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► To cite this version:

E. Courtens. Hydrodynamics of acoustic phonon-molecular reorientation coupling in plastic crystals; vh scattering. Journal de Physique Lettres, 1976, 37 (1), pp.21-24. 10.1051/jphyslet:0197600370102100 . jpa-00231222

HAL Id: jpa-00231222

<https://hal.science/jpa-00231222>

Submitted on 1 Jan 1976

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Classification
 Physics Abstracts
 8.820 — 7.340 — 7.260

HYDRODYNAMICS OF ACOUSTIC PHONON-MOLECULAR REORIENTATION COUPLING IN PLASTIC CRYSTALS; VH SCATTERING

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(Reçu le 8 octobre 1975, révisé le 10 novembre 1975, accepté le 10 novembre 1975)

Résumé. — On développe un modèle qui décrit le couplage entre la réorientation de molécules anisotropes et les modes acoustiques dans un cristal plastique. Le modèle est appliqué au calcul de spectres de diffusion dépolarisée VH pour les cristaux plastiques cubiques. Il prédit deux modes de réorientation suramortis, et l'apparition d'une raie de cisaillement ayant une forme de résonance, en parfait accord avec l'expérience.

Abstract. — A model is developed to describe the coupling between the reorientation of anisotropic molecules and acoustic modes in a plastic crystal. The model is applied to the calculation of depolarized VH light-scattering spectra of cubic plastic crystals. It predicts two distinct overdamped reorientation-like modes and the appearance of shear phonon-like modes with resonance line-shapes, in agreement with experimental observation.

The statistical reorientation of optically anisotropic molecules gives rise to a depolarized Rayleigh wing in light-scattering spectra, as observed both in liquids [1] and in plastic crystals [2]. From the molecular-rotation viewpoint the latter behave very much as liquids, while translationally they are crystalline solids [3]. In liquids there also exists a *dynamical* coupling between reorientational and translational motion (a *static* coupling is forbidden) [4] which leads to characteristic light-scattering lineshapes [5]. Their exact interpretation has retained considerable attention [4]. The present letter considers the corresponding situation in plastic crystals. Though their threshold for plastic deformation is small, plastic crystals do sustain static stresses able to lower their symmetry thereby causing molecular reorientation. Hence *static* correlation between the anisotropic polarizability density and microscopic strains is allowed. This coupling has recently been observed directly for the first time in light-scattering measurements reported separately [6], [7]. The present model gives spectra in full agreement with experiments.

The orientation of molecule *a* at lattice position $\mathbf{R}_a$ is described by the traceless part $\vec{\alpha}^a$ of its optical polarizability tensor (Lorentz-Lorenz corrections will not appear explicitly). Summing over all molecules in volume *V* one obtains the anisotropic polarizability density

$$\vec{\mathbf{A}}^{\mathbf{q}} = \sum_a \vec{\alpha}^a \exp(-i\mathbf{q} \cdot \mathbf{R}_a).$$

The hydrodynamic anisotropy field is

$$\vec{\alpha}(\mathbf{r}) \equiv \frac{1}{\mathcal{N}} \sum_{\mathbf{q}} \vec{\mathbf{A}}^{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}), \quad (1)$$

where the sum extends over the $\mathcal{N}$ modes of the first Brillouin zone centered at $\mathbf{q} = 0$ (assuming one molecule per primitive cell, the extension being straightforward). The strain field $\vec{\epsilon}(\mathbf{r})$ is defined in terms of local displacements $\mathbf{u}$ of the molecular centers by

$$\epsilon_{ij}(\mathbf{r}) \equiv (\partial u_i / \partial x_j + \partial u_j / \partial x_i) / 2.$$

The Lagrangian density for the coupled system is written

$$\mathcal{L} = \mathcal{F} - \mathcal{V} = \frac{1}{2} \rho \dot{\mathbf{u}} \cdot \dot{\mathbf{u}} - \frac{1}{2} \vec{\epsilon} \cdot \vec{\mathbf{C}} \cdot \vec{\epsilon} - \frac{1}{2} \vec{\alpha} \cdot \vec{\mathbf{B}} \cdot \vec{\alpha} - \vec{\alpha} \cdot \vec{\mathbf{D}} \cdot \vec{\epsilon}. \quad (2)$$

The first term is the kinetic-energy density which does not include a reorientational contribution as the corresponding modes are usually overdamped. The second term is the elastic potential, and the third term the orientational potential produced by the center of mass interactions and the orientational interactions, respectively. The orientational potential is directly related to the high-frequency Kerr effect [8]. The last term in (2) represents coupling between anisotropy density and strain as explained above. It should be noted that $\vec{\mathbf{C}}$ is the *high*-frequency elastic tensor. At low frequencies the elastic tensor is *dressed* by mole-

cular reorientations. Its value is obtained by minimization of $\mathcal{U}$ with respect to $\vec{\alpha}$ at constant $\vec{\epsilon}$ and is

$$\vec{\mathcal{C}}^{\text{eff}} = \vec{\mathcal{C}} - \vec{\mathcal{D}} \cdot \vec{\mathcal{B}}^{-1} \cdot \vec{\mathcal{D}}.$$

For cubic crystals of point group higher than T there are three elastic constants in $\vec{\mathcal{C}}$, two orientational constants in $\vec{\mathcal{B}}$, and two coupling constants in $\vec{\mathcal{D}}$. Indeed, the tracelessness of $\vec{\alpha}$ allows to impose

$$B_{11} + 2 B_{12} = D_{11} + 2 D_{12} = 0,$$

using the abbreviated subscript notation. The dressed low-frequency $\mathcal{C}^{\text{eff}}$ is given by

$$C_{11}^{\text{eff}} + 2 C_{12}^{\text{eff}} = C_{11} + 2 C_{12}, \quad C_{11}^{\text{eff}} - C_{12}^{\text{eff}} = C_{11} - C_{12} - (D_{11} - D_{12})^2 / (B_{11} - B_{12}),$$

and

$$C_{44}^{\text{eff}} = C_{44} - D_{44}^2 / B_{44}.$$

Static stability demands that $\mathcal{U}$ be positive definite, which in the cubic case requires that $C_{11} + 2 C_{12}$, $C_{11} - C_{12}$, C_{44} , $B_{11} - B_{12}$, B_{44} , $C_{11}^{\text{eff}} - C_{12}^{\text{eff}}$, and C_{44}^{eff} all be positive.

The presence of frictional forces is accounted for by a dissipative function equal to half the rate of entropy production [9]. Results obtained in this manner are equivalent to those obtained with the more usual hydrodynamic calculation of entropy production following the lines of irreversible hydrodynamics [10]. Each potential term having its associated dissipative part one writes

$$f = \frac{1}{2} \dot{\vec{\epsilon}} \cdot \vec{\Gamma}^{\epsilon} \cdot \dot{\vec{\epsilon}} + \frac{1}{2} \dot{\vec{\alpha}} \cdot \vec{\Gamma}^{\alpha} \cdot \dot{\vec{\alpha}} + \dot{\vec{\alpha}} \cdot \vec{\Gamma}^{\alpha\epsilon} \cdot \dot{\vec{\epsilon}}, \quad (3)$$

where the $\vec{\Gamma}$'s are transport coefficients having a microscopic expression in terms of time dependent correlation functions [11]. The symmetries of the $\vec{\Gamma}$'s are identical to those of the potential constants. One also defines a dressed elastic loss $\vec{\Gamma}^{\epsilon, \text{eff}}$ which is the high-frequency loss as seen below. Dynamical stability requires that f be positive definite, leading to conditions on the Γ 's similar to those on the potential constants.

Application of Lagrange equations of motion for continuous dissipative systems gives a set of eight coupled eq. [12] :

$$\rho \ddot{u}_i - C_{ijkl} \partial^2 u_k / \partial x_j \partial x_l - D_{ijkl} \partial \alpha_{kl} / \partial x_j = \Gamma_{ijkl}^{\epsilon} \partial^2 \dot{u}_k / \partial x_j \partial x_l + \Gamma_{ijkl}^{\alpha\epsilon} \partial \dot{\alpha}_{kl} / \partial x_j, \quad (4a)$$

$$B_{ijkl} \alpha_{kl} + D_{ijkl} \partial u_k / \partial x_l = - \Gamma_{ijkl}^{\alpha} \dot{\alpha}_{kl} - \Gamma_{ijkl}^{\alpha\epsilon} \partial \dot{u}_k / \partial x_l, \quad (4b)$$

where tensor symmetries have been used to replace strains by unsymmetrized gradients. In the absence of coupling ($\vec{\mathcal{D}} = \vec{\Gamma}^{\alpha\epsilon} = 0$), (4a) gives the usual acoustic phonons with the q^2 dependence of their width, and (4b) gives overdamped reorientation modes. With

coupling and in the high-frequency limit the left-hand side of (4b) becomes negligible and the right-hand side gives $\dot{\alpha}$ in terms of $\nabla \dot{u}$. The introduction of this value in (4a) shows that $\vec{\Gamma}^{\epsilon, \text{eff}}$ is the high-frequency loss. Eq. (4) are space Fourier transformed using (1) and a similar relation between $\mathbf{u}(\mathbf{r})$ and $\mathbf{U}^{\mathbf{q}}$, and then Laplace transformed with the notation

$$\vec{\mathcal{A}}^{\mathbf{q}}(s) = \int_0^{\infty} e^{-st} \vec{\mathcal{A}}^{\mathbf{q}}(t) dt,$$

and similarly for $\mathbf{U}^{\mathbf{q}}(s)$. For a general direction $\mathbf{q}$ an 8×8 system results. However for $\mathbf{q}$ in the $(\bar{1}10)$ plane one identifies in the cubic case, to which the remaining discussion is restricted, a subset of three coupled equations between

$$\mathcal{U} \equiv (\mathcal{U}_1 - \mathcal{U}_2) / \sqrt{2}, \quad \mathcal{A}_1 \equiv (\mathcal{A}_{11} - \mathcal{A}_{22}) / \sqrt{2},$$

and

$$\mathcal{A}_2 \equiv \sqrt{2}(\mathcal{A}_{13} - \mathcal{A}_{23}).$$

This geometry has the advantage that only one pure shear mode is active in VH scattering. In that case $\mathcal{A}_1$ and $\mathcal{A}_2$ are also the only components needed to calculate the spectrum.

The depolarized spectrum produced by molecular motion (excluding deformation of electronic shells and anisotropic local fields) is given by [13]

$$I(\mathbf{q}, \omega) \propto V I_0 \text{Re} \int dt e^{i\omega t} \frac{1}{2 \mathcal{N}} \left\langle \sum_{a,b} \alpha_{ij}^a(t) \alpha_{kl}^b(0) \times \exp \{ - i \mathbf{q} \cdot [\mathbf{r}_a(t) - \mathbf{r}_b(0)] \} \right\rangle n_i^0 n_j^0 n_k^0 n_l^0, \quad (5)$$

where ω is the frequency shift, I_0 is the incident intensity, and V is the scattering volume containing $\mathcal{N}$ lattice points. The sum extends over all pairs. The position of molecule a is $\mathbf{r}_a = \mathbf{R}_a + \mathbf{u}_a$. The polarization vectors of the incident and scattered fields are $\mathbf{n}^0$ and $\mathbf{n}^s$, respectively. The angular bracket indicates ensemble averaging. The correlation range of $\vec{\alpha}^a$ and $\vec{\alpha}^b$ being finite, the bracketed part reduces to $\langle A_{ij}^a(t) A_{kl}^a(0) \rangle + \dots$. The further terms are smaller by a factor of the order of $|\mathbf{q} \cdot \mathbf{u}|^2$ and are negligible. These additional terms could not be neglected if $\vec{\alpha}^a$ and $\vec{\alpha}^b$ had long-range correlation, as in the case of polarized scattering, or for orientationally ordered anisotropic molecules. These terms contribute then to the usual Pockel's piezooptic coefficients. For the VH scattering geometry of figure 1, and with

$$\mathbf{n}^s = [1, 1, 2m] / (2 + 4m^2)^{1/2},$$

one obtains from (5) and the definitions above :

$$I(\mathbf{q}, \omega) \propto [V I_0 / \mathcal{N} (4 + 8m^2)] \times \text{Re} \langle \mathcal{A}_1^{\mathbf{q}}(s = -i\omega) \mathcal{A}_1^{-\mathbf{q}}(t = 0) + m \mathcal{A}_1^{\mathbf{q}} \mathcal{A}_2^{-\mathbf{q}} + m \mathcal{A}_2^{\mathbf{q}} \mathcal{A}_1^{-\mathbf{q}} + m^2 \mathcal{A}_2^{\mathbf{q}} \mathcal{A}_2^{-\mathbf{q}} \rangle, \quad (6)$$

where the arguments are explicitly shown in the first bracketed term.

Solving the Laplace transformed equations, the dynamical correlation functions entering (6) are expressed in terms of static correlation functions such as $\langle A_1^q A_1^{-q} \rangle$. The latter are calculated from equipartition using the Hamiltonian

$$\mathcal{H} = \int dV (\mathcal{F} + \mathcal{V}).$$

FIG. 1. — The scattering geometry : $\mathbf{n}_0$ and $[\bar{1}10]$ are perpendicular to the plane of the paper, $\mathbf{k}^0$ and $\mathbf{k}^s$ are the incident and scattered wavevectors, respectively, and $\mathbf{q}$ is the momentum exchange.

The results are simplified by defining new constants

$$B_1 \equiv B_{11} - B_{12}, \quad B_2 \equiv B_{44},$$

$$D_1 \equiv (D_{11} - D_{12})/\sqrt{2}, \quad D_2 \equiv D_{44},$$

$$C \equiv [C_{44} + \frac{1}{2}(C_{11} - C_{12} - 2C_{44})\sin^2 \varphi],$$

where

$$\mathbf{q} = q[\sin \varphi, \sin \varphi, \sqrt{2} \cos \varphi]/\sqrt{2}.$$

The undressed phonon velocity is written $v = \sqrt{C/\rho}$. New dissipative constants $\Gamma_1^a, \Gamma_2^a, \Gamma_1^{ae}, \Gamma_2^{ae}$, and Γ^e are defined similarly. Finally, the dynamical equations are simplified by using complex constants of the type $\mathcal{B}_1 = B_1 + s\Gamma_1^a$, and similarly for $\mathcal{B}_2, \mathcal{D}_1, \mathcal{D}_2$ and $\mathcal{C}$. The poles of the response function, which are the eigenfrequencies of the new hybrid modes, are given by the quartic

$$\mathcal{B}_1 \mathcal{B}_2 (\rho s^2 + C q^2) - q^2 \cos^2 \varphi \mathcal{B}_1 \mathcal{D}_2^2 - q^2 \sin^2 \varphi \mathcal{B}_2 \mathcal{D}_1^2 = 0. \quad (7)$$

These poles are written $s_j = z_j + \delta_j$ ($j = 1$ to 4), where the z_j 's are the values in the absence of coupling. One identifies two reorientational modes (assumed non-degenerate)

$$z_j = -B_j/\Gamma_j^a \quad (j = 1, 2)$$

and the complex conjugated phonon modes, which for small phonon damping are $z_{3,4} \cong \pm ivq - \Gamma^e q^2/2\rho$. Lowest order in the couplings one finds then

$$\delta_1 = [q^2 \sin^2 \varphi \mathcal{D}_1^2 / \rho \Gamma_1^a (s^2 + v^2 q^2)]_{s=z_1}, \quad (8a)$$

with a similar expression for δ_2 obtained by interchange of the subscripts 1 and 2 and of $\sin \varphi$ and $\cos \varphi$, whereas for the phonon

$$\delta_{3,4} = [(q^2/2\rho s) (\mathcal{D}_1^2 \sin^2 \varphi / \mathcal{B}_1 + \mathcal{D}_2^2 \cos^2 \varphi / \mathcal{B}_2)]_{s=\pm ivq}. \quad (8b)$$

The depolarized spectrum is the sum of three components $I_1 + I_2 + I_p$. The first two are Rayleigh wings corresponding to s_1 and s_2 . Using (6) one finds to same order in the couplings :

$$I_1(\mathbf{q}, \omega) \propto \frac{I_0 \pi N}{\beta \Gamma_1^a |s_1|} \frac{2}{1 + 2m^2} L(\omega, s_1) \times \left\{ 1 + \frac{q^2 \sin \varphi \mathcal{D}_1}{\rho(s^2 + v^2 q^2)} \cdot \left[2 \sin \varphi \frac{v^2 q^2 \Gamma_1^{ae} - s \mathcal{D}_1}{\Gamma_1^a (s^2 + v^2 q^2)} + \frac{2m \cos \varphi \mathcal{D}_2 + m^2 \sin \varphi \mathcal{D}_1}{\mathcal{B}_2} \right] \right\}_{s=z_1}, \quad (9a)$$

where $\beta = 1/kT$, and $L(\omega, s_1) \equiv |s_1|/\pi(\omega^2 + s_1^2)$ is the normalized Lorentzian profile. The component $I_2(\mathbf{q}, \omega)$ is obtained from $I_1(\mathbf{q}, \omega)$ by the same interchange as above, and replacing m by $1/m$ within curly brackets only, after which the whole expression is multiplied by m^2 . The third component corresponds to $s_{3,4}$. It consists of the Stokes and anti-Stokes parts of the shear phonon. In lowest order

$$I_p(\mathbf{q}, \omega) \propto [I_0 \pi N / \beta C (1 + 2m^2)] \times \text{Re} \{ [P(\omega, s_3) + P(-\omega, s_3)] \times [\sin \varphi \mathcal{D}_1 / \mathcal{B}_1 + m \cos \varphi \mathcal{D}_2 / \mathcal{B}_2]^2 \}_{s=ivq}, \quad (9b)$$

where

$$P(\omega, -\Gamma + i\Omega) = [\Gamma + i(\Omega - \omega)]/\pi[\Gamma^2 + (\Omega - \omega)^2].$$

I_p is purely Lorentzian in the limits of very small or very large q . For intermediate q it has a resonance or Breit-Wigner lineshape [14]. Moreover, if the dissipative part of the coupling is small, the line disappears at high q .

A measurement as a function of crystal orientation determines unambiguously all parameters of the theory including the relative sign of all four coupling constants. An excellent agreement is obtained between theory and experiment in succinonitrile [6]. The results can also be compared to the low-frequency elastic constants $\tilde{\mathbf{C}}^{\text{eff}}$ known from ultrasonics, and to the high-frequency optical Kerr-effect susceptibility $\tilde{\chi}^{\text{NL}}$ which is a $\mathbf{q} = t = 0$ measurement of the correlation function within angular brackets in eq. (5). From equipartition one obtains

$$B_1 = N^2 L_P^2 L_0/2 (\chi_{11}^{\text{NL}} - \chi_{12}^{\text{NL}}),$$

where N is the number of molecules per unit volume

and L_p , L_0 are Lorentz-Lorenz local field factors [8]. The ratio B_1/B_2 is related to the optical Kerr-effect anisotropy ζ by $B_1/B_2 = 2 - 4\zeta$.

Finally one should note that (5) implies that the anisotropic part of the Pockels piezooptic effect $\vec{p}$ arises entirely from the coupling considered here. Without coupling $p_{44} = p_{11} - p_{12} - 2p_{44} = 0$ and the pure shear mode does not scatter light. This in fact is approximately true for highly symmetric systems such as the rare-gas solids [15]. It thus seems legitimate to account for the shear-phonon scattering strength observed in plastic crystals entirely on the

basis of the present-coupling. In cases where the observed phonons have a frequency much above the reorientational frequency their strength would come from the dissipative terms $\vec{\Gamma}^{ae}$, whereas in the opposite limit it would come from the static term $\vec{D}$. Detailed comparison of theory and experiment would be needed to distinguish these contributions from piezooptic effects of other origins.

Acknowledgements. — The author expresses his appreciation to Prof. N. Gershon, J. Feder, and H. Thomas for a number of fruitful discussions.

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$$\frac{\partial}{\partial t} (\partial \mathcal{L} / \partial \dot{\eta}) + \sum_k \frac{\partial}{\partial x_k} [\partial \mathcal{L} / \partial (\partial \eta / \partial x_k)] - \partial \mathcal{L} / \partial \eta =$$

$$= - \partial f / \partial \dot{\eta} + \sum_k \frac{\partial}{\partial x_k} [\partial f / \partial (\partial \dot{\eta} / \partial x_k)] .$$
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