A coupled-mode model relating Raman line shape to high ionic conductivity

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A phenomenological model, based on the generalized Langevin equation scheme first developed by Bruesch, Zeller, and co-workers, is employed to calculate the Raman band shapes for metal–halogen stretching modes in ionic conductors of the Ag_2HgI_4 class. The observed strong broadening of the Hg–I_4 stretch mode near 122 cm^{-1} is explained as arising from coupling to the mobile ion diffusive mode. Below the $\beta \rightarrow \alpha$ phase transition, the Ag–I mode is oscillatory, and the coupling effect is negligible on either Ag–I or Hg–I. In the conducting phase, the long time diffusive character of the Ag–I motion results in a strong effective damping of the Hg–I motion, leading to the observed broadening. The coupling effects are strong only when one of the two modes is indeed diffusive, thus explaining the apparent value of the Raman linewidth as a screening device for possible new ionic conductor crystals.

I. INTRODUCTION

Most so-called fast-ion conductor or superionic conductor systems show high conductivity ($\sigma \gtrsim 10^{-3}\,\Omega^{-1}\,cm^{-1}$) of one or more ion types in a high-temperature solid phase.[1] There exist, for these systems, one or more low-temperature phases for which the ionic conductivity is at least several orders of magnitude lower. Structural work reveals that for most such systems, particularly binary and ternary conductors of the silver halide class, the high-temperature (α-) phase exhibits disorder of the mobile ions among several (equivalent or inequivalent) sites, where the lower-temperature phases are ordered. Indeed the possibility of structural disorder seems a necessary, but not sufficient, property for ionic conductor crystals.[1]

Work in this laboratory over the past four years has established[2-4] that upon undergoing the $\beta \rightarrow \alpha$ phase transition, ternary Ag_2HgI_4-type conductors exhibit marked and characteristic changes in their Raman spectrum. Our studies have concentrated on materials of the M_2NX_4 class, where the mobile ion M is Ag^+, Cu^+, In^+, Tl^+, or K^+, the metal N is Hg^{2+} or Zn^{2+}, and X is Br^- or I^-. Generally, the bands tentatively assigned to symmetric M–X modes decrease in intensity nearly to zero, after broadening considerably with temperature as the phase transition point was approached from below. Other workers have found similar effects.[5,6]

The bands assigned to symmetric N–X_4 stretching modes, on the other hand, broaden remarkably and generally exhibit one or more new features upon undergoing the phase transition. This behavior, which is exhibited

for Ag_2HgI_4 in Fig. 1, seems typical of all the materials which we have studied, indeed, it has even been suggested[4] that this behavior in the Raman spectrum might be useful as a diagnostic tool to screen possible new ionic conductors.

The observed line shapes have to date not been understood with any satisfactory microscopic model. In the present paper, we present a phenomenological microscopic model for interpretation of the Raman spectra of these systems. It is based on ideas originally put forward[7,8] by Bruesch, Zeller, and co-workers for modeling the infrared spectrum of binary Ag–X conductors. The essential idea is simply that, upon undergoing the $\beta \rightarrow \alpha$ transition, the mobile-ion restoring force in the long time limit goes to zero, thus causing the mobile-ion motions to become diffusive; the short-time behavior remains oscillatory. This is the essence of the Bruesch-Zeller model. We then propose that the vanishing of the harmonic interaction between X and M changes the compliance of the X species in its other motions, including the N–X vibrations; this manifests itself in changed spectral shapes. These latter changes will be large only if the M–X forces undergo very substantial changes (vanish as $t \rightarrow \infty$) at the phase transition, and of course this vanishing of the effective restoring force on the mobile ion is precisely the requirement for ionic conductivity. Our model is thus both classical and phenomenological, but we feel that it indeed offers a reasonable explanation for the line shapes that have been observed.

The present paper describes the model, and uses it to calculate the Raman spectrum in both α- and β-phases for typical M_2NX_2 conductors. The observed Raman data are briefly sketched in Sec. II, and the generalized Langevin model is presented in detail in Sec. III. Section IV presents a calculation of the Raman spectrum

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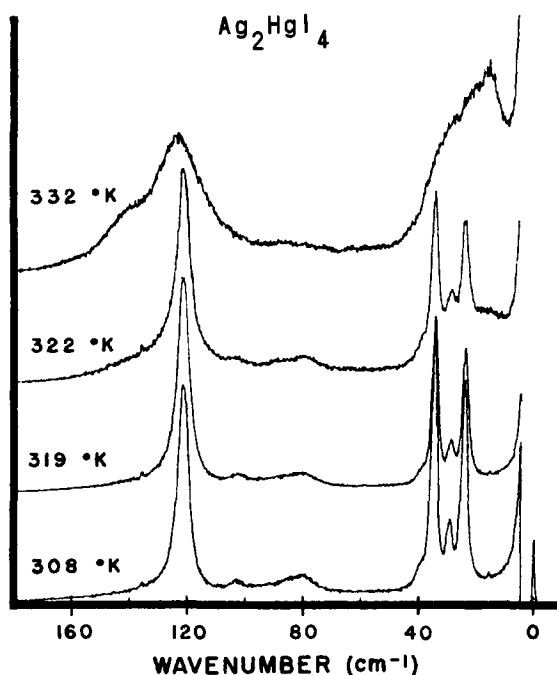
FIG. 1.   Raman spectrum of Ag_2HgI_4 in the vicinity of the phase transition (323 °K).   From Refs. 2 and 3.

employing our generalized Langevin model, and some remarks are presented in Sec. V.

II. THE OBSERVED RAMAN SPECTRUM[1]

The Raman selection rules in well-ordered solids limit Raman activity to zone-center ($k = 0$) optical branches. For the M_2NX_4 species, this means that one can employ the point group in the unit cell to describe the expected Raman spectrum at low temperatures. Such an assignment[2] has been carried out for Ag_2HgI_4 by Grieg, although, since complete single crystal spectra are lacking, the assignments must still be viewed as tentative. Grieg assigns the low-temperature (β phase) peaks as follows: the feature at 122 cm^{-1} is assigned to the a_1 symmetric stretch model of HgI_4^{2-}, while the series of peaks between 80 and 110 cm^{-1} is assigned as the Ag–I stretching region. These assignments are based on analogy to a number of crystalline and solution-phase spectra, and we are quite confident in the assignment. The lower frequency modes, in the region 20–40 cm^{-1}, are assigned to metal–halogen deformation motion; no more precise assignment has been possible.

Upon heating up to and through the $\beta \rightarrow \alpha$ phase transition, the modes from 80 to 110 cm^{-1} broaden, red shift very slightly (~ 2 cm^{-1}), and lose intensity. At the same time, both the 122 cm^{-1} mode and the 20–40 cm^{-1} region broaden precipitously at the transition. At higher temperatures, a new feature is visible as a high frequency shoulder at ~ 142 cm^{-1}. Figure 2 shows[3] a computer-generated least-squares fit of the α-Ag_2HgI_4 spectrum at 323 °K (the fit is to a product of Gaussian and Cauchy functions), in which the main peaks (at 84.8 and 123.5 cm^{-1}, respectively) and the shoulder (at 142.3) are resolved. The sudden broadening of the high-frequency mode, as well as the near disappearance of one mode

assgned to the M–X symmetric stretch, and the essentially complete disappearance of the other (106 cm^{-1}) M–X mode, are very typical of the whole M_2NX_4 class of fast-ion conductors, and are the features which we wish to characterize by our microscopic model.

III. THE GENERALIZED LANGEVIN EQUATION MODEL

Because of the complexity of the full microscopic quantum-mechanical description of phonon dynamics in crystals such as those we are considering here, we wish to develop a simple, classical, phenomenological model to aid in the interpretation of our spectra and to relate the spectral shapes to the dynamics. The simplest way to do this is to consider displacements along modes q_1 and q_2 as the independent variables of our problem; the associated frequencies are ω_1 and ω_2, while the reduced masses are m_1 and m_2. We will take q_1 as the unit-cell coordinate corresponding to M–X symmetric stretching motion in the β phase, and q_2 as describing N–X stretching motion. In the α phase, the M–X motion becomes diffusive, while the N–X motion remains oscillatory. Since, however, the compliance of X in N–X motion depends on the M–X interaction, vanishing X–M restoring forces will lead to marked change in the N–X spectrum. For the binary materials such as AgI, M, and N are identical, and therefore the motion of the mobile ions is simply related to that of the halides.[8] For the ternary species, however, the situation is more complex, and we must assume a form for the q_1–q_2 interaction.

Consider first the case where we assume that there is no coupling between q_1 and q_2. The phenomenological equations of motion are then written in the form

$$m_1 \ddot{X}_1 = - m_1 \Gamma_1 \dot{X}_1 - m_1 \omega_1^2 \int^t M(t - t') \dot{X}_1(t') dt' + f_1 , \quad (1)$$

$$m_2 \ddot{X}_2 = - m_2 \Gamma_2 \dot{X}_2 - m_2 \omega_2^2 X_2 + f_2 . \quad (2)$$

Here the left side is simply the Newton's Law acceleration. The force terms on the right are, respectively, the viscous drag due to lattice interactions, the restor-
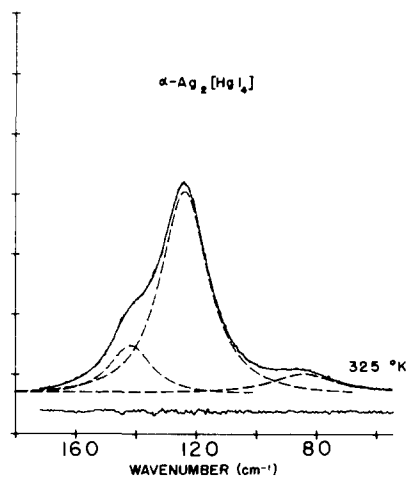

FIG. 2.   Computer resolved Raman spectrum of α-Ag_2HgI_4 at 325 °K, in the 120 cm^{-1} region.   The lower curve represents the difference between the observed spectrum and fitted curves.

ing force term, and the random driving force due to the lattice motion. The first and last forces are related to one another by the fluctuation dissipation theorem

$$\langle f_1(t) f_1(t+\tau)\rangle = 2m_1 k_B T \Gamma_1 \delta(\tau) \ , \tag{3}$$

$$\langle f_2(t) f_2(t+\tau)\rangle = 2m_2 k_B T \Gamma_2 \delta(\tau) \ . \tag{4}$$

In the β phase we require that

$$M(t) = 1 \quad \text{(all } t) \ . \tag{5}$$

Equation (1) then becomes similar in form to Eq. (2), both describing two independent Brownian harmonic oscillators which correspond (assuming small anharmonicities) to the normal modes associated with the M–X and N–X stretching motions. The frequencies ω_1 and ω_2 are to be taken as the observed β-phase frequencies.

The transition to the α phase is characterized by structural changes in the crystal which open the possibility for a diffusive motion of the M ions. Within the phenomenological model, Eqs. (1) and (2), we expect the following changes:

(a) The modes X_1, X_2 are no longer independent. In principle we may seek the new, α-phase, normal modes. If we stick to the old coordinates we expect a new coupling term. We assume that this coupling potential is of the simplest bilinear form. The equations of motion for the mode coordinates in the α phase are then

$$f_1 = m_1 \ddot{X}_1 + m_1 \Gamma_1 \dot{X}_1 + m_1 \omega_1^2 \int_0^t M(t-t') \dot{X}_1(t') \, dt'$$

$$+ m_1 \int_0^t N(t-t')[\dot{X}_1(t') - \dot{X}_2(t')] \, dt' \ , \tag{6}$$

$$f_2 = m_2 \ddot{X}_2 + m_2 \Gamma_2 \dot{X}_2 + m_2 \omega_2^2 \int_0^t \dot{X}_2(t') \, dt'$$

$$+ m_1 \int_0^t dt' N(t-t') \cdot [\dot{X}_2(t') - \dot{X}_1(t')] \ , \tag{7}$$

where the function $N(t)$ determines the dynamics of the interaction between the two modes.

(b) In the α phase the motion along q_1 should be diffusive for long time, but for short times, however we expect the motion along q_1 to be oscillatory even here, since the structure and the predicted potential indicate that there remains a harmonic restoring force for very small displacements along q_1. This determines the asymptotic behavior of the function $M(t)$ in the α phase,

$$\lim M(t) = 1 \quad t \to 0 \ , \tag{8}$$

$$\lim M(t) = 0 \quad t \to \infty \ . \tag{9}$$

Similarly, the long and short time behavior of the q_1 mode will be reflected in the coupling N, and we require

$$\lim N(t) = b \quad t \to 0 \ , \tag{10}$$

$$\lim N(t) = 0 \quad t \to \infty \ , \tag{11}$$

where the b parameter measures the coupling strength. Furthermore, the function N has to satisfy

$$\int_0^\infty N(t) \, dt = 0 \ , \tag{12}$$

which ensures the absence of mode–mode coupling on

the long time scale. Equations (8)–(12) express the fact that for short times the two modes behave as simple coupled harmonic oscillators, while on the long time scale the two motions are decoupled and one of them becomes diffusive.

We are now forced to choose specific algebraic forms for the memory functions $M(t)$ and $N(t)$ which must fulfill Conditions (8)–(11) in the α phase and Condition (5) together with the condition

$$N(t) = 0 \quad \text{all } t \tag{13}$$

in the β phase. In principle, the forms of $M(t)$, $N(t)$ may be determined starting from the complete system Hamiltonian and proceeding to reduce the dynamics via a Fokker–Planck equation; such a task for a system like Ag_2HgI_4 is awesome. We therefore proceed by making the simplest relaxation-time *ansatz* consistent with the conditions on M, N. That is, we define[7,8]

$$M(t) = e^{-t/\tau_1} \ , \tag{14}$$

$$N(t) = b(1 - t/\tau_2) e^{-t/\tau_2} \ , \tag{15}$$

where the τ are relaxation times, which will be finite in α phase but essentially infinite in β phase. These same forms have been used by the Brown–Boveri group in their studies of AgI.[7,8]

The generalized Langevin form which we have presented seems, physically, to contain all of the crucial ingredients: high-frequency oscillatory and low-frequency diffusive behavior for the mobile ion in the α phase, coupling between the mobile ions and the remaining stretching modes, and oscillatory behavior for the mobile-ion species in the β phase. By employing Brownian-type damping and random force terms, we have avoided the explicit introduction of the other phonon modes. Most importantly, the bilinear coupling term should provide the microscopic mechanism for broadening the q_2 stretching mode due to diffusive motion in q_1.

IV. CALCULATION OF THE RAMAN LINE SHAPE

The general study of Raman line shapes is a complicated issue.[9] For simplicity, we will assume that the Raman features due to the q_1 and q_2 modes can be well separated from the other, lower frequency distortion, librational and translational modes. In that case, the vibrational isotropic part of the scattering line shape is simply given, from linear response theory, as a transform of the polarizability autocorrelation function[10]

$$I_{jk}(\Omega) = \int_{-\infty}^\infty dt \, e^{-i\Omega t} \langle \alpha_{jk}(t) \alpha_{jk}(0)\rangle \ , \tag{16}$$

where $\alpha_{jk}(t)$ is the polarizability tensor and the average is performed over any chosen ensemble. For the vibrational component of interest here, we expand the operator $\alpha(t)$ in the normal modes

$$\alpha_{jk}(t) = \alpha_{jk}^0(t) + \sum_\lambda \alpha_{jk}^{1;\lambda}(t) X_\lambda(t) + \cdots \ , \tag{17a}$$

where λ labels the vibrational mode and, formally,

$$\alpha_{jk}^{1;\lambda} \equiv \partial \alpha_{jk}/\partial X_\lambda \big|_{X=0} \ . \tag{17b}$$

Then, using the fact that within our classical discussion

the correlation functions must be symmetric in time, we can write

$$I_{jk}^{\text{vib}}(\Omega) = \sum_{\lambda,\mu} C_{\lambda\mu} \int_0^\infty dt\, e^{-i\Omega t} \langle X_\lambda(t) X_\mu(0)\rangle \ . \qquad (18)$$

Finally, we replace the displacement correlation function by the velocity–velocity function (this equivalence holds semiclassically). Thus,

$$I_{jk}^{\text{vib}}(\Omega) = \sum_{\lambda,\mu} C_{\lambda\mu} \Omega^{-2} \int_0^\infty dt\, e^{-i\Omega t} \langle \dot X_\lambda(t) \dot X_\mu(0)\rangle \ . \qquad (19)$$

The constants $C_{\lambda\mu}$ include the derivatives in (17b), so that there will be constant intensity factors, corresponding to derivative matrix elements, which will appear in the experimental lineshape but not in the Fourier integral of (19). Thus, when we choose $\lambda = \mu = 1$ or 2, we will obtain the lineshape in the regions near ω_1 and ω_2, but the relative intensities of these bands will not be given correctly.

To evaluate the integrals in (19), we multiply both sides of (8) and (9) by $\dot X_1(0)$ and by $\dot X_2(0)$. We then obtain

$$\frac{d}{dt} F_{11}(t) + \Gamma_1 F_{11}(t) + \omega_1^2 \int_0^t M(t-t') F_{11}(t')\, dt'$$

$$+ \int_0^t N(t-t') \cdot [F_{11}(t') - F_{21}(t')]\, dt' = 0 \ , \qquad (20)$$

and three similar equations with differing indices. The correlation functions are defined by

$$F_{ij}(t) \equiv \langle \dot X_i(t) \dot X_j(0)\rangle \ . \qquad (21)$$

We can solve the system of four equations by Laplace transforming. We then obtain

$$s\tilde F_{11} + \Gamma_1 \tilde F_{11} + \omega_1^2 \tilde M \tilde F_{11} + \tilde N \tilde F_{11} - \tilde N \tilde F_{21} = F_{11}(0) \ , \qquad (22)$$

$$s\tilde F_{12} + \Gamma_1 \tilde F_{12} + \omega_1^2 \tilde M \tilde F_{12} + \tilde N \tilde F_{12} - \tilde N \tilde F_{22} = 0 \ , \qquad (23)$$

$$s\tilde F_{22} + \Gamma_2 \tilde F_{22} + \omega_2^2 \tilde F_{22}/s + m\tilde N \tilde F_{22} - m\tilde N \tilde F_{12} = F_{22}(0) \ , \qquad (24)$$

$$s\tilde F_{21} + \Gamma_2 \tilde F_{21} + \omega_2^2 \tilde F_{21}/s + m\tilde N \tilde F_{21} - m\tilde N \tilde F_{11} = 0 \ , \qquad (25)$$

$$m \equiv m_1/m_2 \ .$$

We have defined the Laplace transform by

$$\tilde F_{ij} \equiv \tilde F_{ij}(s) \equiv \int_0^\infty e^{-st} F_{ij}(t)\, dt \ . \qquad (26)$$

These can, finally, be solved by substitution to yield

$$\tilde F_{22}(s) = \frac{k_B T/m_2}{s + \Gamma_2 + \omega_2^2/s + m\tilde N - m\tilde N^2/(s + \Gamma_1 + \omega_1^2 \tilde M + \tilde N)} \ , \qquad (27)$$

$$\tilde F_{11}(s) = \frac{k_B T/m_1}{s + \Gamma_1 + \omega_1^2 \tilde M + \tilde N - m\tilde N^2/(s + \Gamma_2 + \omega_2^2/s + m\tilde N)} \ . \qquad (28)$$

If we now associate the Laplace variable

$$s \to i\Omega \ , \qquad (29)$$

where Ω is the spectral frequency as in (18), then $\tilde F_{11}$ and $\tilde F_{22}$ are precisely the integrals in (19).

To evaluate (27) and (28) analytically, we require the Laplace transforms $\tilde M$ and $\tilde N$, which are

$$\tilde M = \frac{\tau_1}{1 + i\Omega\tau_1} \ , \qquad (30)$$

$$\tilde N = \frac{i\Omega b}{(i\Omega + 1/\tau_2)^2} \ . \qquad (31)$$

By substituting these into (27) and (28) and taking the real part and dividing by Ω^2, we have, from (18) the line shape functions in the q_1 and q_2 regions.

The calculations are characterized by a large number of parameters: the frequencies ω_1 and ω_2 with corresponding reduced masses m_1 and m_2, the correlation times τ_1 and τ_2, the coupling strength b, and the damping strengths Γ_1 and Γ_2. All of these, however, are directly interpreted microscopically; thus, none is a truly free parameter. The frequencies are fixed by β-phase spectrum; the masses should correspond to L–X and M–X modes, but since they are assumed totally symmetric,

$$m = m_1/m_2 \cong 1.0 \ . \qquad (32)$$

The damping values Γ, again, are determined by the line shape in the β phase. The strength parameter $m_1 b$, is, as is clear from (7), just the force constant for interaction between q_1 and q_2; reasonable values for $b = \omega_{\text{interaction}}^2$ are thus of order 1000–5000 cm^{-1}. The memory time τ characterizes the timescale for lattice relaxation following mobile-ion motion; it is related simply to the dc conductivity.[7] Finally, the fluctuation–dissipation theorem requires, in the diffusive regime,

$$\tau_1 = \frac{k_B T/m_1 D - \Gamma_1}{\omega_1^2} \ , \qquad (33)$$

where D is the observed diffusion coefficient.

Figure 3 presents simulated spectral features due to $\tilde F_{22}$ in both α- and β-phases, as well as the parameters which have been employed in their calculation. Note the marked broadening, without substantial shift, of the 122 cm^{-1} (Hg–I) peak; these are the dominant experimental features observed for the whole conducting M_2NX_4 class upon undergoing the $\beta \to \alpha$ transition. The parameters chosen seem reasonable. Our calculations reproduce the observed (5 cm$^{-1} \to$ 20 cm^{-1}) half-width increase, but do not correctly reproduce the observed intensification, which may arise from disorder (cf. below).

Our identification of the 106 cm^{-1} mode as diffusive certainly seems strange at first, since it is an a_1 vibration, and therefore displacement along it cannot lead to symmetry breaking, or to the Ag$^+$ escaping from the I$^-$ tetrahedron and diffusing. The β-phase mode which really becomes diffusive in the α phase may correspond to an AgI$_4$ distortion of T_2 symmetry in the 20–40 cm^{-1} range of the Raman spectrum (see Fig. 1). Within a phenomenological model, however, this seems satisfactory. One imagines the q_1 mode restoring force going to zero in the diffusive regime just because the lower-frequency, lower-symmetry Ag–I mode does. In a sense, we have an effective three-mode model, with the coupling existing between the two a_1 modes, one of which becomes of diffusive type because the Ag$^+$ indeed diffuses. The actual appearance of Fig. 3 is not strongly dependent upon the value of ω_1, as can be seen from (28), or by comparing Figs. 3(a) and 3(b).

V. DISCUSSION

We have presented a phenomenological coupled-mode model for the Raman spectrum of ternary fast-ion con-
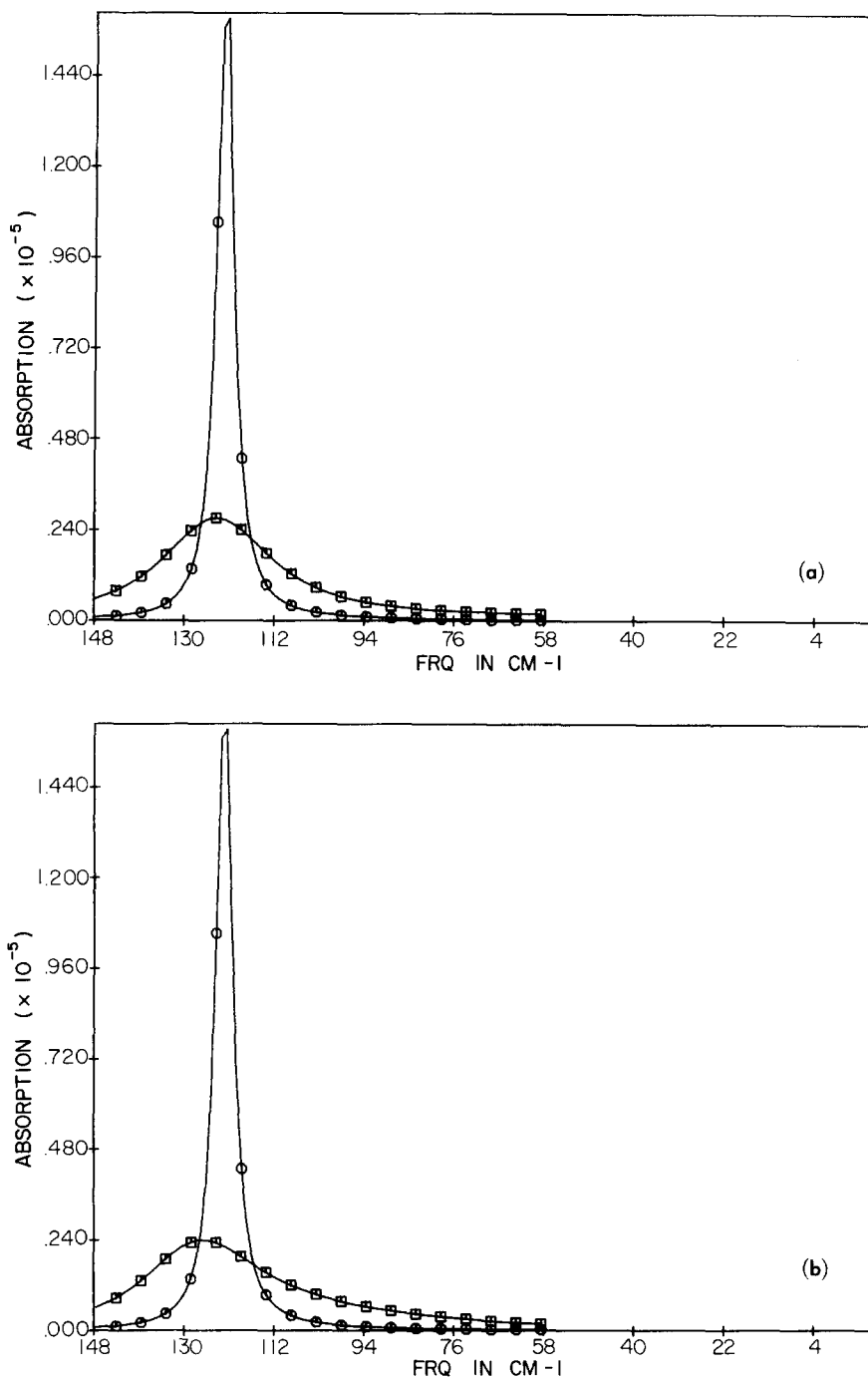
FIG. 3. (a) The line shape function $\Omega^{-2} \tilde{F}_{22}(\Omega)$ corresponding to Raman scattering from the 122 cm^{-1} Hg–I$_4$ stretch. The α-phase parameter values: $\tau_1^{-1} = \tau_2^{-1} = 65$ cm^{-1}, $\Gamma_1 = 6$, $\Gamma_2 = 4$ cm^{-1}, $\omega_1 = 106$ cm^{-1}, $\omega_2 = 122$ cm^{-1}, $b = 3600$ cm^{-2}. In the β phase, $\tau_1^{-1} = \tau_2^{-1} 10^{-5}$ cm^{-2}, $b = 0$. (b) Same as 3(a), except $\omega_1 = 36$ cm^{-1}.

ductors. The model is based on the idea that when the motion of one ionic type becomes diffusive rather than oscillatory, the forces felt by the other ions are modified considerably; this modification manifests itself by a change in the vibrational potentials, and therefore in the vibrational spectrum. The interaction which we envision is a dynamic one, and the characteristic broadening of the Raman line is thus seen as a dynamically based, homogeneous effect.

There exist two other obvious explanations of the broadening of the q_2 mode at the phase transition. The first of these is based upon inhomogeneous effects—essentially, it says that the disordered phase contains many different local environments, and that the ob-served spectrum arises from a superposition of narrow lines due to each environment. The other possible explanation involves a breakdown in the Raman selection rules when the disordering transition occurs, so that the zone-center phonon is no longer the only active mode, and much of the phonon dispersion spectrum is in fact sampled. This explanation was favored by Grieg,[2] and certainly seems reasonable. Indeed, Burns and co-workers have explained[11] the observed line broadening in a number of ionic conductors in terms of a broadened density of states due to greater disorder in one phase than the other. Their explanation for several Ag–ion conductors seems quite convincing. If either of these (static) explanations of the broadening were correct, however, one would expect roughly equivalent broaden-
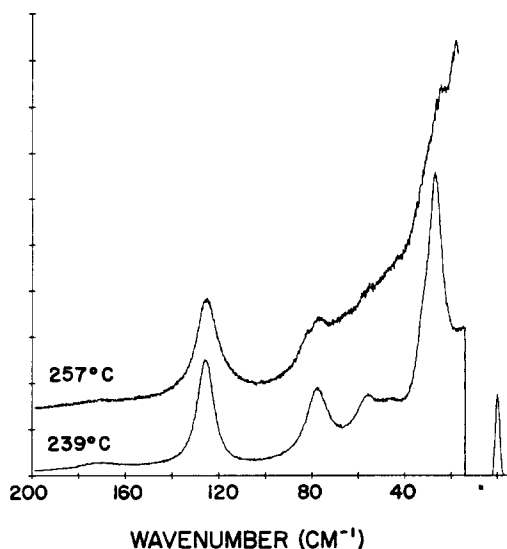
FIG. 4. Raman spectrum of Tl_2ZnI_4 in β, α phases (transition temperature = 250 °C). From Refs. 2 and 3.

$$\text{FWHM} = \Gamma_2 + \frac{2mb\,\omega_2^2\tau_2^3}{(1 + \omega_2^2\tau_2^2)^2} \; . \tag{35}$$

Thus, the linewidth will increase with the coupling b, and with the damping parameter Γ_2. For $\tau_2\omega_2 \gtrsim \sqrt{3}$, we expect the linewidth to decrease with increasing τ_2, while for $\tau_2\omega_2 \lesssim \sqrt{3}$, it should increase. For reasonable parameters ($1/\tau_2 \sim 50$ cm^{-1} as found for AgI by Bruesch et al.[8]), we are just in the borderline range, and, indeed, our calculations have shown the expected behavior for τ much above or below 0.1 psec. From general notions regarding driven oscillators, we might have expected, as we find, that the broadening is most effective for $\omega_2\tau_2 \sim 1$.

Although our model is phenomenological, the microscopic origins of the terms in (8) and (9) do imply relationships both among the parameters of the present scheme and between our dynamic coupling explanation and the disordered-crystal explanation of the linewidth. In the β phase, the mobile-ion M is limited to small displacements and therefore executes nearly harmonic motion. Thus the memory time τ becomes very long (the behavior never is diffusive). By implication, the phonon problem is solvable by standard procedures, and the normal modes sufficiently describe the observed spectrum; thus the Raman activity is limited to the $k = 0$ phonons (ordered system) and the coupling parameter $b \to 0$. In the α phase, the effective potential for M motion can be thought of as multiply periodic.[7,8] For short times ($< \tau$), the motion is then close to harmonic, but for larger diffusion coefficients, from (33), the time τ becomes smaller, the effective motion is less harmonic, the coupling b therefore increases and, since the phonon description starts to fail, the $k = 0$ selection rule is inoperative. Thus the possibility of dynamic, as well as static, disorder can lead to relaxation of the $k = 0$ selection rule. This would account for the larger intensities of the α-phase Ag_2HgI_4 spectrum than is shown in Fig. 3 or predicted from (8) and (9) alone. This additional intensification, however, arises from the same dynamic mechanism as does the original broadening. Thus it will not be found in poor conductors like Tl_2ZnI_{84} (low $D \to$ large τ, small b, little dynamic disorder), but will be in better conductors like Ag_2ZnI_4.

ing in all M_2NX_4 materials. Experiments have shown that within the M_2NX_4-class materials the large broadening of the N–X band on the $\beta \to \alpha$ transition is far more pronounced for good than for poor conductors; Fig. 4 shows[2,4] the Raman spectrum in α- and β-phases for Tl_2ZnI_4, where transition temperature is 250 °C. Note that for this material, which is a much poorer ionic conductor than Ag_2HgI_4 (activation energies for conduction of 84 and 37 kJ/mol, respectively)[4] the broadening is far smaller. This general trend (increased broadening for better conductors) is general in the ternaries, and seems to demand a dynamic, rather than static, explanation. If we calculate the spectrum for Tl_2ZnI_4 using the same parameters as in Fig. 3 but changing both τ and b by the appropriate factors as suggested from the conductivity[2,3] by (33) (τ increases by ~ 500, b decreases by 500), the computed α-phase spectrum is nearly superposable on β phase, just as in Fig. 4.

We also note that in the α phase, the reduced Raman spectrum of materials like Ag_2HgI_4 continues to show broadening as the temperature is increased[3]; this is in contrast to statically disordered structures like As_2S_3 and may signal important dynamic coupling processes of the type involved here.

The relationship between mobility and linewidth is easily understood within our model. From (33), we see that if the β-phase M–X line is not too broad (Γ_1 not too large), we have

$$D = k_B T/m_1\,\omega_1^2\tau_1 \; . \tag{34}$$

In the α phase, the time τ_1 represents the transitional time between diffusive motion of the M species (for times greater than τ_1) and oscillatory motion (for times smaller than τ_1). Thus τ_1 may be roughly interpreted as the time[7] required for the lattice relaxation in the α phase, following Ag–ion motion. For reasonable parameters ($\Gamma_2 \sim \Gamma_1$, $\omega_1 \sim 100$ cm^{-1}, $\omega_2 \sim 120$ cm^{-1}), the α-phase linewidth, from (27), is roughly

The coupled-mode model has several attractive features; it seems physically reasonable, all of the parameters are physically meaningful, and it explains both the β-phase and α-phase spectrum. Most important, it provides a theoretical understanding of the experimental observation that, for the Ag_2HgI_4 class and for several other ionic conductors which undergo sharp $\beta \to \alpha$ transitions, the onset of the high conductivity region is associated with anomalously large Raman line broadening, whereas for similar compounds of lower conductivity the broadening is smaller, even though the thermal transition, and therefore the expected disorder, are similar. We feel that both static (disorder) and dynamic (mode coupling) effects in fact contribute to the observed broadening in the M_2NX_4 species considered here,[12] and that both more precise calculations[11,13] and new experimental data (such as on quenched materials) are needed to understand quantitatively the relationship among disorder,

dynamic coupling, phase transition, and Raman line-width.

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