new feature in dynamic scattering law Eq. (4.17) is the appearance of a dynamic central peak. It

accounts for the slow dynamics at structural arrest. There are experimental indications for such a phenomenon,³⁴⁻³⁶ which is still a subject of current research.

The static and dynamic phenomena which are typical for a nonergodic instability seem to account for the experimental situation in $\text{K}(\text{CN})_x\text{Br}_{1-x}$ for $x \approx 0.5$.²² This value is close to x_c , where for $x > x_c \approx 0.57$ the system still exhibits a second-order phase transition.⁴⁴ In Table I we have demonstrated that the nonergodic instability is suppressed at low values of x . Here random-field effects dominate in comparison with the collective interaction, and the freezing process is a local phenomenon.

The concepts which are at the basis of the present theory are rather general. Substitutional disorder leads to random strain fields, which have two effects: (i) linear coupling to the order parameter and (ii) scattering of dy-

namic waves, giving rise to a nonergodic instability. It is still an open and interesting problem to investigate whether (ii) applies also to other glass-forming mixed crystals such as $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$.⁴⁵ Here the influence of local random fields on the proton freezing has been studied.⁴⁶ Neutron-scattering results⁴⁷ suggest that dynamic phenomena, possibly associated with a nonergodic instability, are important.

ACKNOWLEDGMENTS

The authors are grateful to W. Götze, K. Knorr, A. Loidl, C. Garland, R. Pick, D. Walton, P. Wochner, and J. Krüger for useful discussions. Financial support has been obtained from the Interuniversitair Instituut voor Kernwetenschappen, Belgium.

- ¹N. E. Cusack, *The Physics of Structurally Disordered Matter* (Hilger, London, 1987).
- ²K. Binder and A. P. Young, *Rev. Mod. Phys.* **58**, 801 (1986).
- ³J. M. Rowe, J. J. Rush, D. G. Hinks, and S. Susman, *Phys. Rev. Lett.* **43**, 1158 (1979).
- ⁴K. H. Michel and J. M. Rowe, *Phys. Rev. B* **22**, 1417 (1980).
- ⁵K. H. Michel, *Phys. Rev. Lett.* **57**, 2188 (1986); *Phys. Rev. B* **35**, 1405 (1987).
- ⁶L. J. Lewis and M. L. Klein, *Phys. Rev. Lett.* **57**, 2698 (1986).
- ⁷K. Knorr and A. Loidl, *Phys. Rev. B* **31**, 5387 (1985).
- ⁸J. O. Fossum and C. W. Garland, *Phys. Rev. Lett.* **60**, 592 (1988).
- ⁹T. Schneider and E. Pytte, *Phys. Rev. B* **15**, 1519 (1977).
- ¹⁰A. B. Harris and H. Meyer, *Can. J. Phys.* **63**, 3 (1985).
- ¹¹K. H. Michel, *Phys. Rev. B* **35**, 1414 (1987).
- ¹²A. P. Mayer and R. A. Cowley, *J. Phys. C* **21**, 4835 (1988).
- ¹³K. H. Michel, *Z. Phys. B* **68**, 259 (1987).
- ¹⁴W. Götze, *Solid State Commun.* **27**, 1393 (1978); *J. Phys. C* **12**, (1279); *Philos. Mag. B* **43**, 219 (1981).
- ¹⁵E. Leutheusser, *Phys. Rev. A* **29**, 2765 (1984).
- ¹⁶U. Bengtzelius, W. Götze, and A. Sjölander, *J. Phys. C* **17**, 5915 (1984).
- ¹⁷C. Bostoën and K. H. Michel, *Z. Phys. B* **71**, 369 (1988).
- ¹⁸C. W. Garland, J. Z. Kwiecien, and J. C. Damien, *Phys. Rev. B* **25**, 5818 (1982).
- ¹⁹U. G. Volkman, R. Böhmer, A. Loidl, K. Knorr, U. T. Höchli, and S. Haussühl, *Phys. Rev. Lett.* **56**, 1716 (1986).
- ²⁰K. Knorr, U. G. Volkman, and A. Loidl, *Phys. Rev. Lett.* **57**, 2544 (1986).
- ²¹J. J. Vanderwal, Z. Hu, and D. Walton, *Phys. Rev. B* **33**, 5782 (1986).
- ²²J. Hessinger and K. Knorr, *Phys. Rev. Lett.* **63**, 2749 (1989).
- ²³K. H. Michel and J. Naudts, *Phys. Lett.* **39**, 212 (1977); *J. Chem. Phys.* **67**, 547 (1977).
- ²⁴D. G. Bounds, M. L. Klein, and I. R. McDonald, *Phys. Rev. Lett.* **46**, 1682 (1981); S. D. Mahanti and S. Sahu, *ibid.* **48**, 936 (1981); *Phys. Rev. B* **26**, 2981 (1982).
- ²⁵R. Kubo, *J. Phys. Soc. Jpn.* **12**, 570 (1957); L. P. Kadanoff and P. C. Martin, *Ann. Phys. (NY)* **24**, 419 (1963).
- ²⁶H. Mori, *Progr. Theor. Phys. Jpn.* **33**, 423 (1965); R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. Brittin and L. Dunham (Wiley, New York, 1961), Vol. 3, p. 135.
- ²⁷K. H. Michel, *J. Chem. Phys.* **84**, 3451 (1986); *Z. Phys. B* **61**, 45 (1985).
- ²⁸K. Kawasaki, *Phys. Rev.* **150**, 291 (1966); *Ann. Phys. (NY)* **61**, 1 (1970).
- ²⁹W. Götze, *Liquid-Glass Transition*, Lecture Notes Université de Neuchâtel, 1987 (unpublished); *Z. Phys. B* **56**, 139 (1984).
- ³⁰C. De Dominicis, *Phys. Rev. B* **18**, 4913 (1978); S.-K. Ma and J. Rudnick, *Phys. Rev. Lett.* **40**, 589 (1978); J. A. Hertz and R. A. Klemm, *ibid.* **21**, 1397 (1978).
- ³¹H. Sompolinsky and A. Zippelius, *Phys. Rev. B* **25**, 6860 (1982).
- ³²W. Götze and L. Sjögren, *J. Phys. C* **17**, 5759 (1984).
- ³³A. Loidl, T. Schröder, R. Böhmer, K. Knorr, J. K. Kjems, and R. Born, *Phys. Rev. B* **34**, 1238 (1986); T. Schröder, A. Loidl, T. Vogt, and V. Frank, *Physica B* **156&157**, 195 (1989).
- ³⁴A. Loidl, T. Schröder, K. Knorr, R. Böhmer, B. Mertz, G. J. McIntyre, T. Vogt, H. Mutka, M. Müllner, H. Jex, and S. Haussühl, *Z. Phys. B* **75**, 81 (1989).
- ³⁵P. Wochner, E. Burkel, J. Peisl, C. M. E. Zeyen, and W. Petry, in *Dynamics of Disordered Materials*, Vol. 37 of *Springer Proceedings in Physics*, edited by D. Richter, A. J. Dianoux, W. Petry, and J. Teixeira (Springer, Berlin, 1989).
- ³⁶Z. Hu, J. J. Vanderwal, and D. Walton, *Phys. Rev. B* **37**, 9072 (1988).
- ³⁷J. M. Rowe, J. J. Rush, N. J. Chessier, D. L. Hinks, and S. Susman, *J. Chem. Phys.* **68**, 4320 (1978).
- ³⁸S. K. Satija and C. H. Wang, *Solid State Commun.* **28**, 617 (1978).
- ³⁹A. Loidl, R. Feile, and K. Knorr, *Phys. Rev. Lett.* **48**, 1263 (1982).
- ⁴⁰K. H. Michel, J. Naudts, and B. De Raedt, *Phys. Rev. B* **25**, 5818 (1982).
- ⁴¹Z. Hu, D. Walton, and J. J. Vanderwal, *Phys. Rev. B* **38**, 10830 (1988).
- ⁴²M. Boissier, R. Vacher, D. Fontaine, and R. M. Pick, *J. Phys.* **39**, 205 (1977).
- ⁴³J. M. Rowe and A. Loidl (private communication).
- ⁴⁴J. Ortiz-Lopez and F. Luty, *Phys. Rev. B* **37**, 5452 (1988).
- ⁴⁵E. Courtens, *Jpn. J. Appl. Phys.* **24**, Suppl. 24-2, 70 (1985).
- ⁴⁶R. Pirc, B. Tadic, and R. Blinc, *Phys. Rev. B* **36**, 8607 (1987).
- ⁴⁷E. Courtens, R. A. Cowley, and H. Grimm, *Ferroelectrics* **78**, 275 (1988); H. Grimm, in *Dynamics of Disordered Materials* (Ref. 35), p. 274.