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Quasi elastic coherent neutron scattering in the disordered phase of CBr_4 : experimental evidence of local order and rotational dynamics of molecules

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Résumé. — Nous présentons des résultats expérimentaux de diffusion diffuse des neutrons dans la phase plastique de CBr_4 ($T > 320$ K). La dépendance en \mathbf{q} et en température des intensités et des largeurs des pics quasi élastiques est analysée. Deux composantes sont observées : la première provient des corrélations entre molécules voisines et la seconde est due à la rotation propre de la molécule isolée. Les temps caractéristiques pour les deux processus sont évalués à 5 ps et 2,2 ps.

Abstract. — Experimental results on neutron diffuse scattering in the plastic phase of CBr_4 ($T > 320$ K) are reported. The wave vector and temperature dependences of intensities and widths of quasi elastic lines are analysed. We observe two components : one arising from correlations between neighbouring molecules and the other due to the self-rotation of a single molecule. Characteristics times for the two processes have been evaluated to be 5 ps and 2.2 ps respectively.

Results of diffuse scattering in the orientationally disordered f.c.c. phase ($47^\circ\text{C} < T < 92^\circ\text{C}$) of CBr_4 have been reported previously [1, 2].

It has been shown that local order is due to steric hindrance between neighbouring molecules and this effect is displayed by diffuse cigar-shaped spots near the (220) Bragg peaks.

Figure 1 shows the intensity $I_c(\mathbf{Q})$ (integrated over energy) corresponding to the static coherent scattering cross section $d\sigma/d\Omega$ in the $[\bar{1}\bar{1}\bar{2}]$ scattering plane. The maximum was found near (2.1, 2.1, 0) for $|\mathbf{Q}| \approx 2.1 \text{ \AA}^{-1}$ and the anisotropy is $\Delta Q_{\parallel}/\Delta Q_{\perp} \approx 4$ (ΔQ_{\parallel} and ΔQ_{\perp} are the widths parallel and perpendicular to the lines of high intensity).

It was pointed out that, because of the dynamical nature of the molecular correlations, this scattering is inelastic and some results have been given previously.

In this paper, we report some new measurements on coherent quasi-elastic scattering which provide new conclusions about the molecular motions. Experimental conditions for the sample have been described before [1].

In the case of CBr_4 , coherent scattering represents 93,5 % of the total scattering cross section from which

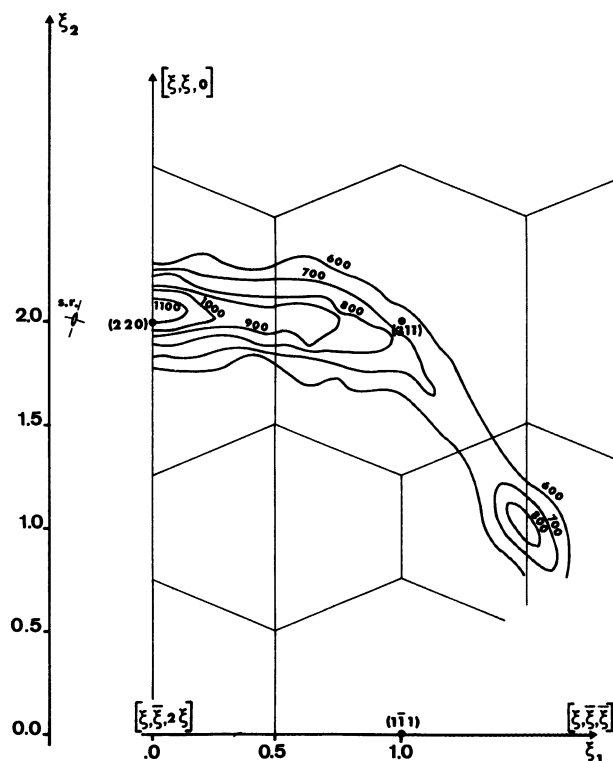


Fig. 1. — Diffuse scattering in the $(\bar{1}\bar{1}\bar{2})$ plane. (Instrument D 10 — sample 0.3 cm^3 — background 500 counts.)

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we can assume that the all measured signal is due to elastic or inelastic *coherent* scattering. Undesirable « background » arises only from the quartz container of the crystal and is essentially elastic. Unfortunately, this elastic scattering is distributed on a broad sphere with a radius of 1.5 \AA^{-1} which is not far from the diffuse scattering at $|\mathbf{Q}| = 2.1 \text{ \AA}^{-1}$. Hence, an elastic component is always included in diffuse scattering principally in the reciprocal region of interest. The energy width of the observed elastic peak is equal to the instrumental energy resolution function. A high energy resolution is thus required and our measurements were performed on the H_1 triple axis spectrometer at Saclay and on the IN12 spectrometer at Grenoble both installed on cold sources. The use of a double graphite monochromator for H_1 , a vertically curved graphite monochromator for IN12, flat pyrolytic graphite analysers, cold beryllium filters and severe collimation of the beams leads to a good resolution. Typically the estimated instrumental energy width was : 0.024 THz (0.09 meV) FWHM at $\lambda_i = 5 \text{ \AA}$, or 0.055 THz (0.22 meV) FWHM at $\lambda_i = 4.05 \text{ \AA}$.

Measurements of quasi elastic widths of the pure inelastic components obtained after deconvolution indicate that we have essentially to consider two different regions of reciprocal space : the first in the vicinity of the (220) Bragg spots corresponds to a sharp and intense peak due to the strong correlated molecular motions (Fig. 2) and the second, extending everywhere else, corresponds to weakly correlated or uncorrelated motions which give broad and weak diffuse peaks (Fig. 3).

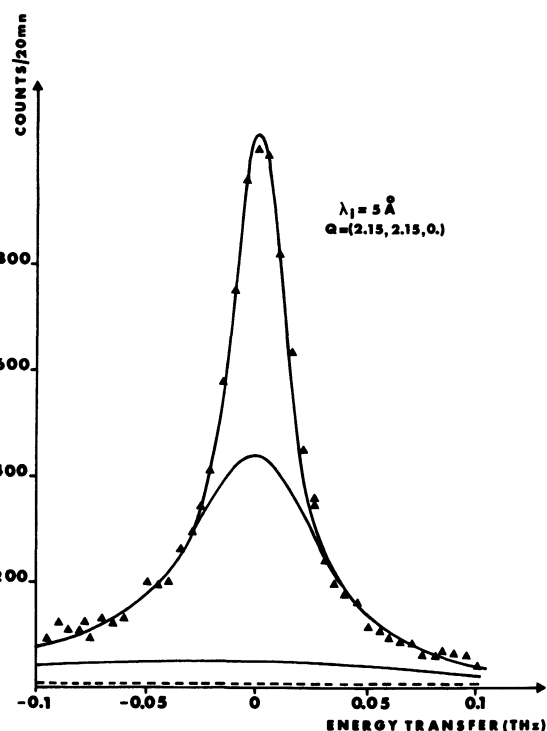


Fig. 2. — Constant \mathbf{Q} — scan at the point $\mathbf{Q} = (2.15, 2.15, 0)$ ($\lambda_i = 5 \text{ \AA}$ — resolution : 0.024 THz FWHM) showing an elastic peak and a Lorentzian (0.03 THz HWHM).

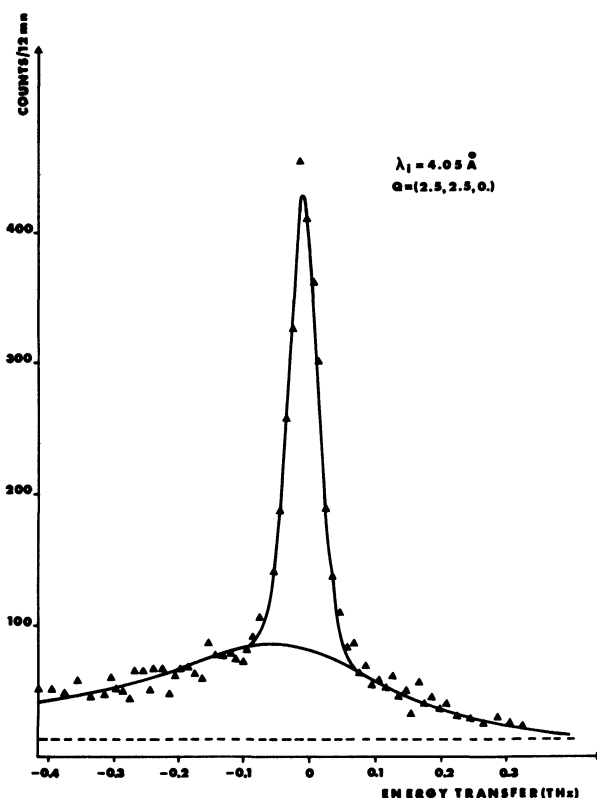


Fig. 3. — Constant \mathbf{Q} — scan at $\mathbf{Q} = (2.5, 2.5, 0)$ $\lambda_i = 4.05 \text{ \AA}$ — resolution 0.055 THz FWHM) showing an elastic peak and a Lorentzian (0.27 THz HWHM).

Indeed we deduce from measurements in the « correlated » region that intensity and width of the spectrum are functions of the wave vector \mathbf{q} indicating the collective or « correlative » nature of molecular motions. Figure 4 shows the evolution of intensity and width *versus* wave vector \mathbf{q} in directions [110] and [111]. The fact that the diffuse peak is only seen in the vicinity of the (220) Bragg spot is due to the effect of the scattering structure factor. This varies

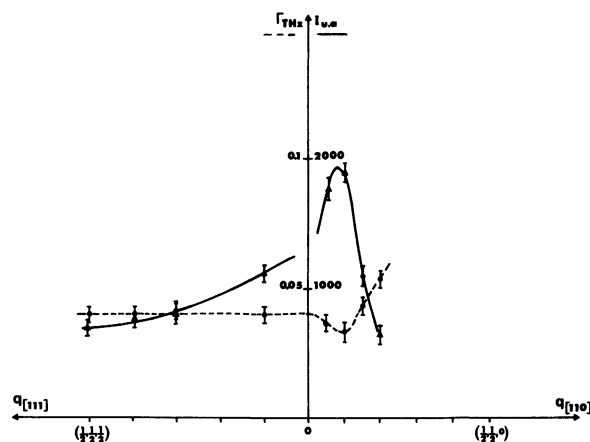


Fig. 4. — Evolution of intensity (full line) and width (dashed line) of the diffuse peak *versus* the wave vector \mathbf{q} in the direction [111] and [110]. (Instrument IN 12 — ILL.)

with Q as the static structure factor $S(Q)$ as long as the approximation $S(Q, \omega) \simeq S(Q) F(\omega)$ is valid and it has been shown [1] that $S(Q)$ is at maximum on the sphere of radius 2.1 \AA^{-1} and that maxima arise around (220).

Because, CBr₄ exhibits a structural phase transition of the order-disorder type at 47 °C, it is interesting to study the temperature effects. These effects on intensity and width can be summarized on figures 5a and 5b. We can see that intensity increases while width decreases when the temperature T approaches the transition temperature. Nevertheless, in contrast to the CD₄ case [3], we do not observe critical slowing down of orientational fluctuations according to the first-order nature of the transition and this fact partially explains the success of the « all or nothing » model for steric hindrance in CBr₄ proposed by Coulon and Descamps [2].

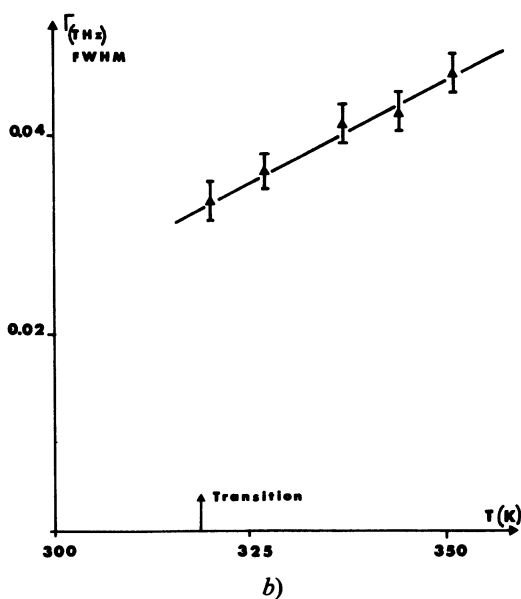
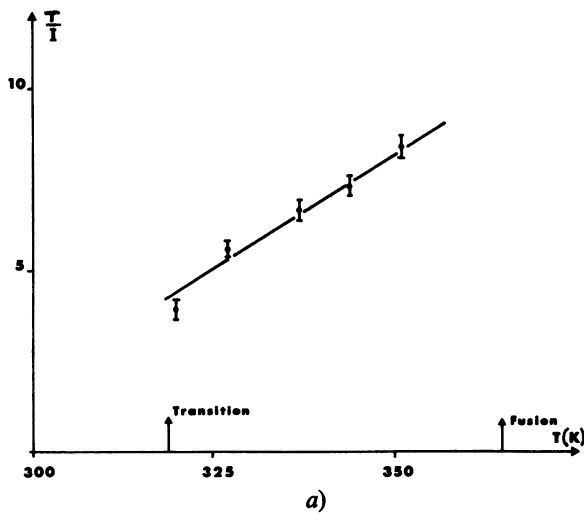


Fig. 5. — Variations of $T/\text{intensity}$ (5a) and width (5b) of the diffuse peak at $Q = (2.1, 2.1, 0)$ versus temperature.

Finally at 52 °C, we deduce from the width of the diffuse peak, $\Gamma = 0.030 \pm 0.008 \text{ THz}$ (HWHM), a relaxation time of the correlations which is approximately equal to 5×10^{-12} second.

The second component of the diffuse scattering is different from the first one. Indeed from the figure 3 for $Q = (2.5, 2.5, 0)$ we can see that the diffuse peak broadens out and the intensity decreases. We have measured an experimental width of 0.27 THz (HWHM) at this point. Systematic study throughout the reciprocal space was then performed. The IN 8 spectrometer at ILL (Grenoble) was used, because the width is now larger. It provides a thermal neutron beam of good intensity and an energy-resolution of 0.26 THz FWHM (1.0 meV) is sufficient for our purpose.

Figure 6 shows the results of the energy analysis of diffuse scattering along a line going from (112) to (222). We can see here that the scattering is not wave vector dependent. We only observe for all directions in the reciprocal space a small variation of the width with $|Q|$ (Fig. 7). It should be noted that, at large $|Q|$, measurements are only made for a positive energy transfer due to the angular limitations of the instrument. This is the reason why error bars are larger for $|Q| > 3 \text{ \AA}^{-1}$.

As elastic intensity from the container is always present and is generally larger than the diffuse intensity, we cannot measure the integrated intensity to obtain the static scattering function $S(Q)$. What we can do is only to perform measurements at a given

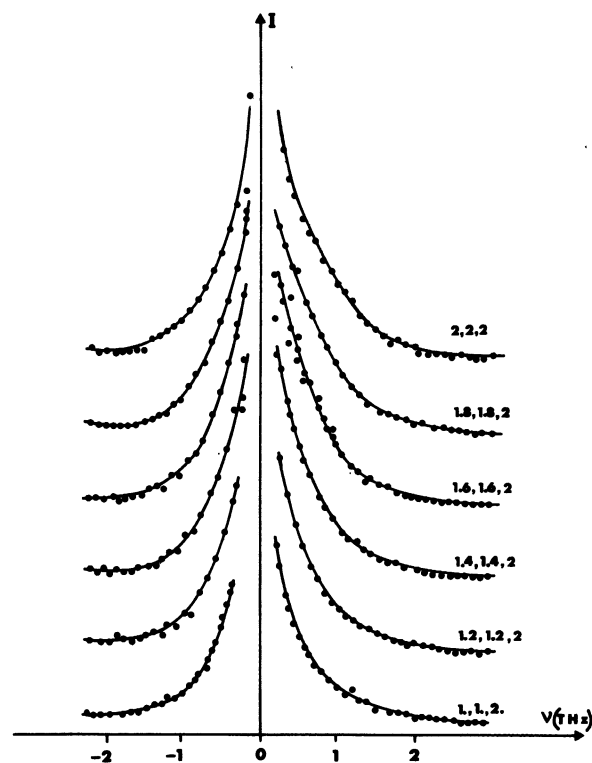


Fig. 6. — Energy analysis of diffuse scattering along a line going from (112) to (222). Intensity is in arbitrary units. (Instrument IN 8-ILL.)

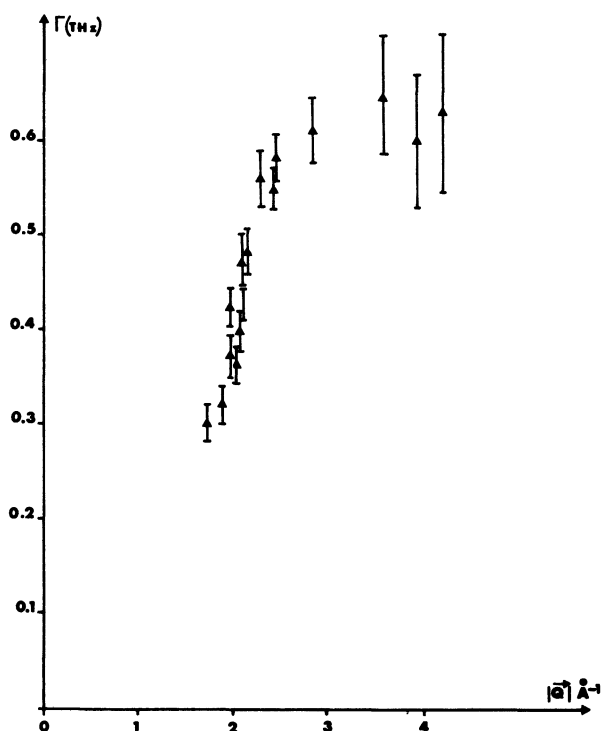


Fig 7. — $|Q|$ dependence of the width Γ of the second component of diffuse scattering considered as a single Lorentzian.

energy transfer with an energy window in such a way that elastic intensity is eliminated. Figure 8 represents scans in several directions of the reciprocal space with an energy transfer of 0.8 THz and a window equal to the instrumental energy resolution (0.26 THz). We can deduce that scattering is approximately isotropic. Some discrepancies appear at $|Q| = 4 \text{ \AA}^{-1}$ for directions $[111]$ and $[423]$. It has

been shown elsewhere [4] that one phonon scattering is responsible for a small amount of intensity in this region.

Whereas scattering by collective motions results from interferences between scattered waves and leads to scattering functions which are well localized in space and wave-vector-dependent, the scattering encountered here is more like « incoherent » scattering. We shall see below that it could be explained with a simple model of molecular self correlations.

The scattering cross section obtained from an assembly of independent molecules has been written using symmetry properties of the self-orientational density function (s.o.d.f.) [5]. Complete calculation can be made if we choose a model for the s.o.d.f. We have applied to our case a model of rotational diffusion as used by Sears [6] in calculations for liquid methane, and where the conditional probability to observe orientation Ω_2 at time t if orientation is Ω_1 at time 0 is :

$$G(\Omega_1, \Omega_2, t) = \sum_{lm} \frac{2l+1}{8\pi^2} F_{lm}^l(t) \times \sum_{\mu} U_{m\mu}^l(\Omega_2) U_{m\mu}^{l*}(\Omega_1)$$

$U_{m\mu}^l(\Omega)$ are the rotator functions of James and Keenan [7] and

$$F_{mm}^l(t) = \delta_{mm} \exp \{ -l(l+1) D_r t \} .$$

In the case of CBr_4 and taking account of the symmetry, the intermediate rotational scattering function can be written :

$$I_{\text{coh}}^{R(\text{self})}(\mathbf{Q}, t) = 4 b_{\text{Br}}^2 \sum_{l \neq 0} (2l+1) j_l^2(Q\rho) (1 + 3 P_l(-\frac{1}{3})) F_{00}^l(t)$$

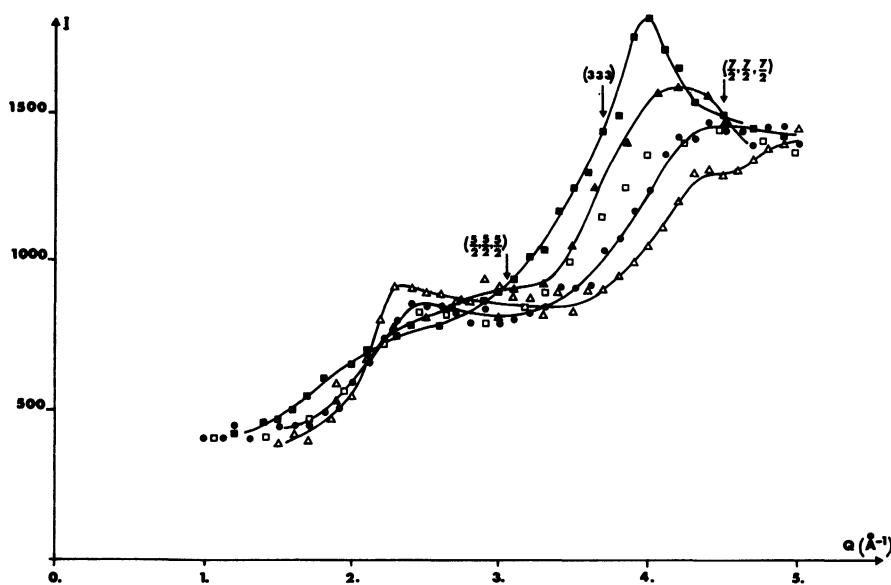


Fig 8. — Intensity proportional to $S(\mathbf{Q}, \omega_0)$ with $\omega_0 = 0.8 \text{ THz}$ for various directions of reciprocal space. [Directions : $\bullet = [513]$; $\Delta = [1\bar{1}0]$; $\blacktriangle = [\bar{4}23]$; $\blacksquare = [111]$; $\square = [3\bar{1}1]$.]

where b_{Br} is the scattering length of bromine, $j_l(Q\rho)$ the spherical Bessel function of order l and $P_l(-\frac{1}{3})$ the Legendre — polynomial of order l .

As the total scattering function is :

$$I_{coh}^{self}(Q, t) = I_{coh}^{T(self)}(Q, t) \cdot I_{coh}^{R(self)}(Q, t).$$

We have to take account of the translational part $I_{coh}^{T(self)}(Q, t)$ of the scattering function. For the sake of simplicity we have used a simple Debye model for the translations (with $v_{Debye} = 0.5$ THz according to the Debye Waller factor). Figure 9 shows the calculated scattering function $S^{self}(Q, \omega')$ for $\omega' = 0.8$ THz. The dashed line corresponds to the amount of multiphonons scattering calculated in the Placzek « incoherent approximation » [8]. In view of the results, the rotational diffusion is a fairly good approximation. The model predicts an enlargement of the diffuse peaks according to the law $l(l + 1) D_r t$. From the best comparison with experiment (Fig. 8), we deduce $D_r \approx 0.012$ THz. This value gives correct widths at large Q [for example at $|Q| = 3.5 \text{ \AA}^{-1}$, the relevant components are $\Gamma_6 = 0.5$ THz and $\Gamma_7 = 0.67$ THz] but the calculated widths are too

low at smaller $|Q|$. [We find for example at $|Q| = 2.5 \text{ \AA}^{-1}$ (Fig. 3), $\Gamma_3 = 0.14$ THz and $\Gamma_4 = 0.24$ THz.] In the Debye theory $D_r = 1/6 \tau$ and then the characteristic time for the self correlations would be roughly 2.2×10^{-12} second. This time should be compared with the value 5×10^{-12} second found before for the relaxation time of the correlations. As the latter is the same order as the former, the molecules are often reorientating.

The method we have used throughout this paper describes diffuse scattering in CBr₄ as formed of two components, one arising from correlations between neighbouring molecules, and the other due to the self correlations of the molecules. A rotational diffusion model is used to take account of the latter component.

In a recent work concerning the dynamics of molecular correlations in CBr₄, M. Descamps [9] showed that correlations are due to steric hindrance between molecules. With the use of a one parameter phenomenological potential, this author was able to describe the two components of the diffusion in a unified way which means that a molecule is in fact more or less correlated with the other one at a given time.

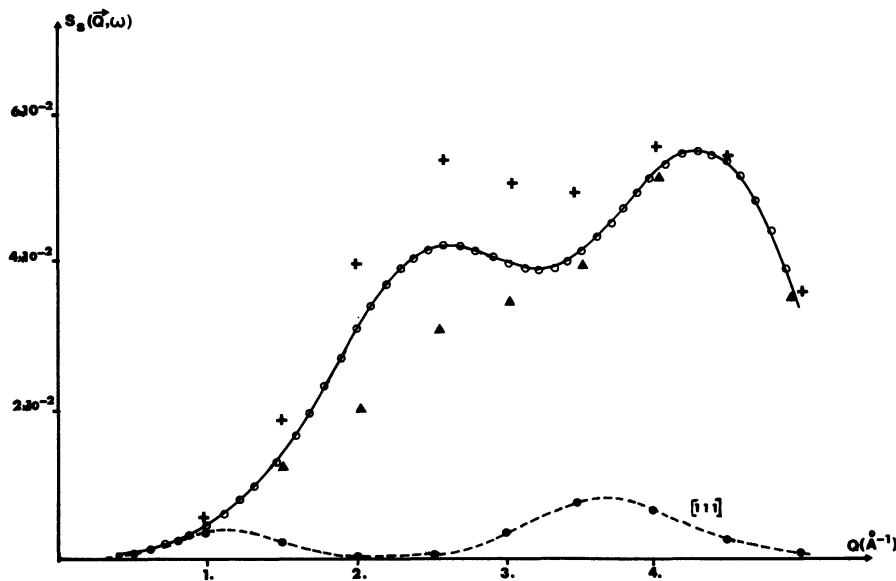


Fig. 9. — Calculated $S^{self}(Q, \omega)$ from the isotropic rotational diffusion model [dashed line corresponds to multiphonons correction]. + $D_r = 0.017$, $\circ D_r = 0.012$, $\triangle D_r = 0.008$.

References

[1] MORE, M., LEFEBVRE, J., HENNION, B., POWELL, B. M. and ZEYEN, G. M. E., *J. Phys. C* **13** (1980) 2833-46.
 [2] COULON, G. and DESCAMPS, M., *J. Phys. C* **13** (1980) 2847-56.
 [3] HULLER, A., PRESS, W., *Phys. Rev. Lett.* **29** n° 5 (1972) 266.
 PRESS, W., HULLER, A., STILLER, H., STIRLING, W., CURRAT, R., *Phys. Rev. Lett.* **32** n° 24 (1974) 1354.
 [4] MORE, M., Thèse d'Etat (1982) Lille.
 [5] PICK, R. M. and YVINEC, M., *J. Physique* **41** (1980) 1053.
 [6] SEARS, V. F., *Canad. J. Phys.* **45** 2 (1967) 237.
 [7] JAMES, H. M. and KEENAN, T. A., *J. Chem. Phys.* **31** (1959) 12-41.
 [8] MARSHALL, W. and LOVESEY, S. W., *Theory of Thermal Neutron Scattering* (Oxford-Clarendon Press) 1971.
 [9] DESCAMPS, M., *J. Physique* **45** (1984) to be published.