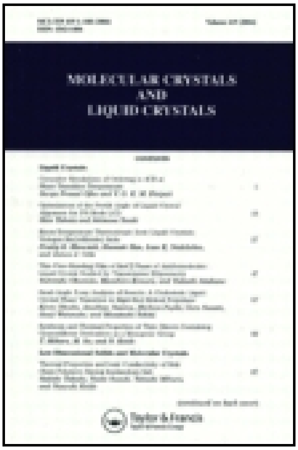

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A Method to Investigate Orientational Order in Plastic Crystals with Unknown Orientation by Depolarized Rayleigh Scattering.: Application to Succinonitrile

J. P. Bonnet [a]
[a] Université des Sciences et Techniques du Languedoc, Laboratoire de Spectrométrie Rayleigh-Brillouin, Equipe de Recherche Associée au C.N.R.S., N° 460, Pl. E. Bataillon, 34060, Montpellier Cédex, France

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A Method to Investigate Orientational Order in Plastic Crystals with Unknown Orientation by Depolarized Rayleigh Scattering.

Application to Succinonitrile

J. P. BONNET
Université des Sciences et Techniques du Languedoc, Laboratoire de Spectrométrie Rayleigh-Brillouin, Equipe de Recherche Associée au C.N.R.S. N° 460, Pl. E. Bataillon, 34060 Montpellier Cédex, France.

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The properties of orientational order in the cubic plastic phases may be described by two parameters (short-range orientational order and long-range orientational anisotropy). The principle of the determination of these parameters by depolarized Rayleigh scattering on non-oriented crystals is described. The method is applied to succinonitrile, giving a satisfactory agreement with Kerr effect measurements on oriented crystals.

I INTRODUCTION

A liquid crystal may be characterized by a long-range orientational order of the molecules, associated with a more or less complete translational disorder. In a plastic crystal the orientational order is a short-range property and is associated with a long-range translational order allowing molecular rotations in a crystalline lattice.

Another long-range property, characteristic of plastic phases, has recently been shown: the long-range orientational anisotropy which is related to the symmetry of the crystal.[1–3]

This characteristic orientational order is described by two parameters in a cubic crystal[2,3] and by three parameters in an hexagonal crystal.[3] These parameters have been obtained from Kerr effect measurements in the (cubic) plastic phase of succinonitrile.[1] The depolarized Rayleigh scattering also is a way to measure these order parameters.[3]

Plastic crystals are often grown in glass cells because of their hygroscopicity or tendencies towards sublimation and flow, which are frequent in these compounds. Their crystallographic axes are thus difficult to determine. The aim of this paper is to describe a method allowing the measurement of the order parameters by Rayleigh scattering on such crystals.

Firstly we recall the essential results of the Rayleigh scattering theory in plastic crystals. Next we present the method of determination of the order parameters; this method is then applied to succinonitrile.[4]

II THE RAYLEIGH DIFFUSE LINE IN PLASTIC CRYSTALS

A theory of Rayleigh scattering in plastic crystals has been recently proposed.[3] We recall here some results, limiting ourselves to the case of the Rayleigh diffuse line (RDL) in cubic crystals.

The RDL is due to anisotropy fluctuations induced by the rotational motion of optically anisotropic molecules. These motions are correlated over short distances and are considered here as decoupled from the translational motions. The intensity of the RDL is therefore independent from the scattering wave vector and gives information only on the orientational part of the order.

The order of the cubic plastic phases is described by a short-range orientational order parameter and a long-range orientational anisotropy parameter (two parameters of the latter type for hexagonal symmetry). In a Rayleigh scattering experiment this order appears by means of an anisotropy in the scattered intensity, that is the RDL intensity is a function of the Eulerian angles $(\alpha\beta\gamma)$ locating the crystallographic frame with respect to the laboratory frame. This intensity is also a function of the dynamics of the molecular reorientations through the rotational correlation function of the polarizability tensor $\Gamma_{\mu\nu}(t)$.

$\Gamma_{\mu\nu}(t)$ is a reducible spherical tensor and is defined as:

$$\Gamma_{\mu\nu}(t) = \left\langle \sum_{ij} \beta^2_\mu(\Omega(i, 0))\beta^2_\nu(\Omega(j, t)) \right\rangle. \tag{1}$$

The physical quantities appearing in Eq. (1) are defined in the crystallographic frame. $\beta^2_\nu(\Omega(j, t))$ is the irreducible polarizability tensor of rank 2 (standard component ν) of molecule j at time t. The β^2 are functions of the orientation of the molecules denoted by $\Omega(j, t) \equiv (\phi(j, t), \theta(j, t), \Psi(j, t))$. The summation extends over the N molecules of the sample, the brackets represent an equilibrium ensemble average.

In the following we will work on the integrated Rayleigh intensity and then concern ourselves with $\Gamma_{\mu\nu} \equiv \Gamma_{\mu\nu}(0)$.

In the general case $\Gamma_{\mu\nu}$ has 25 components ($\mu, \nu, = 0, \pm 1, \pm 2$). In a cubic medium there are 7 non-zero components:

$$\Gamma_{00};\ \Gamma_{-11} = \Gamma_{1-1};\ \Gamma_{-22} = \Gamma_{2-2};\ \Gamma_{22} = \Gamma_{-2-2}. \qquad (2)$$

Two of these are independent due to the relations:

$$\begin{aligned} \Gamma_{00} &= \Gamma_{22} + \Gamma_{-22} \\ \Gamma_{-11} &= \Gamma_{22} - \Gamma_{-22}. \end{aligned} \qquad (3)$$

The choice of the two independent components is made in order to separate the short and long-range effects; furthermore the two chosen parameters have well-defined transformation properties by rotation.

The short-range order parameter is defined as:

$$\Gamma = \sum_{\mu} (-1)^{\mu} \Gamma_{-\mu\mu}, \qquad (4)$$

Γ transforms as an irreducible tensor of rank 0 (it is rotationally invariant). This quantity is identical to the short-range parameter defined in liquids: Γ^{iso}. Therefore at the plastic-liquid transition $\Gamma \rightarrow \Gamma^{\text{iso}}$.

The component Γ_{22} vanishes at this transition and so represents a parameter characteristic of the plastic order: it is the long-range orientational anisotropy parameter. This quantity transforms by rotation as an irreducible tensor of rank 4. It may be noted that this long-range parameter includes a contribution from the short-range orientational order; this is also true for the $\Gamma_{-\mu\mu}$ components defined above.

The normalized intensity of the RDL is then given by:

$$I(\alpha\beta\gamma) = (\tfrac{1}{5})a_{\varepsilon}(\Gamma - 4\Gamma_{22}) + \phi_{\varepsilon}(\alpha\beta\gamma)\Gamma_{22}, \qquad (5)$$

a_{ε} and $\phi_{\varepsilon}(\alpha\beta\gamma)$ are geometical functions which have been tabulated for the usual scattering cases *Vh*, *Vv*, *Hh* and *Hv* indexed here by ε (90° scattering).[3]

The sign of the various $\Gamma_{\mu\nu}$ has not been discussed in reference[3] and has an importance for the experimental method. By construction we have:

$$\begin{aligned} \Gamma_{00}, \Gamma_{-22} &> 0 \\ \Gamma_{-11} &< 0 \\ \Gamma_{22} &> 0 \text{ or } < 0 \\ \Gamma = \Gamma_{00} - 2\Gamma_{-11} + 2\Gamma_{-22} &> 0. \end{aligned} \qquad (6)$$

The sign of Γ_{22} is related to the geometrical properties of the reorientational motion of molecules. This may be shown in the simple case of self-correlated motions of symmetric top molecules (polarizability tensor with $D_{\infty h}$ symmetry). In this case we have for one molecule

$$\Gamma_{22} \propto \langle P_4(\cos\theta_i)\rangle = (\tfrac{1}{8})\langle 35\cos^4\theta_i - 30\cos^2\theta_i + 3\rangle. \qquad (7)$$

We also have for cubic symmetry:

$$\langle P_2(\cos\theta_i)\rangle = (\tfrac{1}{2})\langle 3\cos^2\theta_i - 1\rangle = 0. \tag{8}$$

So according to Eqs. (7) and (8):

$$\Gamma_{22} \propto \langle 5\cos^4\theta_i - 1\rangle. \tag{9}$$

Equation (9) may also be obtained from a molecular field approximation. So, in this simple case, the sign of Γ_{22} depends on the relative magnitude of $\langle\cos^4\theta_i\rangle$ and $\frac{1}{5}$: this is a geometrical characteristic of the reorientational model.

III DETERMINATION OF THE ORDER PARAMETERS IN CRYSTALS WITH UNKNOWN ORIENTATION

The problem of Rayleigh scattering studies of non-oriented plastic crystals has recently been considered.[5] In this last reference the adopted method is an orientation of the crystal by the Rayleigh scattering itself. An alternative method is to work directly on the non-oriented crystal. It is this approach that we consider here.

For an oriented single crystal the knowledge of the geometrical functions a_ε, $\phi_\varepsilon(\alpha\beta\gamma)$ and Eq. (5) allow the determination of the order parameters from two measures. In a non-oriented single crystal we measure $I(\alpha\beta\gamma)$ for a number of unknown $(\alpha\beta\gamma)$ angles. From these a maximal and a minimal value of the scattered intensity (I_M and I_m) are deduced. In the following we discuss the crossed polarization cases (Vh, Hh, Hv for 90°-scattering) where the RDL appears alone. In the chosen polarizations we have $a_\varepsilon = \frac{1}{2}$ and $0 \leq \phi_\varepsilon(\alpha\beta\gamma) \leq 1$. The expression of I_M and I_m may be obtained from Eq. (5) but will vary according to the sign of Γ_{22}.

$$\Gamma_{22} > 0 \begin{cases} I_M = (\tfrac{1}{10})(\Gamma + 6\Gamma_{22}), & (10.a) \\ I_m = (\tfrac{1}{10})(\Gamma - 4\Gamma_{22}), & (10.b) \end{cases}$$

$$\Gamma_{22} < 0 \begin{cases} I_M = (\tfrac{1}{10})(\Gamma - 4\Gamma_{22}), & (11.a) \\ I_m = (\tfrac{1}{10})(\Gamma + 6\Gamma_{22}), & (11.b) \end{cases}$$

Equations (10) and (11) give:

$$I_M - I_m = |\Gamma_{22}|. \tag{12}$$

It may be noted from Eq. (12) that the RDL anisotropy, $I_M - I_m$, is simply related to the long-range orientational anisotropy of the crystal.

From the knowledge of I_M and I_m we can only evaluate the absolute value of Γ_{22}. It is also possible to obtain another $\Gamma_{\mu\nu}$ component by noting that:

$$I_M + I_m = \Gamma_{-22}. \tag{13}$$

where we have used Eqs. (2) to (4).

A third experimental datum is then necessary. We introduce $\langle I\rangle_{\alpha\beta\gamma}$, the scattered intensity averaged over the crystal orientations with respect to the laboratory frame.

$$\langle I\rangle_{\alpha\beta\gamma} = \frac{1}{8\pi^2}\int \mathrm{d}\alpha \sin\beta \,\mathrm{d}\beta \,\mathrm{d}\gamma \, I(\alpha\beta\gamma). \tag{14}$$

We find:

$$\langle I\rangle_{\alpha\beta\gamma} = (\tfrac{1}{10})\Gamma, \tag{15}$$

which is obviously the result obtained in the case of an isotropic medium. This quantity is interesting because it gives a measurement of the short-range order parameter independent of the assumption referring molecular orientations to symmetry properties of the crystal. Such a measurement may give an a-posteriori verification of formulas of type (3) based upon symmetry considerations. Equations (10), (11) and (15) then give us,

$$I_M + I_m - 2\langle I\rangle_{\alpha\beta\gamma} = (\tfrac{1}{5})\Gamma_{22}, \tag{16}$$

from which we can determine the sign of Γ_{22}.

The averaged intensity $\langle I\rangle_{\alpha\beta\gamma}$ is only a way to determine the sign of Γ_{22}. Given this sign, a temperature dependent study implies measurements of $I_M(T)$ and $I_m(T)$ only.

IV EXPERIMENTAL RESULTS

The succinonitrile ($NCCH_2CH_2CN$) shows a plastic phase between 233.3 K and 331.3 K, the lattice is bcc. This crystal exhibits an orientational and conformational disorder as a result of the existence of two gauche and one trans isomers for the molecule.[6] Each of these isomers may occupy 12 equilibrium positions.[7]

The theory summarized in Section II is k-independent and does not apply strictly to succinonitrile. Actually in this crystal there is a coupling between translational and rotational modes which gives rise to transverse Brillouin lines. Nevertheless these lines which modify the profile of the RDL in certain crystal orientations, have a very negligible contribution to the integrated intensity (area of the RDL). We have chosen succinonitrile to test the method because it is the only crystal for which data (on oriented samples) are available.

The experimental device has already been described elsewhere.[5] The source is a single frequency (4880 Å) argon ion laser. The measurements were performed with a 2.5 mm thick plane Pérot–Fabry interferometer; its free spectral range is 60 GHz, its finesse 70. The sample is held on an orientation set-up giving the mechanical equivalent of the Eulerian angles $(\alpha\beta\gamma)$. Index matching is insured by a mixture of carbon tetrachloride and ethyl alcohol.

The temperature dependence of the order parameters has been already obtained from Kerr effect; our light scattering measurements have been made at only one temperature ($T = 22°\mathrm{C}$) for the purpose of comparison with Kerr results.

A systematic study of the intensity as a function of $(\alpha\beta\gamma)$ has been carried out in Vh and Hv polarization. The continuity in the variations of these intensities allows us to think that the values of I_M and I_m are determined with a satisfactory precision. This study leads to the determination of the intensities averaged over crystal orientations: $\langle I_{Vh}\rangle_{\alpha\beta\gamma}$ and $\langle I_{Hv}\rangle_{\alpha\beta\gamma}$. Averaging over 30 orientations in each polarization case gives us $\langle I_{Vh}\rangle_{\alpha\beta\gamma} = \langle I_{Hv}\rangle_{\alpha\beta\gamma}$ which corresponds to the "isotropisation" of the crystal, the value $\rho = I_{Vh}/I_{Hv} = 1$ being characteristic of an isotropic medium. So we obtain:

$$\langle I\rangle_{\alpha\beta\gamma} = \langle I_{Vh}\rangle_{\alpha\beta\gamma} = \langle I_{Hv}\rangle_{\alpha\beta\gamma}.$$

Our results, together with those previously obtained by Kerr effect are reported in Table I. These are given in a relative form (normalization by Γ_{00}); agreement may be considered as satisfactory.

TABLE I

Comparison between Rayleigh and Kerr measurements (normalized parameters at $T = 22°\mathrm{C}$).

	Rayleigh	Kerr
Γ/Γ_{00}	3.3 ± 0.3	3.4
Γ_{22}/Γ_{00}	$0.28_5 \pm 0.03$	0.26

As pointed out by Courtens[3] these normalized parameters depend little if at all on short-ranged angular correlations, they are rather characteristic of the long-range aspect of the orientational order (Γ_{22}/Γ_{00} is equal to the tensor anisotropy ζ of Ref. 2). On the other hand, absolute measurement of Γ is necessary for the investigation of the short range order. These absolute values introduce some discrepancy between Kerr and Rayleigh results; this is due to the necessary calibration making use of a reference compound. Calibration has been made against the isotropic intensity (Rayleigh plus Brillouin) scattered by benzene. Birefringence of CCl_4 was used in Kerr measurements.

TABLE II

Comparison between Rayleigh and Kerr measurements (order parameters in Å^6 at $T = 22°C$).

	Rayleigh	Kerr
Γ	3.0 ± 0.5	4.1
Γ_{22}	0.26 ± 0.04	0.31

On both cases local field corrections are taken into account by Lorentz-Lorenz factors. These absolute results are given in Table II.

CONCLUSION

In conclusion we believe that this method may be useful in certain cases where the traditional techniques of crystal orientation are delicate. We believe also that the method may give results with a precision comparable to that obtained by Rayleigh scattering on oriented crystals, when applied to a compound more simple than succinonitrile.

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