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NEUTRON QUASI-ELASTIC SCATTERING STUDY OF TRANSLATIONAL MOTIONS IN THE SMECTIC H, C AND A PHASES OF TBBA

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Résumé. — On présente des expériences de diffusion quasi-élastique de neutrons sur les phases smectiques H, C et A du TBBA, faites en utilisant la technique de *backscattering*. Les résultats sont analysés en termes de mouvements translationnels et on définit un coefficient de self diffusion apparent D_{ap}. La signification physique de D_{ap} est discutée en fonction du tenseur de self diffusion et d'autres types de mouvements translationnels.

Abstract. — Neutron quasi-elastic scattering experiments in the smectic H, C and A phases of TBBA are presented, using the high resolution backscattering technique. The data are analyzed in terms of translational motion and are characterized by an apparent self diffusion coefficient D_{ap}. The physical meaning of D_{ap} is discussed in terms of the true bulk self diffusion tensor and other kinds of translational motions.

Continuing our study of terephtal-bis-butyl-aniline (TBBA) by incoherent neutron scattering [1, 2, 3, 4] we have used the very high resolution backscattering technique [5, 6], to measure the broadening of the quasi-elastic line in the smectic H, C and A phases due to translational motions [7, 8]. In previous work [1] we showed that the quasi-elastic spectra are composed of a very narrow line superimposed on a much broader one arising from rotational motions. In the SmH phase, this broad line is about 100 μeV FWHM and preliminary experiments of a similar nature show that the width is notably greater in the C and A phases. On the scale of the present measurements (experimental window of ± 7 μeV around $\hbar\omega = 0$) the above rotational contribution to the spectra can be considered to a good approximation as a flat signal, any broadening of the narrow central line is probably due to translational motions.

The polydomain sample used [partially deuterated specimen DTBBA [1] completely deuterated on the butyl chains], the container and the temperature regulation system were the same as in previous work [1]. Three scattering angles were measured simultaneously for elastic Q of 0.15, 0.28 and 0.54 Å^{-1}. The instrumental energy resolution (about 1 μeV FWHM) was derived from the spectrum obtained in the crystalline (room temperature) phase of the same sample.

Examples of spectra (corrected for container scattering) obtained at $Q = 0.28$ Å^{-1}, for four temperatures around the SmH-SmC and SmC-SmA transitions are shown in figure 1 together with the experimental resolution. The full curves are the best fit of a lorentzian curve (FWHM : ΔE) convoluted numerically with the experimental resolution, together with a flat background. The width ΔE was found
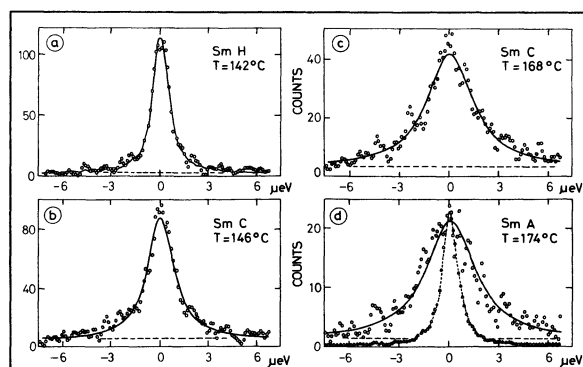
Fig. 1. — Neutron quasi-elastic spectra (corrected for container scattering) of a powder sample of partially deuterated TBBA obtained by the backscattering technique, for four temperatures in the smectic phases. Neutron momentum transfer $Q = 0.28$ Å^{-1}. The experimental resolution function is shown on spectrum *d*. The full curves are the best fit of a lorentzian curve convoluted with the resolution function together with a flat background. This background is shown by dashed lines.

to be proportional to Q^2 for all temperatures : an apparent diffusion coefficient D_{ap} can be defined by the relation

$$\Delta E = 2\ \hbar D_{ap}\ Q^2. \qquad (1)$$

Figure 2 shows a plot of D_{ap} as a function of $10^3/T$ where T is the absolute temperature. The features of this result are : (i) D_{ap} is very small and practically constant in the H phase, (ii) there is a drastic jump
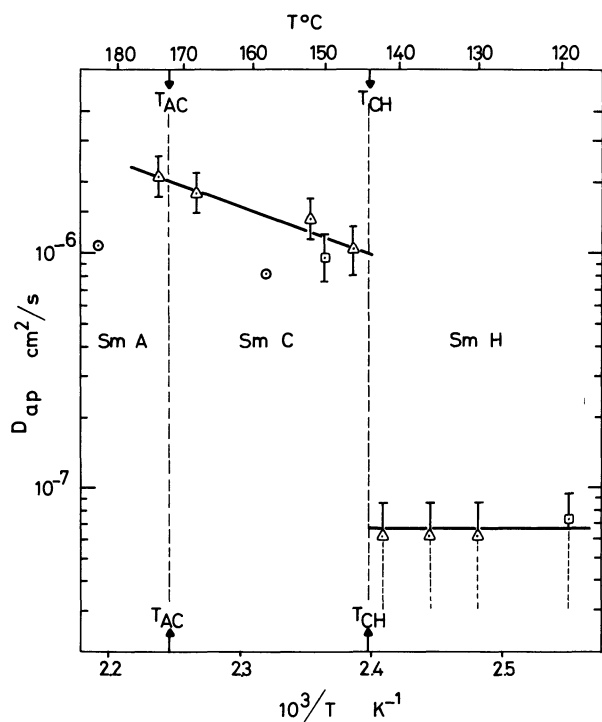

FIG. 2. — Diffusion coefficients in TBBA versus $10^3/T$.— △, □ : apparent self diffusion coefficients D_{ap} calculated from relation (1). The widths ΔE were deduced from spectra obtained in two different experiments. Sample used : partially deuterated TBBA. — 0 : average value of the self diffusion coefficient measured by a multi-pulse NMR technique [12]. Sample used : normal TBBA. — The slope of the straight line in the smectic C and A phases is about 9 kcal/mole.

(more than one order of magnitude) at the SmH-SmC transition, (iii) D_{ap} increases with temperature in the C phase and (iv) no discontinuity is apparent at the SmC-SmA transition.

One might question the choice of a lorentzian shape for the theoretical expression of the translational part of the scattering law. In view of the relatively poor statistics a fit with more than two parameters (width and background) would be meaningless. However, as can be seen from figure 1, the experimental spectra are all slightly more peaked than the single lorentzian, as expected from a system where the self diffusion is anisotropic (see the discussion in section 3 of ref. [9]). We shall now discuss the physical meaning of the experimental values of D_{ap} found in the various smectic phases.

a) Smectic H phase : Comparing the resolution function (in Fig. 1*d*) and the direct spectrum (Fig. 1*a*), ᵢ

the reader will see that the broadening is very small ($\approx 1/10$ of the resolution). It is not clear wether the measured, temperature independent, coefficient $D_{ap} \approx 6 \times 10^{-8}$ cm²/s is meaningful or not.

Since our sample is in powder form, this slight broadening could reflect self diffusion through grain boundaries, it may be that the bulk self diffusion is in fact much smaller. This view is supported by a similar unsuccessful experiment [10] performed by us on a smectic H monodomain and also a recent NMR measurement [1] where the self diffusion coefficient was found to be smaller than 10^{-8} cm²/s.

b) Smectic C and A phases : Here there is a marked broadening of the spectra and the values of D_{ap} can be considered to be accurate within ± 20 %. This rather poor accuracy arises both from the low statistics in these experiments and the finite Q resolution. The latter is due to the width of the analyzer crystals and can be calculated exactly. In our case, its contribution is much smaller than that due to the statistics.

Macroscopic self diffusion coefficients have been measured recently by NMR [11, 12]. The self diffusion was found to be anisotropic in both the smectic C and smectic A phases. The corresponding averages for two temperatures are shown in figure 2. These values are smaller by a factor $\sim \frac{1}{2}$ than D_{ap}. If the NMR technique gives the true bulk self diffusion coefficients [13], some translational motion other than the self diffusion also contribute to the broadening of the neutron spectra. We have thought of two possible explanations :

(i) Self diffusion through grain boundaries : in the present case, we had a powder sample whereas in the NMR measurements the sample was aligned with a 15 kG field yielding large monodomains.

(ii) The second possibility is related to the ondulation modes [14] present in both smectic A and C phases.

De Gennes [15] has calculated the incoherent scattering function $G(\omega)$ associated with these modes and shown that, in certain conditions, this function must diverge at low frequencies, typically 10^8 Hz ~ 1 µeV. This corresponds exactly to the present energy range. Moreover, one condition for observing such effects is to work at Q values of the order 0.2 Å^{-1}, which again is the case here. Finally, we have verified that the convolution of $G(\omega)$ (eq. (10) of ref. [15]) with a lorentzian curve (simulating the resolution function) produces a spectrum whose behaviour versus Q^2 is very similar to that produced by the self diffusion mechanism.

To decide in favour of explanation (*b*), more accurate neutron experiments are needed : with a single domain and better statistics. We hope to carry out such experiments in the near future.

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(¹) Blinc R., private communication.

References and footnotes

[1] HERVET, H., VOLINO, F., DIANOUX, A. J. and LECHNER, R. E., *J. Physique Lett.* **35** (1974) L-151.

[2] HERVET, H., VOLINO, F., DIANOUX, A. J. and LECHNER, R. E., *Phys. Rev. Lett.* **34** (1975) 451.

[3] VOLINO, F., DIANOUX, A. J., LECHNER, R. E. and HERVET, H., *J. Physique Colloq.* **36** (1975) C1-84.

[4] VOLINO, F., DIANOUX, A. J. and HERVET, H., submitted to *Phys. Rev. Lett.*

[5] BIRR, M., HEIDEMANN, A. and ALEFELD, B., *Nucl. Instrum. Methods* **95** (1971) 435.

[6] ALEFELD, B., *Kerntechnik* **14** (1972) 15.

[7] TOPLER, J., ALEFELD, B. and SPRINGER, T., *Mol. Cryst. Liq. Cryst.* **26** (1974) 297.

[8] LEADBETTER, A. J., TEMME, F. P., HEIDEMANN, A. and HOWELLS, W. S., to be published in *Chem. Phys. Lett.*

[9] DIANOUX, A. J., VOLINO, F. and HERVET, H., *Mol. Phys.* (in print).

[10] We are indebted to Dr. J. Doucet for providing the TBBA monocrystal and participating in the corresponding measurements.

[11] BLINC, R., BURGAR, M., LUZAR, M., PIRŠ, J., ZUPANČIČ, I. and ŽUMER, S., *Phys. Rev. Lett.* **33** (1974) 1192.

[12] BLINC, R., PIRŠ, J. and ZUPANČIČ, I., *Phys. Rev. Lett.* **30** (1973) 546.

[13] In fact, the true value of the self diffusion coefficient can be obtained only in the limit $Ql \ll 1$ where l is the greatest molecular dimension and $1/Q$ the distance over which the translational motion is observed. In a NMR experiment using a field gradient, one usually follows the diffusing particles over semi-macroscopic distances so that the above condition is always verified. This technique should thus give the true bulk self diffusion coefficients. With the neutron technique, even with the smallest Q available $Q \simeq 0.15$ Å^{-1}, and $l \approx 25$ Å, we have $Ql > 1$. Consequently, any low frequency large amplitude (of the order of the molecular length) oscillation, can produce similar effects to the self diffusion.

[14] DE GENNES, P. G., *J. Physique Colloq.* **30** (1969) C 4-65.

[15] DE GENNES, P. G., *J. Physique* **36** (1975) 603.