Soft modes and central peak in orientationally disordered crystals

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The coupled dynamics of translations and rotations is studied with respect to mixed molecular crystals. At high temperatures the dynamic scattering law exhibits a Brillouin doublet which softens with decreasing temperature (fast orientational relaxation regime). In diluted molecular crystals of type $(KCN)_c(KX)_{1-c}$, $X = Cl$ or Br, the structural phase transition is suppressed and one reaches the slow orientational relaxation regime at low temperatures. Then the Brillouin doublet frequency passes through a minimum and increases again with decreasing temperature. At the same time a well-defined central resonance rises in the spectrum as a consequence of slowing-down orientational relaxation. The theory describes recent neutron-scattering experiments in mixtures by Rowe and Rush and recent Brillouin-scattering results by Satija and Wang.

I. INTRODUCTION

The study of soft modes and central peaks is a subject of extensive current research. So far, one has investigated mainly these features in crystals which exhibit displacive or order-disorder phase transitions.[1] For a brief review of the recent literature, the reader should consult Ref. 2. From the experimental and theoretical work it is clear that there can exist several reasons for the occurrence of a central peak. It needs not be an intrinsic effect but could also be due to the presence of static impurities.[3] Since the width of the central peak is in many cases smaller than the experimental resolution,[4] it is very difficult to clarify unambiguously the nature of this phenomenon in order-disorder and in displacive systems.

There exists another class of crystals which are also of interest for the study of soft modes and central peaks, namely, molecular crystals or complex crystals. As complex crystals, we consider those crystals where part or all of the atoms form molecules or molecular ions. We assume that these molecules have orientational degrees of freedom. In an orientationally disordered phase, the collective dynamics of orientational relaxation[5] gives rise to a central peak which is measurable by coherent inelastic neutron scattering. The measurability depends crucially on the experimental energy resolution compared with the intrinsic frequency of the relaxation process. If the orientational relaxation is extremely fast, the corresponding central peak is broad and flat. Such a feature is easily lost in the experimental background. This is the case in the disordered phase of CD_4 at high temperature. With decreasing temperature, one approaches the orientational phase transition and the central peak emerges from the background as a consequence of critical slowing down.[6] On the other hand, in the disordered phase of ND_4Cl, the orientational relaxation is very slow, the corresponding central peak has a width smaller than the experimental resolution.[7]

In many systems, as for instance also in ND_4Cl, the coupling between orientational and translational degrees of freedom is relevant. Then, for given experimental conditions, the relative magnitude of typical phonon frequencies ω_1 with respect to the orientational relaxation frequency λ is relevant. For the case of a two states orientational system like ND_4Cl, we refer to Ref. 8. A general microscopic study of the coupled dynamics of orientations and translations is given in Ref. 9. In discussing the resonances of the dynamic displacement-displacement correlation function, one distinguishes two extreme cases: (a) fast orientational relaxation, $\lambda > \omega_1$, the inelastic scattering law exhibits a soft-mode Brillouin doublet structure, there is no central peak; (b) slow orientational relaxation, $\omega_1 > \lambda$, in addition to a nonsoft Brillouin doublet there appears a well-defined central mode due to collective orientational relaxation. In KCN one has the fortunate situation, that both regimes are accessible to experiment. In fact ultrasonic methods,[10,11] Brillouin scattering,[12-15] and neutron scattering at small wave vectors[16,17] measure case (a). On

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the other hand, by increasing the momentum transfer in neutron scattering,[17] one is also able to reach case (b).

Since λ should decrease with decreasing temperature, the question arises whether it should be possible to reach case (b) by decreasing the temperature. In pure KCN, this is prevented by the occurrence of the (first-order) phase transition near 168 K before λ becomes sufficiently small. It is therefore of interest to lower the transition temperature by adding spherical symmetric impurities. These impurities are inert in the sense that they have no orientational degrees of freedom as is the case for the CN molecular ion. One therefore considers $(KCN)_c(KX)_{1-c}$ mixtures where X stands for a spherical Br or Cl atom. The lowering of the phase transition temperature with increasing Cl concentration is confirmed by experiment.[11,18,19] From our theoretical discussion, it is obvious that a study of dynamic properties in $(KCN)_c(KX)_{1-c}$ mixtures will be most instructive. This statement is supported by recent inelastic neutron-scattering[20] and Brillouin-scattering experiments.[21] In mixtures with CN concentration $c \lesssim 0.7$, one finds[20,21] that the soft-mode frequency decreases with decreasing temperature, reaches a finite minimum value and then increases with decreasing temperature. In addition, the shape of the neutron-scattering[20] spectra at small wave vectors changes as a function of decreasing temperature from the two peak structure which characterizes the fast relaxation regime to the three peak structure which characterizes the slow relaxation regime.

The purpose of the present paper is to give a theoretical description of these features in the framework of a microscopic dynamic theory. In Sec. II, we recall some basic concepts of a Hamiltonian with translational and orientational degrees of freedom. In Sec. III we recall the dynamic equations which allow us to calculate the inelastic neutron and Brillouin-scattering laws. In particular, we give a detailed description of the dynamic displacement-displacement correlation function (Sec. IV). The resonances of this correlation function are studied in Sec. V, both for the case of pure crystals and for mixtures. Finally, a qualitative comparison with experiment is given in Sec. VI.

II. MODEL

In this section, we recall some basic features of a model Hamiltonian for a pure crystal with translational and rotational degrees of freedom.[22] As a concrete example, we refer to KCN in the orientationally disordered cubic phase above 168 K.

To describe the interaction between translations and rotations, one has to start from a potential which contains both degrees of freedom. As is common in lattice dynamics, one expands the potential in terms of deviations from well-defined equilibrium positions. This is meaningful for the translational coordinates in a periodic crystal. For the orientational coordinates, generally specified in terms of Euler angles, such an expansion is only allowed in the case where the amplitudes of orientational oscillations (librations) are very small. It becomes very questionable in the case of large amplitude orientational oscillations and it breaks down for the case of orientationally disordered phases.[5] For the same reason, the use of so-called tunneling models[23,24] which select a restricted number of molecular orientations[25,26] is relevant only at low temperatures. In order to overcome these fundamental difficulties, one should use symmetry adapted functions,[27] i.e., adequate combinations of spherical harmonics or of Wigner's D functions as dynamic variables. These functions are adequate to describe the dynamics of orientational phase transitions.[5]

Starting from a repulsive overlap force model which describes the motion of a linear (dumbbell) molecule or molecular ion in an octahedral environment, we have recently derived a Hamiltonian which contains both translational and rotational degrees of freedom.[22] The result of that derivation reads

$$H = H^T + H^R + H^{TR} . \tag{2.1}$$

Here H^T describes the pure translational part

$$H^T = \sum_{\vec{k}} \left(\frac{p_i^\dagger(\vec{k})p_i(\vec{k})}{2m} + \tfrac{1}{2}M_{ij}(\vec{k})s_i^\dagger(\vec{k})s_j(\vec{k}) \right) . \tag{2.2}$$

$s_i(\vec{k})$ denotes the Fourier transformed center of mass displacement of the unit cell, $p_i(\vec{k})$ is the conjugate momentum, and m is the total mass per unit cell; $i = x, y, z$ labels Cartesian coordinate axes. The coupling factor M_{ij} accounts for the harmonic part of the translational interaction potential. Since we are only interested in long-wavelength phenomena (elastic properties, for instance) we need only consider the translational center of mass motion. Wave vectors are denoted by $\vec{k}$.

The pure rotational part of the Hamiltonian is taken to be of the form

$$H^R = K + V^R . \tag{2.3}$$

Here the kinetic energy of rotation is given by

$$K = \sum_{\vec{k}} \frac{L_i^\dagger(\vec{k})L_i(\vec{k})}{2I} , \quad i = (1, 2) , \tag{2.4}$$

where $\vec{L}$ denotes the angular momentum (1, 2 di-

rection of principal axes of the dumbbell) and I is the moment of inertia. The orientational potential is to be taken of the form

$$V^R = V^0(\vec{k} = 0),\qquad(2.5)$$

where V^0 is a single-particle orientational potential. It describes the motion of a simple molecule in a rigid octahedral environment.[28] Expanding this potential in terms of cubic harmonics, we obtain as a first term in this expansion the so called Devonshire potential which is proportional to $K_4(\theta_n, \varphi_n)$. The orientation of the nth dumbbell is specified by the polar angles θ, φ,

The translation-rotation interaction Hamiltonian H^{TR} is found to be (up to first order in translations)

$$H^{TR} = \sum_{\vec{k}} i\hat{v}_{\alpha i}(\vec{k}) Y_\alpha^\dagger(\vec{k}) s_i(\vec{k}) .\qquad(2.6)$$

The orientational motion is described in terms of five symmetry adapted functions $Y_\alpha(\theta_n, \varphi_n)$, $\alpha = 1-5$. Two of these functions have E_g symmetry, the remaining three have T_{2g} symmetry. The importance of these functions for the interpretation of Raman scattering experiment has been stressed in Ref. 29. An explicit derivation of the interaction (2.6) is given in Ref. 22. Here, we recall that $\hat{v}_{\alpha i}(\vec{k})$ is a 5×3 matrix. All elements of this matrix are completely specified in terms of the microscopic overlap potential.

Here and in the following, Fourier transforms are defined according to

$$A(\vec{n}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} A(\vec{k}) e^{i\vec{k}\cdot\vec{X}(\vec{n})} ,\qquad(2.7)$$

where $\vec{n}$ labels the unit cells and when N is the total number of unit cells.

We remark that we have not taken into account explicitly a direct interaction among rotating dumbbells. As we have shown previously,[22] the bilinear interaction (2.6) among translation and rotation gives rise already to an effective orientational interaction of the form

$$V_{eff} = -\frac{1}{2} \sum_{\vec{k}} Y_\alpha^\dagger(\vec{k}) C^{\alpha\beta}(\vec{k}) Y_\beta(\vec{k}) ,\qquad(2.8a)$$

with

$$C^{\alpha\beta}(\vec{k}) = \hat{v}_{\alpha i}(M^{-1})_{ii}\hat{v}_{\beta i} .\qquad(2.8b)$$

The elements $C^{\alpha\beta}$ have been given in Ref. 22. In the long-wavelength limit $C^{\alpha\beta}(\vec{k})$ depends only on $\vec{k}/k$. This corresponds to a R^{-3} dependence in real space, R being the distance between the CN molecular ions. Consequently, Eq. (2.8a) corresponds to an elastic dipole interaction between CN ellispsoids. The relevance of this interaction

has been inferred by Lüty *et al.*[19] and by Rehwald *et al.*[11] from experiments.

III DYNAMIC EQUATIONS

Using the Hamiltonian described in Sec. II, we have previously derived coupled dynamic equations for the translational and rotational dynamic response functions. We recall that Kubo's relaxation function[30] for two operators A, B is given by

$$\Phi_{AB}(z) = -i \int_0^\infty dt\, e^{izt} \Phi_{AB}(t)$$

$$= -\frac{1}{z}[\chi_{AB}(z) - \chi_{AB}(0)] ,\qquad(3.1)$$

where $\chi_{AB}(z)$ is the Laplace transform of the retarded Green's function[31]

$$\chi_{AB}(z) = -\langle\langle A^\dagger; B \rangle\rangle_z = i \int_0^\infty dt\, e^{izt} \langle[A^\dagger(t), B(0)]\rangle .\qquad(3.2)$$

Here $\langle\ \rangle$ denotes the equilibrium thermal average. We define $\Phi''(\omega)$ by writing ($z = \omega \pm i\epsilon$, $\epsilon \to 0$):

$$\Phi_{AB}''(\omega) = (1/2i)[\Phi_{AB}(\omega + i\epsilon) - \Phi_{A'B}(\omega - i\epsilon)] .\qquad(3.3)$$

This quantity is related to the dynamic correlation function by[30]

$$S_{AB}(\omega) = -\omega[1 - \exp(-\omega/T)]^{-1} \Phi_{AB}''(\omega) .\qquad(3.4)$$

Therefore, $\Phi''(\omega)$ is the relevant quantity for the interpretation of inelastic neutron or Brillouin-scattering experiments. In Ref. 9 we have derived a coupled set of matrix equations

$$(\tilde{1}z^2 - \tilde{D})\tilde{\Phi}_{ss}(z) - i\tilde{\beta}\tilde{R}\tilde{\Phi}_{\overline{Y}s}(z) = z\tilde{D}^{-1} ,\qquad(3.5a)$$

$$(\tilde{1}z + i\tilde{\lambda})\tilde{\Phi}_{\overline{Y}s}(z) + iz\tilde{\beta}^\tau\tilde{\Phi}_{ss}(z) = i\tilde{\beta}^\tau\tilde{D}^{-1} .\qquad(3.5b)$$

Here we have used a tilde to indicate the matrix character. The first set of Eqs. (3.5a) describes essentially the translational motion with coupling to the rotations. The second set of Eqs. (3.5b) acounts for the dynamics of rotations with coupling to the translations. Instead of $Y_\alpha(\vec{k})$, we have used the orthogonalized orientational variables $\overline{Y}_\alpha$ defined by

$$\overline{Y}_\alpha(\vec{k}) = Y_\alpha(\vec{k}) - s_i(\vec{k})D_{ij}(\vec{k})(s_j(\vec{k}), Y_\alpha(\vec{k})) .\qquad(3.6)$$

Static susceptibilities are defined by brackets

$$(A, B) \equiv \chi_{AB}(z = 0) ,\qquad(3.7)$$

[compare Eq. (3.2)] and the quantities $\tilde{\beta}$ and $\tilde{D}$ entering Eqs. (3.5a) and (3.5b) are defined by

$$D_{ij}(\vec{k}) = (s(\vec{k}), s(\vec{k}))_{ij}^{-1} ,\qquad(3.8)$$

$$\beta_{\alpha i}^\tau(\vec{k}) = (\overline{Y}_\alpha(\vec{k}), \mathcal{L}p_i(\vec{k})) .\qquad(3.9)$$

In Eq. (3.9) β^τ stands for the transposed element

and $\mathcal{L}$ denotes the Liouville operator.

The relaxation of orientational correlations is accounted for in Eq. (3.5b) by the transport coefficient[9]

$$\lambda_{\alpha\beta}(\vec{k}, i\epsilon) = \Lambda_{\alpha\gamma}(\vec{k}, i\epsilon)X_{\alpha\beta}(\vec{k}), \qquad (3.10)$$

where

$$\Lambda_{\alpha\gamma}(\vec{k}, i\epsilon) = -(\mathcal{L}Y_\alpha, (i\epsilon - Q\mathcal{L})^{-1}\mathcal{L}Y_\gamma), \qquad (3.11a)$$

and

$$X_{\alpha\beta}(\vec{k}) = (\overline{Y}(\vec{k}), \overline{Y}(\vec{k}))^{-1}_{\alpha\beta}. \qquad (3.11b)$$

The operator Q in Eq. (3.11a) selects the non-secular motion.[32] In Eq. (3.5a), $\tilde{R}$ stands for the single-particle susceptibility

$$R_{\alpha\beta} = (\mathrm{Tr}\, e^{-V^0/T}\, {}^T Y_\alpha^\dagger Y_\beta)/\mathrm{Tr}\, e^{-V^0/T}, \qquad (3.12)$$

where the potential V^0 is given by Eq. (2.5) and where the trace Tr stands for an integration over the polar angles θ, φ.

By eliminating $\Phi_{\overline{Y}_s}$ from Eqs. (3.5a) and (3.5b), we obtain a closed equation for Φ_{ss}.

$$[\tilde{1}z^2 - \tilde{D} - z\tilde{\beta}\tilde{X}(\tilde{1}z + i\tilde{\lambda})^{-1}\tilde{\beta}^\tau]\Phi_{ss}(z)$$
$$= [\tilde{1}z - \tilde{\beta}\tilde{X}(\tilde{1}z + i\tilde{\lambda})^{-1}\tilde{\beta}^\tau]\tilde{D}^{-1}. \qquad (3.13)$$

Here the orientational relaxation leads to resonances at $\tilde{1}z = -i\tilde{\lambda}$.

IV. DYNAMIC DISPLACEMENTS CORRELATION FUNCTION

Since the relevant quantities entering Eq. (3.13) are functions of temperature, we should be able to study the scattering law as a function of temperature. As we have shown previously,[9] Eq. (3.13) becomes diagonal for $\vec{k} = (0,0,k)$. One obtains

$$[z^2 - \Omega_i^2 - z\sigma_i(z)]\Phi_{ss}^{ii}(z) = [z - \sigma_i(z)]\Omega_i^{-2}, \qquad (4.1)$$

with

$$\Omega_i^2 = D_{ii}, \quad i = 1, 2, 3 \qquad (4.2)$$

and

$$\sigma_i(z) = \beta_i'^2/(z + i\lambda_i), \qquad (4.3)$$

where

$$\beta_i'^2 = \omega_i^2 - \Omega_i^2, \qquad (4.4)$$

with

$$\omega_i^2 = M_{ii}. \qquad (4.5)$$

We note that

$$\Omega_1^2 = \Omega_2^2 = (V_g/m)k^2 c_{44}, \qquad (4.6a)$$

$$\Omega_3^2 = (V_g/m)k^2 c_{11}, \qquad (4.6b)$$

$$\omega_1^2 = \omega_2^2 = (V_g/m)k^2 c_{44}^0, \qquad (4.7a)$$

$$\omega_3^2 = (V_g/m)k^2 c_{11}^0, \qquad (4.7b)$$

where c_{44}, c_{11} are the elastic constants (Voigt's notation) in the presence of orientational interaction while c_{44}^0, c_{11}^0 are the bare elastic constants in absence of orientational interaction.[33] In Eq. (4.6) V_g denotes the volume of the unit cell. The orientational relaxation matrix (3.10) is given by

$$\lambda_1 = \lambda_2 = \Lambda_{44}X_{44}, \qquad (4.8a)$$

$$\lambda_3 = \Lambda_{11}X_{11}, \qquad (4.8b)$$

where, according to Eqs. (3.11a) and (3.11b), Λ_{44} and X_{44} are defined with functions Y_4 of T_{2g} symmetry while Λ_{11} and X_{11} are defined with functions Y_1 of E_g symmetry (see Sec. III).

In Ref. 22 we have shown that c_{44} and c_{11} are given by

$$c_{44} = c_{44}^0(1 - y\delta/T), \qquad (4.9a)$$

$$c_{11} = c_{11}^0(1 - x\gamma/T). \qquad (4.9b)$$

Here δ and γ are constants related to the eigenvalues of the effective interaction matrix C defined by Eq. (2.8b). The quantities y and x are elements of the single-particle susceptibility matrix Eq. (3.12), $y = R_{44}$ and $x = R_{11}$ which correspond to T_{2g} and E_g symmetry, respectively. The temperature-dependent functions x and y are calculated by numerical integration.[22] Using Eqs. (B9) and (B10) of Ref. 9, we can write

$$X_{11} = \gamma\omega_3^2/(\omega_3^2 - \Omega_3^2) = T/x, \qquad (4.10a)$$

$$X_{44} = \delta\omega_1^2/(\omega_1^2 - \Omega_1^2) = T/y. \qquad (4.10b)$$

From Eqs. (4.4) and (4.6a)–(4.7b), (4.9a), and (4.9b) we find

$$\beta_1'^2 = \beta_2'^2 = \omega_1^2 y\delta/T, \qquad (4.11a)$$

$$\beta_3'^2 = \omega_3^2 x\gamma/T, \qquad (4.11b)$$

and similarly

$$\Omega_1^2 = \Omega_2^2 = \omega_1^2(1 - y\delta/T), \qquad (4.12a)$$

$$\Omega_3^2 = \omega_3^2(1 - x\gamma/T). \qquad (4.12b)$$

As we have noted previously, $\delta y > \gamma x$ and at $T_c = y(T_c)\delta$, $\Omega_1^2 = 0$ and equivalently $c_{44} = 0$.

As a final point, we consider the temperature dependence of Λ_{44} and Λ_{11}. A detailed microscopic calculation of this quantity according to Eq. (3.11a) is out of the scope of this work. In describing critical dynamics, one sometimes assumes that Λ is almost constant, the main temperature dependence of λ arising from the susceptibility.[34] Here we will assume that Λ_{44} (and also Λ_{11}) has a characteristic temperature dependence in three different regimes

$$\text{(a)} \quad \Lambda = \Lambda_\infty \quad \text{for } T > 100 \text{ K}, \qquad (4.13a)$$

(b) $\Lambda = \Lambda_\infty \ln(\frac{1}{25} T)(\ln 4)^{-1}$ for $25 < T \leqslant 100$ K (4.13b)

(c) $\Lambda = \Lambda_0 \approx 0$ for $T < 25$ K. (4.13c)

In fact this is a typical temperature behavior which is also exhibited within a good approximation by the single rotator susceptibilities such as x and y. It has its origin in the crystal-field potential V^0 of Eq. (2.5). Two energy barriers are important: the energy of about 3.5 meV,[24] which is required for a CN rotator to reorient between the potential minima in [111] directions in passing across [110] directions, and the energy difference between the potential maxima and minima ([100] direction and [111] directions). The latter energy is not well known. It is estimated to lie between 15 and 30 meV.

The three temperature regions therefore correspond to (i) almost free rotation, (ii) hindered reorientations, and (iii) librations. From experiment we estimate $\hbar\lambda_1 = 3$ meV for $T = 300$ K. Using Eqs. (4.8a) and (4.10b) with $y \approx 0.1$ (see evaluation in Ref. 22), we arrive at $\Lambda_\infty = 10^{-3}$ meV/$\hbar$. From experiment we also arrive at $\hbar\omega_1 = 0.9$ meV for a wave vector k restricted to $\frac{1}{10}$ of the Brillouin-zone distance in [001] direction. These values of ω_1 and Λ are used when we calculate the inelastic scattering law as a function of temperature.

V. RESONANCES

A. Pure crystals

The resonances of the dynamic scattering law are determined from the study of $\Phi''(\omega)$ as a function of frequency. The function $\Phi_{ss}^{ii}(z)$ is determined from Eq. (4.1). Applying Eq. (3.3) we immediately find

$$\Phi''(\omega) = \frac{-\beta_i'^2 f_i(\omega)}{[\omega^2 - \Omega_i^2 - \beta_i'^2 \omega^2 f_i(\omega)/\lambda_i]^2 + [\omega\beta_i'^2 f_i(\omega)]^2},$$
(5.1)

where

$$f_i(\omega) = \lambda_i/(\omega^2 + \lambda_i^2).$$
(5.2)

In Ref. 9 we have shown that Eq. (5.1) leads to a three peak structure. In practice one can easily distinguish two extreme cases, depending on whether the orientational relaxation λ_i is fast or slow in comparison with a typical phonon frequency ω_i. (a) Fast relaxation, $\lambda_i > \omega_i$. There are two resonances off center (Brillouin doublet) with frequency

$$\omega_i^\pm = \pm\Omega_i - i\beta_i'^2/2\lambda_i.$$
(5.3)

Comparing Eqs. (4.6a) and (4.6b) and (4.9a) and

(4.9b) one sees that Ω_i shows soft-mode behavior. On the other hand, there is no central peak. In pure KCN crystals (pure in contradistinction to mixtures), this is the experimental situation[17] at small wavevectors.[35] (b) Slow relaxation, $\lambda_i < \omega_i$. Now Eq. (5.1) has three resonances: a Brillouin doublet

$$\omega_i^\pm = \pm\omega_i - (\tfrac{1}{2}i)\lambda_i\alpha_i^2,$$
(5.4a)

and a central mode

$$\omega_i^0 = -i\lambda_i(1 - \alpha_i^2),$$
(5.4b)

where $\alpha_i^2 = \beta_i'^2/\omega_i^2$. In pure KCN this situation can only be reached at large wave vectors $\vec{k}$ such that $\omega_i(\vec{k}) > \lambda_i$. This is also confirmed by experiment.[17] We note that in this case, the Brillouin doublet frequency ω_i is larger than Ω_i.

From the experimental situation we conclude that in pure KCN, the situation described in case (a) holds for small wave vectors for all temperatures in the orientationally disordered cubic phase down to the phase transition at 168 K.

We now consider in more detail the temperature dependence of λ defined by Eq. (4.8a). This quantity is relevant for the study of the transverse acoustic mode. Since y increases with decreasing temperature, it follows from Eq. (4.10b) that X_{44} decreases with decreasing temperature. According to Eq. (4.13b), also Λ_{44} decreases with decreasing temperature. Consequently, λ decreases with decreasing temperature. In theory it should be possible to start from a temperature where case (a), $\lambda_i > \omega_i$ is realized and to reach case (b), $\lambda_i < \omega_i$ by lowering the temperature (the bare phonon frequency ω_i is practically constant as a function of T). In practice, however, λ_i is so large that the phase transition occurs at T_c before the case (b) can be reached. Therefore, one is always in case (a), $\lambda_i > \omega_i(\vec{k})$ for k being in the acoustical region.

B. Mixtures

The situation just described would be changed if we could dispose of a mechanism which allows to lower T_c. Such a mechanism is known to exist in A-B components mixtures. Suppose that in a pure A system (concentration $c_A = 1$) the interaction among A molecules leads to a second-order phase transition at temperature T_c. Then the admixture of inert B molecules with concentration c_B leads to a lowering of the transition temperature according to $T_c' = c_A T_c$ where $c_A = 1 - c_B$. Note that this result is obtained by a simple random (zero-order or Bragg-Williams) approximation. This simple treatment is sufficient for our purposes as long as the degree of dilution is not too large.[36]

We will be interested in values $1 \geq c_A \geq 0.3$.

We now consider $(KCN)_{c_A}(KX)_{c_B}$ mixtures when X stands for Cl or Br ions. There the spherical X ions play the role of orientationally inert particles in substitution for the CN ions. The lowering of T_c is confirmed by experiment.[11,18,19] A theoretical treatment of the elastic constants of mixtures in the framework of a tunneling model for CN molecules with ferroelastic interaction has been given in Ref. 25. Here we will show how the dynamic equations and the corresponding resonances are modified by considering mixtures. In fact most experiments are done at nonzero frequency and the dynamic theory should be relevant.

The admixture of the inert component leads to a lowering of T_c by a factor $c_A \leq 1$. We can equivalently consider this lowering of T_c as being due to a decrease of the effective collective interaction among CN ions by a factor c_A. This amounts in replacing everywhere in Eqs. (4.9a), (4.9b), and (4.11a)–(4.12b) the effective interaction eigenvalue δ by $\delta' = c_A\delta$. Being interested in the behavior of the transverse acoustical modes as a function of frequency and temperature, we have considered the relaxation function $\Phi_{ss}^{11\,\prime\prime}(\omega)$ given by Eq. (5.1) with

$$\Omega_1^2 = \omega_1^2(1 - c_A y\delta/T) , \tag{5.5}$$

$$\beta_1^{\prime\,2} = \omega_1^2 c_A y\delta/T , \tag{5.6}$$

$$\lambda_1 = \Lambda T/y , \tag{5.7}$$

with Λ given by Eqs. (4.13a)–(4.13c), $\omega_1 = 0.9$ meV/$\hbar$, $\delta = 1355,6$ K. The function $y(T)$ was taken from Ref. 22. It increases continuously with decreasing temperature. We have been interested in the temperature interval $T = 350$–54 K, with y varying, respectively, between 0.101 and 0.124. The phase transition was assumed to be of second order with $T_c = \delta y(T_c) = 154$ K. In reality, the phase transition is of first order with a discontinuity at 168 K. Since our aim is to give here an overall qualitative picture of the dynamics, the neglect of the first-order features of the phase transition should be allowed.

We have inserted the expressions (5.5)–(5.7) into Eq. (5.1) and plotted $\Phi_{ss}^{11\,\prime\prime}(\omega)$ as a function of ω for a temperature range of $350 \geq T \geq 54$ K and a concentration range $1 \geq c_A \geq 0.4$. The results are discussed in Sec. VI.

VI. RESULTS

By plotting $\Phi_{ss}^{11\,\prime\prime}(\omega) \equiv \Phi''(\omega)$ as a function of ω, we obtain as a typical spectrum a Brillouin doublet and eventually [see case (b) of Sec. V] a central peak. For a given concentration c_A, we have followed the evolution of the position $\omega = \pm\omega_+$ of the
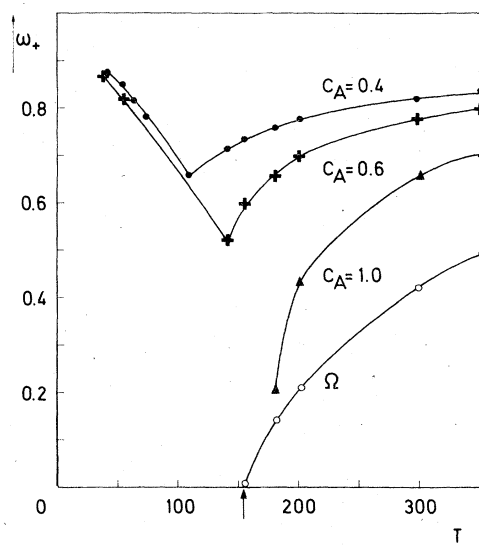

FIG. 1. Transverse acoustical-phonon frequency ω_+ as determined by the dynamic scattering law (theory) for different concentrations as function of temperature. Also the static soft mode Ω in pure KCN is shown. Fixed wave vector of order $\frac{1}{10}$ Brillouin-zone distance.

Brillouin peaks as a function of temperature. This is shown in Fig. 1. For comparison, we have also plotted the evolution of the soft-mode frequency Ω calculated by the static theory for pure KCN. The resonances of $\Phi''(\omega)$ are given by the solution of

$$\omega^2 - [\Omega_1^2 + \omega^2\beta_1^{\prime\,2}/(\omega^2 + \lambda_1^2)] + i\omega\lambda_1\beta_1^{\prime\,2}/(\omega^2 + \lambda_1^2) = 0 . \tag{6.1a}$$

By using Eq. (4.4), this expression can be rewritten as

$$\omega^2 - [\omega_1^2 - \lambda_1^2\beta_1^{\prime\,2}/(\omega^2 + \lambda_1^2)] + i\omega\lambda_1\beta_1^{\prime\,2}/(\omega^2 + \lambda_1^2) = 0 . \tag{6.1b}$$

Consequently, we find that for a given value of T and c_A, ω_+ is in the range $\Omega \leq \omega_+ \leq \omega_1$. If for a given value of c_A, we start from high temperatures such that $\lambda_1 \geq \omega_1$, the evolution of ω_+ with decreasing temperature is mainly governed by the decreasing value of Ω_1^2 while at the same time [see Eqs. (4.4) and (4.12a)], $\beta_1^{\prime\,2}$ and thus the coupling to the orientational mode increases. This coupling [see second term within brackets on the left-hand side of Eq. (6.1a)] tends to slow down the decrease of ω_+ and to counterbalance the influence of decreasing Ω_1. In pure KCN, the phase transition occurs before the coupling to orientational relaxation becomes dominant and tends to increase ω_+. In mixtures, the decrease of ω_+ is retarded in comparison with pure systems. Therefore, the

second term within brackets on the left-hand side in Eq. (6.1a) becomes of increasing importance. Note that the denominator of this term decreases since λ_1 decreases with decreasing T. Therefore, we are able to reach the slow relaxation case (b) described in Sec. VI: $\lambda_1 \lesssim \omega_1$. Now it is more adequate to discuss the soft-mode resonances by considering Eq. (6.1b). We remind that ω_1 is the bare phonon frequency in the absence of any orientational interaction, i.e., $c_A = 0$. With decreasing T and further decrease of λ_1, the second term within brackets on the left-hand side of Eq. (6.1b) becomes less and less important such that ω_+ finally approaches ω_1 which is independent of concentration c_A. This picture is confirmed by Fig. 1 where we have shown the variation of $\omega_+(T)$ for different concentrations. Note that the slowing down of $\omega_+(T)$ by leaving the high-temperature region is retarded with decreasing concentration c_A. Note also that the minimum is displaced to lower temperatures with lower values of c_A. This is experimentally confirmed by Brillouin-scattering measurements.[21] To illustrate our reasoning, we have quoted, in Table I, $\beta_1'^2$, λ_1, and Ω for different temperatures and different concentrations.

Note that neutron-scattering results[20] are most important to confirm our present interpretation in the framework of a dynamical theory. Indeed, experimentally one finds that for $c_A \approx 0.4$, one is in the fast relaxation regime [case (a)], with a soft-mode doublet in the high-temperature region above 150 K, while in the low-temperature region below 100 K, one reaches the slow relaxation regime [case (b)] where in addition to a speeding up Brillouin doublet, there appears a central peak. The present theory confirms this picture as is illustrated in Fig. 2 for $c_A = 0.4$. A similar picture holds also for $c_A = 0.6$. As is apparent from Fig. 1, we were not able to localize the phonon peaks in the region around $T = 100$ K for $c_A = 0.6$. The spectrum has there the shape of a large central peak with broad shoulders which extend to values

TABLE I. Calculated values of relevant parameters as function of concentration and temperature. Units of $(meV/\hbar)^2$ for Ω^2 and β'^2, $meV/\hbar$ for λ, and K for T.

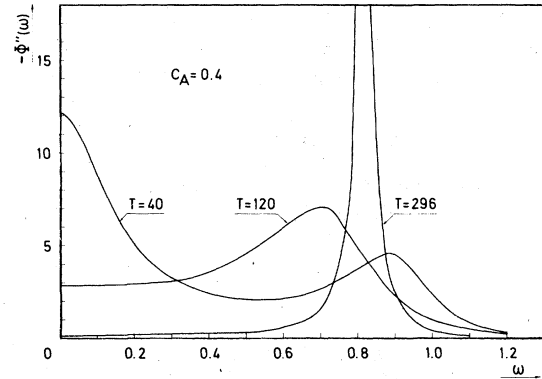| $C_A = 1$	β'^2	Ω^2	λ
$T = 350$	0.317	0.493	3.47
$T = 200$	0.598	0.212	1.83
$C_A = 0.6$	β'^2	Ω^2	λ
$T = 350$	0.190	0.620	3.47
$T = 200$	0.359	0.451	1.83
$T = 154$	0.486	0.324	1.36
$T = 106$	0.733	0.07	0.89
$T = 54$	1.5	−0.69	0.246

FIG. 2. Inelastic scattering law at $c_A = 0.4$ for different temperatures. Wave-vector $\frac{1}{10}$ Brillouin-zone distance. The figure is symmetric to negative ω side.

of $\omega\hbar$ in the range of 0.6–0.7 meV. These phonons are overdamped. Around $T = 50$ K, the central peak has again sufficiently sharpened and there is a distinct phonon peak at $\omega_+ \approx 0.8$ meV/$\hbar$. We remark that for $T = 40$ K, the values of ω_+ at $c_A = 0.4$ and $c_A = 0.6$ are almost equal and very close to $\omega_1 = 0.9$ meV/$\hbar$. We already mentioned this feature in discussing Eqs. (6.1a) and (6.1b).

At CN concentrations larger than 0.8, the inelastic spectrum is very similar to the case of pure KCN, the soft modes move to $\omega = 0$ with decreasing temperature. Around 150 K the soft-mode doublet has condensed into a central peak which becomes very narrow (0.04 meV) at 130 K. In a real crystal, this should correspond to a structural phase transition. This is observed experimentally.[18,19] On the other hand, the shape of the inelastic spectrum at $c_A < 0.8$ (see Fig. 2) indicates that the spherical ions are sufficiently effective to maintain the stability of the cubic crystal at lower temperatures. Experimentally, no phase transition is found for sufficiently high Cl concentration.[18,19]

We summarize our discussion by stating that the calculated soft-mode behavior is in agreement with both neutron[20] and Brillouin[21] experiments. In addition, the shape of the observed spectra in neutron-scattering experiments[20] fully supports the dynamical interpretation given by the present theory.

Finally, we would like to mention that the behavior of soft sound waves which interact with molecular reorientations as described in the present paper, has close analogies with sound propagation in liquids.[37] There the interaction of a sound wave with some irreversible process characterized by a relaxation time $\tau = 1/\lambda$ leads to the well-known phenomenon of second viscosity.[38] The qualitative shape of sound velocity curves in the critical region of argon[37] is the same as shown

for $(KCN)_{c_A}(KBr)_{c_B}$ in Fig. 1 of the present paper. The analogy is even more close with binary mixtures near the liquid-vapor critical line.[39,40]

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