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Anharmonic dynamics of defect pairs in soft-mode systems

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Molecular-dynamics calculations have been performed for two-dimensional soft-mode systems with defects. An isolated defect, which is softer than the host crystal, produces a localized vibration below the phonon band whose frequency decreases with decreasing temperature $T > T_c$; finally, in the vicinity of T_c, there is a change from oscillator to relaxator behavior connected with the appearance of a central peak, whose height increases rapidly upon approaching T_c. For low defect concentrations c this effect leads to a linear c dependence of the central peak in the dynamical structure factor $S_{\mathbf{q}=0}(\omega)$. In the case of defect pairs, the dynamical structure factors of the localized modes show a strong dependence on the defect distance. For finite defect concentrations this gives rise to a c^2 contribution to the central peak in $S_{\mathbf{q}=0}(\omega)$ and a temperature-dependent distribution of relaxation times, which governs the central-peak shape. The connection to light scattering and dielectric measurements in systems with low defect concentrations is discussed.

I. INTRODUCTION

In the last years much experimental (for a review see Ref. 1) and theoretical[1-5] effort has been devoted to the problem of soft-mode systems with defects. From the experimental point of view this question is interesting for three reasons: Any real crystal contains impurities, many experimental methods[6] use special impurities as probes (NMR, EPR, Mössbauer spectroscopy), and there exist systems which show a drastic change in their physical properties even with low defect concentrations [e.g., $KTaO_3$ with Li (Refs. 7 and 8), Na, or Nb (Refs. 9–11)]. From the theoretical point of view, the anharmonic dynamics of the vibrations localized near the defects and the defect influence on the global dynamics [e.g., the dynamical structure factor of the soft-mode $S_{\mathbf{q}=0}(\omega)$] are of special interest.

A theoretical treatment of the low-concentration problem starts often, in a first step, with a single-defect system. Such a model describes a situation where the defect distances are so large that their interaction can be neglected; it leads to a single localized vibration and a linear concentration dependence of the defect influence on global properties, e.g., on the central-peak intensity of the soft-mode dynamical structure factor. In a second step, isolated pairs with a defect distance **d** can be treated. One expects a **d**-dependent frequency splitting of the localized modes due to the interaction between the two defects.

Earlier mean-field approximation (MFA) investigations[3] of *single-defect systems* yielded, for certain defect parameters, a localized vibration below the phonon band, whose frequency ω_l goes to zero at a temperature T_c^{loc} above T_c. A corresponding two-dimensional (2D) molecular-dynamics (MD) treatment[12,13] yielded, for temperatures far above T_c, a decrease of ω_l parallel to that of the soft-mode frequency. This is in agreement with the respective MFA results. However, in contrast to the MFA results, the frequency does not become zero above T_c, but levels off and approaches the soft-mode frequency; the mode changes its character from oscillator to relaxator which is indicated by the rise of a central peak in the dynamical structure factor. The central peak begins to form at a temperature $T^R > T_c$. It increases with decreasing temperature, exceeds the phonon peak at a temperature T^{OR} with $T_c < T^{OR} < T^R$, and increases strongly at T_c. These effects occur both for order-disorder and displacive defects. The defect relaxator connected with the central peak can be identified with the slow motion which is found above T_c in many measurements on mixed systems with a low concentration of soft defects [e.g., in $KTaO_3$:Nb under high pressure[10,14] or in $KTaO_3$:Li (Refs. 15 and 16).

In the following we present MD calculations for a *two-defect system* and discuss the influence of the defect distance **d** on the dynamics of the system and especially on the oscillator-relaxator transition temperature T^{OR}. The results are used to determine the concentration dependence of the central-peak intensity for a macroscopic crystal with a finite concentration c of defects (particularly the c^2 term). The notations for modes and characteristic temperatures are summarized in Table I.

Section II contains a description of the model and the MD technique. In Sec. III the numerical calculations and the results are presented and discussed. In Sec. IV the defect influence on $S_{\mathbf{q}=0}(\omega)$ for a macroscopic crystal with a finite concentration is derived. In Sec. V, finally, the main results are summarized.

II. MODEL AND MD TREATMENT

The molecular-dynamics calculations are performed for a 2D square lattice with a local 2-4 potential and a harmonic nearest-neighbor interaction. For the sake of simplicity we use a one-dimensional order parameter, i.e., scalar local normal coordinates X_{n}. The Hamiltonian of this system is

$$h=\sum_{\mathrm{n}}\left[\frac{1}{2m}P_{\mathrm{n}}^2+\tfrac{1}{2}(a+\Delta a_{\mathrm{n}})X_{\mathrm{n}}^2+\tfrac{1}{4}(b+\Delta b_{\mathrm{n}})X_{\mathrm{n}}^4\right]-\tfrac{1}{2}\sum_{\mathrm{m,n}}V_{\mathrm{nm}}X_{\mathrm{n}}X_{\mathrm{m}} \tag{2.1}$$

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TABLE I. Notation of modes and of characteristic temperatures.

Indices $\mu = 0$, 1, s, and a	Label soft mode, local single-defect mode, symmetric, and antimetric defect-pair modes, respectively.
Indices $d = 1$, 2, and ∞	Indicate pair separation (in multiples of the lattice constant); $d = \infty$: single defects.
T_μ^R	Temperature at which the central peak of mode μ begins to form.
T_μ^{OR}	Temperature of oscillator-relaxator transition for mode μ.

(with $V_{\mathrm{nm}} = C$ for nearest neighbors and zero otherwise). Introducing reduced quantities $[X_i = (C/b)^{1/2} x_i$, $h = C^2/bH$, $\tau = (1/mC)^{1/2} t$, where τ is the original and t the reduced time] one obtains

$$H = \sum_{\mathrm{n}} \left[\frac{p_{\mathrm{n}}^2}{2} + \frac{1}{2} A_{\mathrm{n}} x_{\mathrm{n}}^2 + \frac{1}{4} B_{\mathrm{n}} x_{\mathrm{n}}^4 \right] - \frac{1}{2} \sum_{\mathrm{m,n}} v_{\mathrm{nm}} x_{\mathrm{n}} x_{\mathrm{m}} \ ,$$

where the interaction is $v_{\mathrm{nm}} = 1$ for nearest neighbors and zero otherwise. Identical defects positioned at $\mathbf{n} = (0,0)$ and $\mathbf{n} = \mathbf{d}$ are described by the local potential parameters

$$A_{\mathrm{n}} = A + \Delta A \delta_{\mathrm{n0}} + \Delta A \delta_{\mathrm{nd}} \ ,$$
$$B_{\mathrm{n}} = 1 + \Delta B \delta_{\mathrm{n0}} + \Delta B \delta_{\mathrm{nd}} \ .$$

The simulation of constant-temperature conditions by stochastic forces $f_n(t)$ and a corresponding friction γ given by

$$\langle f_{\mathrm{n}}(t) f_{\mathrm{m}}(t') \rangle = 2\gamma T \delta(t - t')$$

leads to a Langevin equation of motion:

$$\ddot{x}_{\mathrm{n}} = -A_{\mathrm{n}} x_{\mathrm{n}} - B_{\mathrm{n}} x_{\mathrm{n}}^3 + \sum_{\mathrm{m}} v_{\mathrm{nm}} x_{\mathrm{m}} - \gamma \dot{x}_{\mathrm{n}} + f_{\mathrm{n}}(t) \ . \tag{2.2}$$

Equation (2.2) is integrated numerically with an algorithm similar to that proposed by van Gunsteren and Berendsen.[17] The global behavior of the system is described by the time-dependent correlation function

$$\langle Q_0(t) Q_0(0) \rangle - \langle Q_0^2 \rangle \tag{2.3}$$

of the soft-mode coordinate

$$Q_0(t) = \frac{1}{\sqrt{N}} \sum_{\mathrm{n}} x_{\mathrm{n}}(t) \ . \tag{2.4}$$

Information about the local behavior is obtained from the correlation functions of the symmetric (Q_s) and of the antisymmetric (Q_a) combinations of the defect coordinates x_0 and x_{d}:

$$\begin{aligned} Q_{s_d} &= \frac{1}{\sqrt{2}} (x_0 + x_{\mathrm{d}}) \ , \\ Q_{a_d} &= \frac{1}{\sqrt{2}} (x_0 - x_{\mathrm{d}}) \ . \end{aligned} \tag{2.5}$$

In Eq. (2.5) we assumed, for the sake of simplicity, local modes of the form

$$\begin{aligned} | u^{s_d} \rangle_{\mathrm{m}} &= \frac{1}{\sqrt{2}} (\delta_{\mathrm{m},0} + \delta_{\mathrm{m,d}}) \ , \\ | u^{a_d} \rangle_{\mathrm{m}} &= \frac{1}{\sqrt{2}} (\delta_{\mathrm{m},0} - \delta_{\mathrm{m,d}}) \ , \end{aligned} \tag{2.6}$$

which reflect the main features of the real localized modes of a crystal with a defect pair. This is justified for the determination of the frequency dependence of correlation functions, which is not very sensitive to the assumed local-mode shapes. The scattering intensities, however, depend strongly on the latter. Below, when the defect influence on the dynamical structure factor of the $\mathbf{q} = \mathbf{0}$ mode is discussed, we shall therefore assume more realistic localized modes.

From the time-dependent correlation functions the dynamical structure factors of the interesting modes $v = 0, s, a$ are obtained by Fourier transformation:

$$S_v^* \, | \omega | = \frac{S_v \, | \omega |}{\langle Q_v^2 \rangle} = \frac{1}{\pi} \int \frac{\langle Q_v(t) Q_v(0) \rangle}{\langle Q_v^2 \rangle} \cos(\omega t) dt \ . \tag{2.7}$$

III. NUMERICAL CALCULATIONS AND RESULTS

The numerical calculations were performed for a system of size 15×15. The value $A = 2$ was chosen for the local potential parameter which corresponds to a critical temperature $T_c = 1.93$ (measured in units of C^2/kb). In cases where defects are present, we choose, unless stated otherwise,

$$A_0 = A_{\mathrm{d}} = B_0 = B_{\mathrm{d}} = 0.2 \ .$$

Thus, the defect as well as the host cells are of displacive type.

First, to investigate the *local dynamics*, we determined the dynamical structure factor of the symmetric (Q_s) and antisymmetric (Q_a) localized modes for different defect distances. Figures 1(a) and 1(b) show S_s and S_a for nearest $[\mathbf{d} = (1,0)]$ and third-nearest-neighbor defect pairs $[\mathbf{d} = (2,0)]$, respectively, as functions of the frequency for different temperatures above T_c. For comparison, Fig. 1(c) shows the dynamical structure factor $S_1(\omega)$ of the single-defect localized mode for different temperatures. With increasing d, the structure factors S_s, and S_a converge towards S_1.

In the temperature region with well-defined oscillatory local modes there is a splitting between ω_s and ω_a which increases strongly with decreasing d. This is illustrated in Fig. 2, where the squares of the peak frequencies of the different $S_v(\omega)$ are represented as functions of tempera-

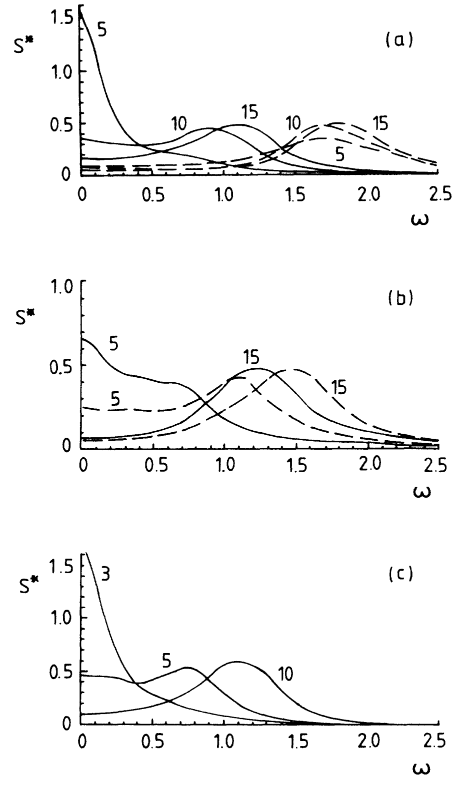

FIG. 1. Reduced dynamical structure factors $S_\lambda^*(\omega)$. The two upper parts of the figure show $S_\lambda^*(\omega)$ for the symmetric (solid lines) and the antimetric modes (dashed lines) of defect-pair systems. Distances between the two defects are (a) $\mathbf{d}=(1,0)$ (s_1 and a_1 modes) and (b) $\mathbf{d}=(2,0)$ (s_2 and a_2 modes). The bottom part (c) shows $S_1^*(\omega)$ for the localized single-defect mode $\lambda=1$. Temperatures in (dimensionless) units of C^2/kb [cf. Eq. (2.1)] are indicated at the curves. Defect parameters are $A_0=A_d=B_0=B_d=0.2$. S^* in reduced units [cf. Eq. (2.7)]. ω in units of $(mC)^{1/2}$ [cf. Eq. (2.1)].

ture. Shown are the frequencies $\omega_0, \omega_1, \omega_s, \omega_a$ of the soft mode, of the local single-defect mode, and of the two local defect-pair modes respectively, the latter for $\mathbf{d}=(1,0)$ and $\mathbf{d}=(2,0)$. The leveling of the $\omega_\nu(T)$ curves for the defect systems in the low-T region is clearly visible for defect pairs with $d=2$ (curves s_2 and a_2) and even more for pairs with $d=1$ (curves s_1 and a_1). For single defects it is noticeable only for defects softer than those described (by curve 1) in Fig. 2. Furthermore, the curves level off at temperatures increasing from single defects over $d=2$ pairs to $d=1$ pairs.

$S_s(\omega)$ shows the strongest d dependence in the low-frequency region. The oscillator-relaxator transition of this mode is shifted to higher temperatures, and the half-width of the central peak decreases drastically if d decreases. This is shown in Fig. 3 where the half-widths $\Delta\omega(d,T)$ are plotted as functions of temperature for $d=1$, $d=2$, and $d=\infty$ (isolated defect). The arrows indicate the oscillator-relaxator transition temperatures T_μ^{OR} for the different modes μ. The central peaks begin to form already at temperatures T_μ^R well above T_μ^{OR}. We obtain the following sequence

$$T_c < T_0^{OR} < T_1^{OR} < T_{s_2}^{OR} < T_{s_1}^{OR} \ ,$$

where T_0^{OR} is the temperature of the oscillator-relaxator transition in a perfect crystal.[18,19]

The defect influence on the *global dynamics* becomes noticeable in the dynamical structure factor $S_{\mathbf{q}=0}(\omega,T)$. This basic quantity is measured in many experiments. In defect-free systems it begins to form a central peak at reduced temperatures T_0^R of about 4 to 5. At $T_0^{OR}=3$ the central peak attains a height equal to that of the oscillating peak. $S_{\mathbf{q}=0}$ is affected by defects only if they are present in a finite concentration. In any computer simulation the lattice has a finite size and consequently an isolated defect or a defect pair correspond to a finite concentration.

Figure 4 shows the influence of defects on $S_{\mathbf{q}=0}(\omega,T)$ for the cases of an isolated defect, of a nearest-neighbor

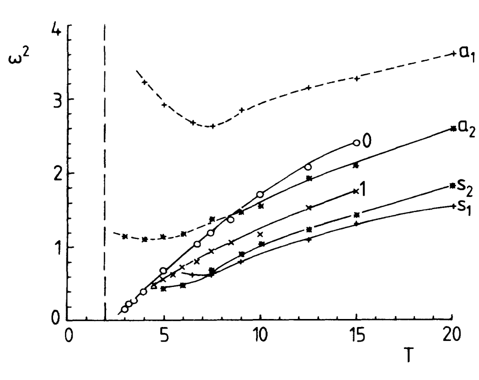

FIG. 2. Frequencies of various modes: soft mode (curve 0), localized single-defect- (curve 1), and defect-pair-modes [curves s_1 and a_1 for $\mathbf{d}=(1,0)$ and s_2 and a_2 for $\mathbf{d}=(2,0)$]. The dashed vertical line is T_c. s is the symmetric and a is the antisymmetric mode. T is in units of C^2/kb [cf. Eq. (2.1)]. ω in units of $(mC)^{1/2}$ [cf. Eq. (2.1)].

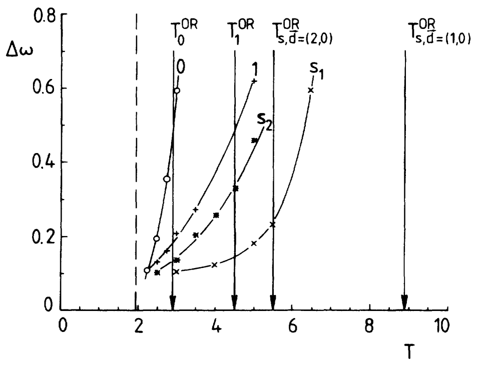

FIG. 3. Width of the central peak of various modes. Curve 0 is the soft mode of the defect-free system. Curve 1 is the localized single-defect mode. Curves s_1 and s_2 are localized symmetric modes of defect pairs with distances $\mathbf{d}=(1,0)$ and (2,0), respectively. The dashed vertical line is T_c. T is in units of C^2/kb [cf. Eq. (2.1)]. $\Delta\omega$ is units of $(mC)^{1/2}$ [cf. Eq. (2.1)].

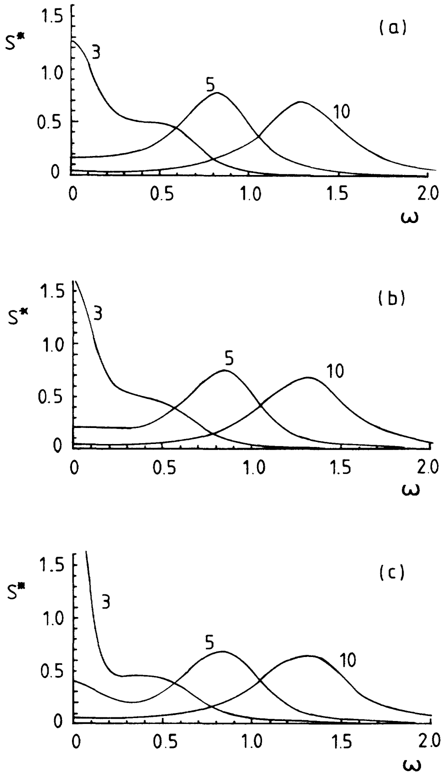

FIG. 4. Dynamical structure factor of the $\mathbf{q}=0$ mode including contributions (a) from the localized single defect mode (1). (b) and (c) from localized symmetric defect pair modes with defects at distances $\mathbf{d}=(2,0)$ (s_2 mode) and $\mathbf{d}=(1,0)$ (s_1 mode), respectively. The numbers at the curves indicate the temperatures in (dimensionless) units of C^2/kb [cf. Eq. (2.1)]. S^* is in reduced units [cf. Eq. (2.7)]. ω is in units of $(mC)^{1/2}$ [cf. Eq. (2.1)].

pair, and of a third-nearest-neighbor pair. The soft-mode frequency (in the temperature region $T>T_0^{OR}$, where the soft phonon is well defined), is not affected by the defects for the low defect concentrations ($\frac{2}{225}$ for the pair and $\frac{1}{121}$ for the single defect) considered. Near $\omega=0$, however, the dynamical structure factor changes drastically, when the temperature is decreased to values in the vicinity of or below the oscillator-relaxator transition temperature T_μ^{OR} of the relevant localized modes ($\mu=1$; $\mu=s$, $d=1$; $\mu=s$, $d=2$). The height, the reciprocal width, and the intensity of the central peak increase with decreasing d. Between T_μ^R and T_0^R, the soft-phonon peak and the central peak are coexistent. It should be stressed that the defects investigated in this paper, though being described by displacive (single-well) local potentials, lead to pronounced central peaks in $S_{\mathbf{q}=0}$ already far above the bulk transition temperature.

To study the influence of a passage of the defect parameters from the regime with distinctly displacive character towards the order-disorder regime, we performed MD simulations with different values of A_0 (and A_d) and B_0 (and B_d). Some results are shown in Figs. 5–7 for single defects and defect pairs described by different sets of potential parameters. Notice, however, that all local potentials used (host as well as defect potentials) are of the displacive (single minimum) type.

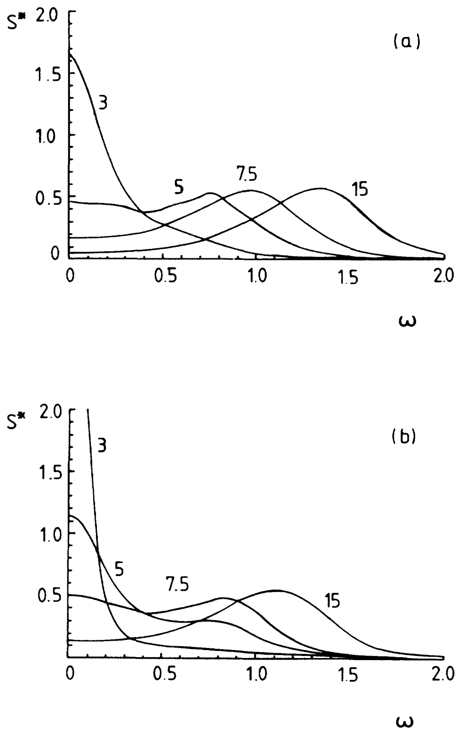

FIG. 5. Reduced [cf. Eq. (2.7)] dynamical structure factors $S_1^*(\omega)$ of single-defect systems, for two sets of defect parameters: (a) $A_0=0.2$, $B_0=0.2$; and (b) $A_0=0$, $B_0=0.1$. The numbers at the curves indicate the temperatures in (dimensionless) units of C^2/kb [cf. Eq. (2.1)]. S^* in reduced units [cf. Eq. (2.7)]. ω in units of $(mC)^{1/2}$ [cf. Eq. (2.1)].

One observes that a decrease of A_0 and B_0 (corresponding to a decrease of the displacive and an increase of the order-disorder characteristics) is accompanied by a pronounced increase of the central-peak height combined with a definite narrowing. The less-displacive-type defects exhibit a central peak already at even higher temperatures. This is shown for one-defect systems in Fig. 5 and for nearest-neighbor two-defect systems in Fig. 6. The temperature dependence of the height of the central peak is shown in Fig. 7 for defect pairs with $d=1$ and $d=2$ and for single defects. There is a gradual passage towards the Halperin- and Varma-type behavior (with a narrow central peak).

IV. $S_{\mathbf{q}=0}(\omega)$ FOR FINITE DEFECT CONCENTRATIONS

The dynamical structure factor $S_{\mathbf{q}=0}(\omega)$ allows the calculation of the imaginary and real parts of the dielectric constant with the help of the dissipation-fluctuation theorem and the Kramers-Kronig relation and is, thus,

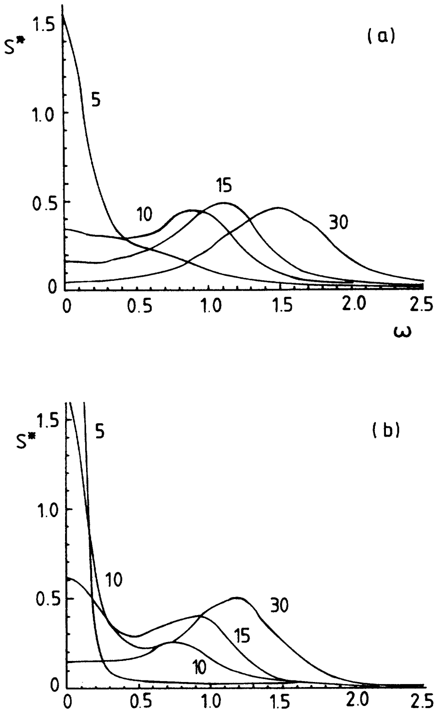

FIG. 6. Reduced [cf. Eq. (2.7)] dynamical structure factors $S_{s,d=1}(\omega)$ for the symmetric localized modes of systems with pairs of defects on nearest-neighbor sites ($d=1$), for two sets of defect parameters: (a) $A_0=0.2$, $B_0=0.2$; and (b) $A_0=0$, $B_0=0.1$. The numbers at the curves indicate the temperatures in (dimensionless) units of C^2/kb [cf. Eq. (2.1)]. S^* in reduced units [cf. Eq. (2.7)]. ω in units of $(mC)^{1/2}$ [cf. Eq. (2.1)].

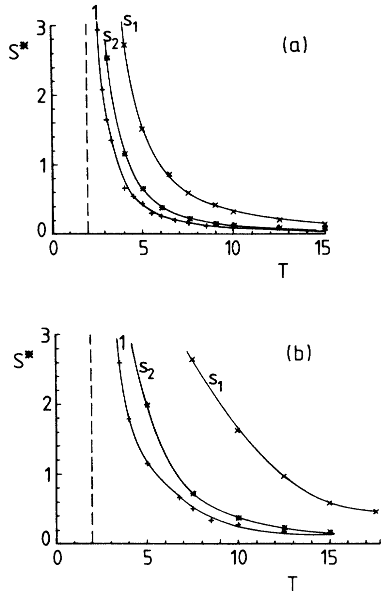

FIG. 7. Height $S^*(\omega=0)$ of the (symmetric) localized mode central peak vs temperature, for defects with two sets of defect parameters: (a) $A_0=0.2$, $B_0=0.2$; and (b) $A_0=0$, $B_0=0.1$. Curves s_1 and s_2 are pairs of defects at distances $d=1$ and 2, respectively. Curve 1 is the isolated defect. The dashed vertical lines indicate T_c. S^* in reduced units [cf. Eq. (2.7)]. T in units of C^2/kb [cf. Eq. (2.1)].

connected to the central quantities measured with light scattering and dielectric methods. The aim of this section is to derive properties of $S_{\mathbf{q}=0}(\omega)$ for a macroscopic crystal with a small but finite defect concentration from the structure factors S_1 and S_s calculated with the help of MD simulations.

For temperatures between T_μ^{OR} and T_c, $S_{\mathbf{q}=0}(\omega)$ shows a pronounced central peak, which represents a pure defect contribution above T_0^R and a superposition of both defect and soft-mode relaxations below T_0^R. In the following we derive a simple expression for $S_{\mathbf{q}=0}(\omega)$ which is valid in the temperature range $T_0^R<T<T_\mu^R$ and for ω below the soft-mode frequency.

In general, the total $S_{\mathbf{q}=0}(\omega)$ for a crystal with an isolated defect (or a defect pair) can be represented as

$$S_{\mathbf{q}=0}(\omega)=\sum_{\mu,\nu} S_{\nu\mu}(\omega)\langle u^{\mathbf{q}=0}\,|\,u^{\nu}\rangle\langle u^{\mu}\,|\,u^{\mathbf{q}=0}\rangle\ . \qquad (4.1)$$

The sum runs over a complete basis set $\{\,|u^{\nu}\rangle\}$ formed by the eigenstates of an effective harmonic crystal with a defect (or a defect pair):

$$|u^{\mathbf{q}=0}\rangle,\ \text{with}\ |u^{\mathbf{q}=0}\rangle_{\mathrm{m}}=\frac{1}{\sqrt{N}}$$

is the $\mathbf{q}=0$ mode. In the ω and T range defined above, the main contribution to the scattering intensity in Eq. (4.1) comes from the low-lying localized mode, i.e.,

$$S_{\mathbf{q}=0}(\omega)\approx S_{\tilde\lambda}(\omega)\,|\langle u^{\mathbf{q}=0}\,|\,u^{\tilde\lambda}\rangle|^2\ . \qquad (4.2)$$

The index $\tilde\lambda$ stands for $\tilde 1$ or $\tilde s$ and denotes the localized mode in the set $\{\,|u^{\nu}\rangle\}$. The structure factors $S_{\tilde 1}$ and $S_{\tilde s}$ of these actual localized modes are expressed approximately by the structure factors S_1 and S_s of the simplified modes [Eq. (2.6)]:

$$|u^{1}\rangle_{\mathrm{m}}=\delta_{\mathrm{m}0};\quad |u^{s}\rangle_{\mathrm{m}}=\frac{1}{\sqrt{2}}(\delta_{\mathrm{m}0}+\delta_{\mathrm{md}})$$

by

$$S_{\tilde\lambda}=S_{\lambda}/|\langle u^{\lambda}\,|\,u^{\tilde\lambda}\rangle|^2\ . \qquad (4.3)$$

Equation (4.3) is valid if the interaction between the localized $(\,|u^{\tilde\lambda}\rangle)$ and the extended modes in the set $\{\,|u^{\nu}\rangle\}$ is weak and in the ω range where only the localized modes contribute to the structure factor.

With the help of Eqs. (4.2) and (4.3) the defect contribution to $S_{\mathbf{q}=0}(\omega)$ can be obtained from S_1 or S_s, which were determined by MD, in the following form:

$$S^{\lambda}_{\mathbf{q}=0}(\omega)=\frac{|\langle u^{\mathbf{q}=0}\,|\,u^{\tilde\lambda}\rangle|^2}{|\langle u^{\tilde\lambda}\,|\,u^{\lambda}\rangle|^2}S_{\lambda}(\omega)\ . \qquad (4.4)$$

For exponential spatial decays

$$|u^{\tilde 1}\rangle_{\mathrm{m}}=K_1 z^{|\mathrm{m}|}$$

and

$$|u^{\tilde{s}}\rangle_{\mathrm{m}}=K_s(z^{|\mathrm{m}|}+z^{|\mathrm{m}-\mathrm{d}|})$$

of the localized states, with a temperature dependent decay rate $z(T)$ between 0 and 1 and normalization constants K_1 and K_s, one obtains

$$\frac{|\langle u^{\mathrm{q}=0}|u^{\tilde{1}}\rangle|^2}{|\langle u^{\tilde{1}}|u^{1}\rangle|^2}=\frac{1}{N}\left[\sum_{\mathrm{m}} z^{|m|}\right]^2\equiv\frac{1}{N}p_1(T) \quad (4.5\mathrm{a})$$

and

$$\frac{|\langle u^{\mathrm{q}=0}|u^{\tilde{s}}\rangle|^2}{|\langle u^{\tilde{s}}|u^{s}\rangle|^2}=\frac{2}{N}\frac{\left[\sum_{\mathrm{m}} z^{|m|}\right]^2}{1+z^{|\mathrm{d}|}}\equiv\frac{2}{N}p_s(T,d) \ . \quad (4.5\mathrm{b})$$

For a finite concentration c of defects, which are arranged either as widely separated isolated defects or as widely separated pairs with a distance d between the defects of a given pair, Eqs. (4.4) and (4.5) yield

$$S^{1}_{\mathrm{q}=0}(\omega)\approx cp_1(T)S_1(\omega) \quad (4.6\mathrm{a})$$

and

$$S^{s}_{\mathrm{q}=0}(\omega)\approx cp_s(T,d)S_s(\omega) \ . \quad (4.6\mathrm{b})$$

The approximate results of Eqs. (4.6) were compared with our MD data for systems with (1) an isolated defect, (2) a third-nearest-neighbor pair ($d=2$), and (3) a nearest-neighbor pair ($d=1$). Good agreement was obtained, in the T-ω range defined above, with $z(T)$ varying from 0.45 at $T=T^{OR}_s$ to 0.3 at $T=T^{OR}_0$.

In a real crystal, the three cases studied above (isolated defect, nearest-neighbor pair, and third-nearest-neighbor pair) appear with a certain probability which depends on the defect concentration c and on correlations between the defect sites. For a random distribution, the probability of finding a second defect at a distance d from a given defect is, to first order in c,

$$W_d=ch_d \ ,$$

where h_d is the number of sites at a distance d. Consequently, the probability of finding no second defect in the neighborhood $d\leq D$ of a given defect, i.e., of having an isolated defect (ID), is, to first order in c,

$$W_{\mathrm{ID}}=1-c\sum_{d(\leq D)} h_d \ .$$

For a crystal with a concentration c of random defects we thus obtain the following expression for the defect contribution to the dynamical structure factor:

$$S^{\mathrm{def}}_{\mathrm{q}=0}\approx cp_1S_1+c^2\sum_d h_d[p_s(d)S_{s,d}-p_1S_1] \ . \quad (4.7)$$

Two consequences of Eq. (4.7) for the experimentally observable defect influence in the central peak region are as follows.

(1) In the temperature range $T^R_s>T>T^R_{\tilde{1}}$, where only defect pairs produce a central peak, the intensity depends quadratically on the concentration c. Below $T^R_{\tilde{1}}$ one has, in addition, a linear term which dominates for small concentrations and close to T_c.

(2) Below $T^R_{s,d=1}$, the central peak is a superposition of different relaxators corresponding to defect pairs with different widths d. The number of relaxators and the relaxation time $\tau(d,T)$ increase with decreasing T leading to a temperature-dependent distribution of relaxation times whose average and width increase if T is lowered from $T^R_{s,d=1}$ to T_c.

These general results should be valid also (and even more) for order-disorder-type defects. The consequences discussed in point (2) are in qualitative agreement with dielectric measurements at $\mathrm{KTaO_3}$ doped with Li.[20]

A quantitative theoretical description of the discussed effects for a specific three-dimensional crystal—e.g., the intensively investigated system $\mathrm{KTaO_3}$:Li (or :Nb)—depends on the lattice structure, on correlations between the defect sites, and on the defect potential.[21] It should include long-range dipolar interactions which can produce a glasslike behavior.[22,23]

V. SUMMARY

Molecular-dynamics calculations were performed for a phase transition system with a pair of soft defects. We determined the frequency splitting between the symmetric and antisymmetric defect modes. It turned out to be strongly dependent on temperature and on the distance d of the defects.

The oscillator-relaxator transition temperature of the symmetric mode increases drastically with decreasing d and so do the relaxation times for a given temperature below T^{OR}.

The strong d dependence of the defect dynamics has two consequences for the dynamics of a macroscopic crystal with a finite defect concentration c: In the defect contribution to the dynamical structure factor $S_{\mathrm{q}=0}(\omega)$ a c^2 term arises besides the linear term. The central peak is a superposition of relaxator peaks with a temperature dependent distribution of relaxation times.

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