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# Inelastic Neutron Scattering by Deuterated Para-azoxy-phenetole

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Phonon dispersion curves were measured by inelastic neutron scattering on a deuterated para-azoxy-phenetole single crystal in two symmetry directions which are nearly parallel and perpendicular to the molecular axis. Results were obtained at 77 K and 296 K. The temperature dependence of the dispersion curves is not too pronounced.

## I. INTRODUCTION

In recent years increasing effort has been devoted to studies of the structure and dynamics of liquid crystalline materials.[1–4] This activity is mainly explained by the wide scientific interest in these materials. Both fundamental and applied aspects are of great importance.

Nematic para-azoxy-anisole (PAA) is one of the most widely studied liquid crystalline materials. Mainly because of this we chose PAA as a subject for structure and dynamics studies utilizing neutron scattering experiments.

It was found that solid PAA shows polymorphism[5] and due to "memory effects" traces of different crystalline structures are conserved in the nematic phase. Therefore both the structure and the spectrum of collective excitations of liquid crystalline PAA depend on the prehistory of the sample.

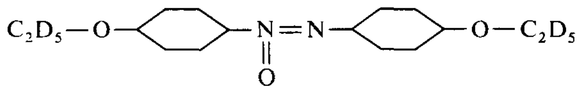
In addition to this complication due to the existence of polymorphism, single crystals of PAA cannot be grown. The study of single crystalline samples could have given the key to the understanding of the observed "phonon like" neutron resonances[6] as obtained in inelastic scattering experiments.

In order to see the change in the collective excitations around the solid-nematic liquid crystal phase transition a molecule similar to PAA, namely para-azoxy-phenetole (PAF), was chosen. This material has liquid crystalline properties similar to those of PAA but does not show temperature dependent polymorphism in the solid phase. Therefore we were able to grow a single crystal of about 0.4 $cm^3$ volume from deuterated PAF.

The present work describes inelastic neutron scattering experiments performed on a triple-axis spectrometer. Dispersion relations of phonons were obtained in two symmetry directions: one is nearly parallel to the axis of PAF molecules in the crystal, the other is nearly perpendicular to this direction. These are the directions in which a successful attempt was made to measure the dispersion relations of collective excitations in liquid crystalline PAA and the same is expected for PAF.

## II. STRUCTURE

The first experiments were aimed at determining the crystalline structure of PAF. In order to get rid of incoherent scattering by hydrogen, deuterated PAF was used in our study. The chemical configuration of the rod-like molecules is $C_{16}D_{18}O_3$ and its structural formula can be given as



The crystalline structure of PAF was first determined by Carlisle and Smith[7] using x-ray diffraction. A monoclinic elementary cell was found with space group 1a (structure A), having four molecules in the unit cell. The lattice parameters were obtained as

$$a = 22.55\,\text{Å}$$
$$b = 5.43\,\text{Å}$$
$$c = 15.84\,\text{Å}$$

and

$$\beta = 130^\circ$$

As our neutron diffraction studies on the deuterated PAF single crystal have not confirmed this structure, careful x-ray studies were performed[8] on our crystal, which turned out to be triclinic with space group $P$ (structure B) and two molecules in the unit cell. The lattice parameters can be given as

$$a = 9.439\,\text{Å} \qquad \alpha = 92^\circ 47'$$
$$b = 8.986\,\text{Å} \qquad \beta = 62^\circ 51'$$
$$c = 9.849\,\text{Å} \qquad \gamma = 94^\circ 19'$$

The axes of the two molecules in the unit cell I and II deviate with an angle of 2.4° and the angle between the molecular axes and the unit cell vectors were obtained as

$$\mathbf{l}_{\mathrm{I}} \sphericalangle \mathbf{a} = 82.7^\circ \qquad \mathbf{l}_{\mathrm{II}} \sphericalangle \mathbf{a} = 82.4^\circ$$
$$\mathbf{l}_{\mathrm{I}} \sphericalangle \mathbf{b} = 60^\circ \qquad \mathbf{l}_{\mathrm{II}} \sphericalangle \mathbf{b} = 62.3^\circ$$
$$\mathbf{l}_{\mathrm{I}} \sphericalangle \mathbf{c} = 36.3^\circ \qquad \mathbf{l}_{\mathrm{II}} \sphericalangle \mathbf{c} = 34.2^\circ$$

and the molecules are found in the (0, 0, 0) and $a/2$, 0, 0) positions as shown in Figure 1 where the alignment of the molecules is shown in two projections.

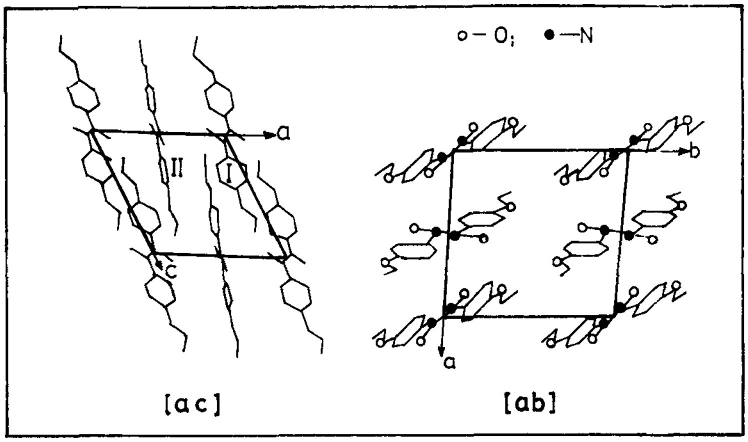


FIGURE 1 Alignment of PAF molecules in triclinic lattice in *ac* and *bc* projections. Symbols I and II indicate the two molecules of the unit cell in positions (0, 0, 0) and ($a$/2, 0, 0) respectively.[8]

To clarify the origin of the existence of two different structures, we carried out investigations using incoherent neutron scattering, Raman scattering and differential calorimetric measurements, in addition to structural investigations.

It was found that structure A is characteristic for crystals obtained from solution although the parameters obtained in Ref. 7 are somewhat different from those of Ref. 8 since

$$a = 17.445\,\text{Å}$$
$$b = 5.437\,\text{Å}$$
$$c = 15.891\,\text{Å}$$

and

$$\beta = 94^\circ 16'$$

were measured.[9] Structure B was obtained from melt. It is a stable configuration and A could not be obtained from B by remelting and crystallization.

A significant change was observed in the phonon spectrum as measured by neutron scattering or Raman spectroscopy when structure A was converted into structure B. The phase transition A → B could also be detected in the calorimetric measurements. Our deuterated single crystal certainly showed the B structure.

## III. INELASTIC NEUTRON SCATTERING

The inelastic neutron scattering experiments were performed on the triple axis spectrometer at the Budapest 5 MW WWR-M reactor.[10] The parameters of the spectrometer are given as follows:

monochromator: Zn (200); mosaic spread: 30′
analyser : Zn (200); mosaic spread 30′ or pyrolytic graphite (200); mosaic spread 90′

the collimation angles were

before the monochromator: 90′
after the monochromator: 30′
before the analyser: 40′
after the analyser: 40′

The PAF single crystal was of good quality, irregularly shaped with maximal dimensions $3 \times 21 \times 20\,\mathrm{mm}^3$. The crystal was grown in the Solid State Physics Institute of the Soviet Academy of Sciences, Chernogolovka, by the zone-melting technique. From rocking curves in some major Bragg-reflections 24′ mosaic spread was found.

Phonon dispersion curves were measured at 300 K and 77 K. For room temperature studies the crystal was glued to an Al-rod while for 77 K runs the orientation was performed together with the small Al-container in which the crystal was fastened mechanically. This container was fixed in the $N_2$-cryostat.

In order to avoid any damage to the crystal during the cooling process the sample temperature of 77 K was reached very slowly in about 30 hours. During cooling the quality of the crystal was continuously monitored by regular measurement of a few Bragg reflections.

First the proper scattering plane was chosen so that the reciprocal lattice plane, shown in Figure 2 should be in the scattering plane. This particular plane was chosen for two reasons.

1) The mean deviation of the PAF molecular axis from the (112) and (301) symmetry directions in this plane is small, namely

$$\mathbf{l} \sphericalangle \tau_{112} \sim 7^\circ$$

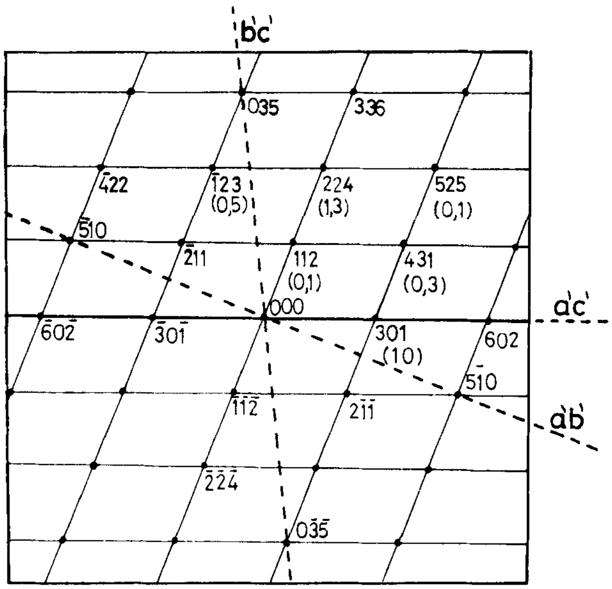


FIGURE 2 Reciprocal lattice plane chosen as scattering plane. Numbers in brackets indicate relative Bragg-peak intensities at 2 Å incoming wavelength with Zn analyzer. Dashed lines correspond to intersections of scattering plane with main symmetry planes.

and

$$\mathbf{l} \sphericalangle \tau_{301} \sim 81^\circ$$

i.e. the molecular axis is nearly parallel and perpendicular to these symmetry directions.

2) Relatively intensive Bragg reflections and phonon reasonances can be expected if the measurements are performed in the Brillouin zones around the (301) and (224) reciprocal lattice points. Some additional measurements were made around the (123) point.

Corrections for the temperature dependence of the lattice parameters were made as described in Ref. 11.

Constant momentum transfer (Q) and energy transfer $\hbar\omega$ scans were measured depending on focusing conditions.

The wavelength of the incident neutron beam was varied between 1.69 Å and 2.4 Å depending on phonon energies and focusing conditions. In some cases a large mosaic spread graphite crystal was used to eliminate second order contamination from the monochromatic ingoing neutron beam.

In order to illustrate the experimental results some of the measured neutron resonances are shown in Figures 3 and 4 for room and nitrogen

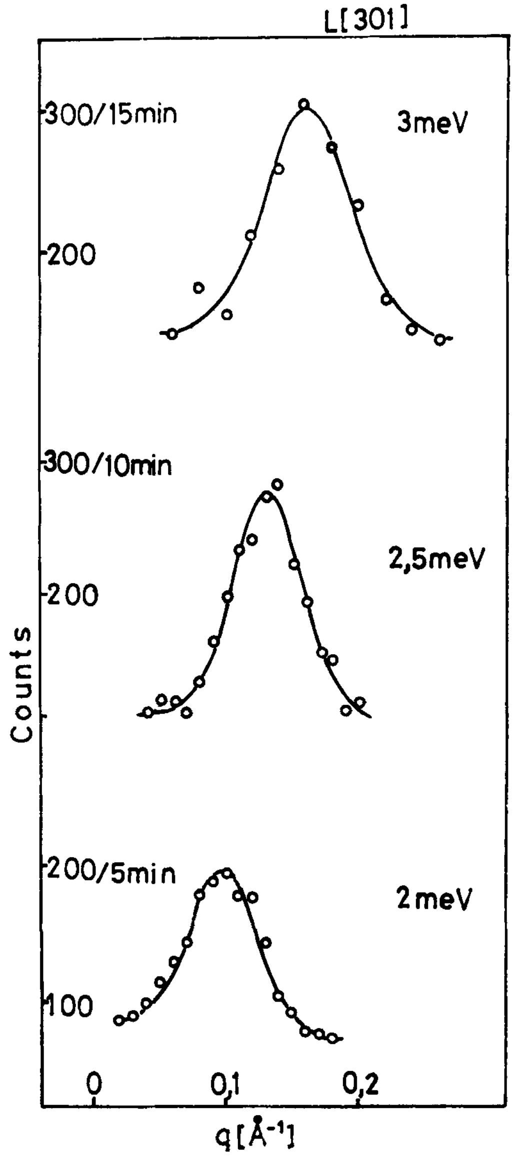


FIGURE 3 Neutron groups as measured by constant $\hbar\omega$ scans in the (301) direction around the (301) reflection at 300 K. Solid lines are computer fitted curves.

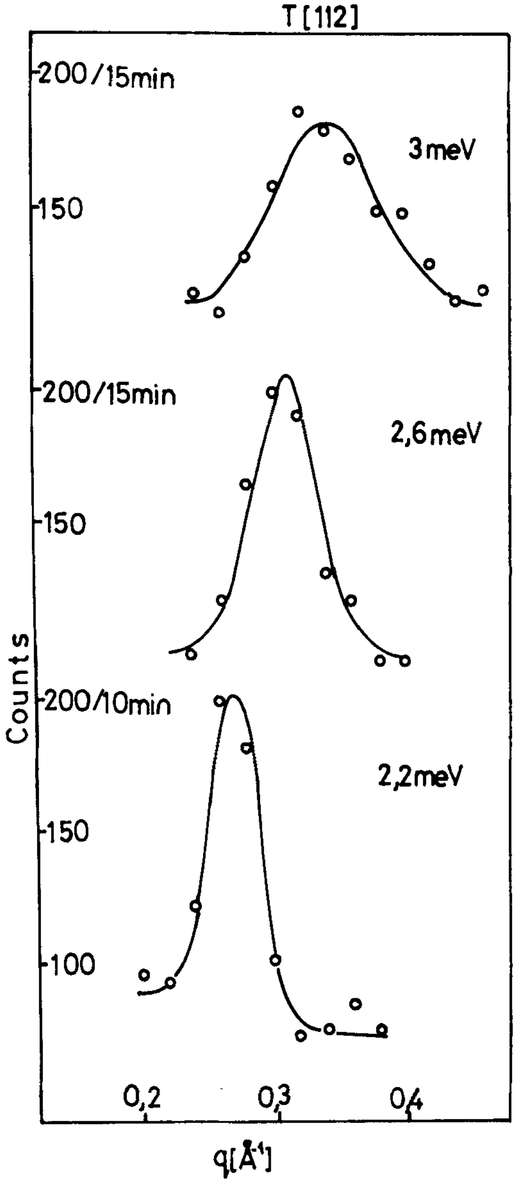


FIGURE 4 Neutron resonances as measured by constant $\hbar\omega$ scans in the (112) direction around the lattice point (3, 0, 1) at 77 K.

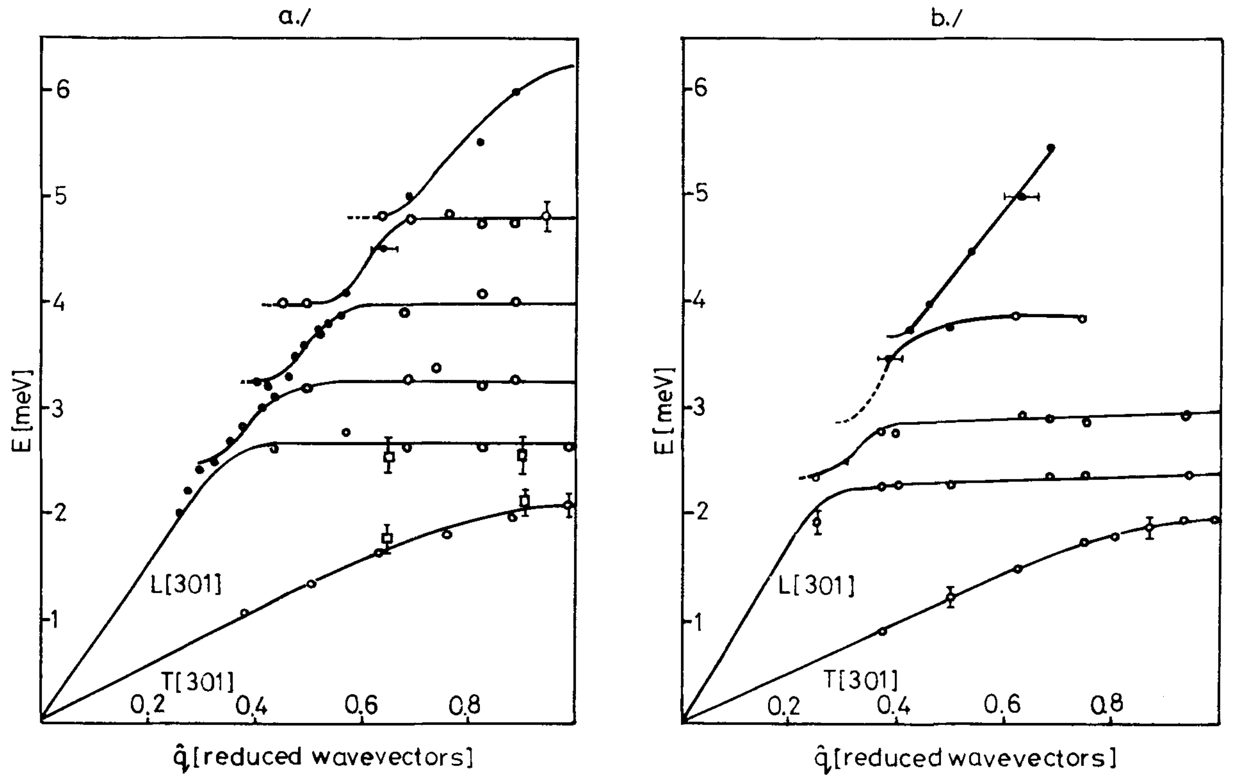


FIGURE 5 Phonon dispersion curves in the (301) direction. ● = constant $\hbar\omega$ scans, ○ = constant **Q** scans, □ = points measured in higher Brillouin zone (a) $T$ = 300 K; (b) $T$ = 77 K.

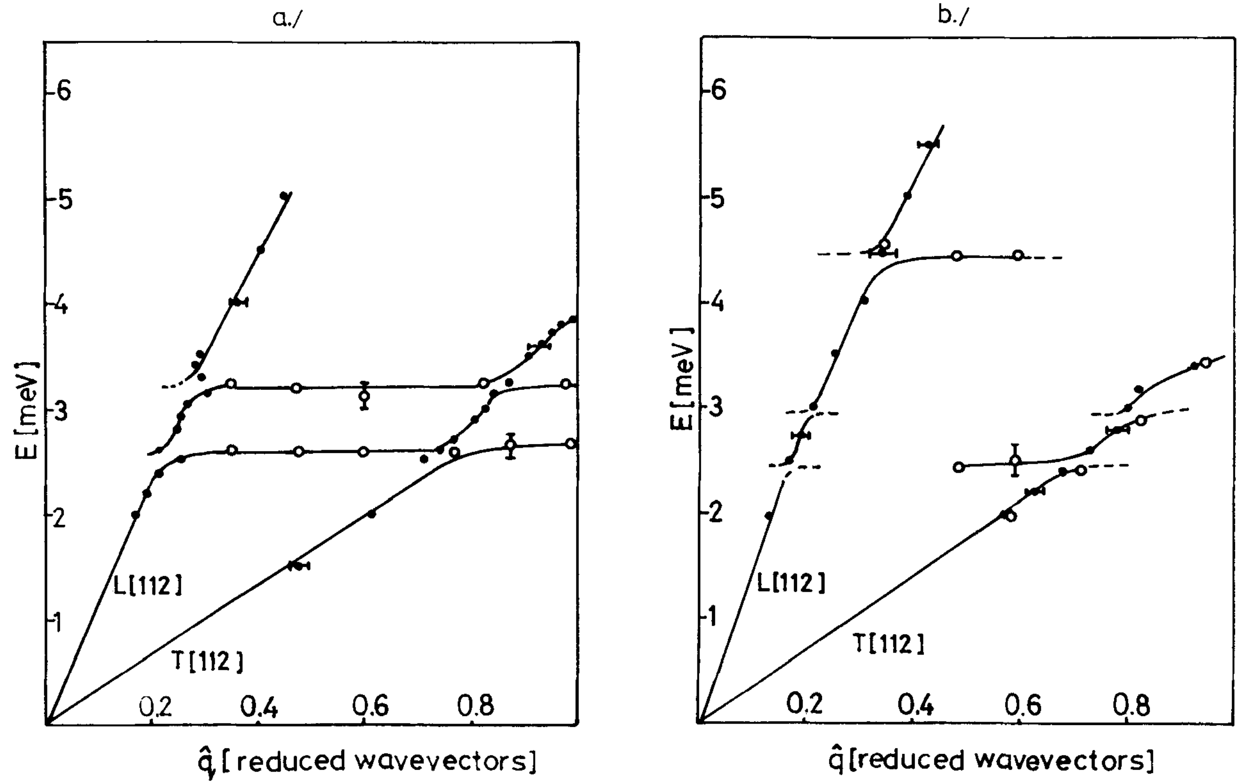


FIGURE 6 Phonon dispersion curves in the (112) direction, ● = constant $\hbar\omega$ scans, ○ = constant **Q**, (a) $T = 300$ K, (b) $T = 77$ K.

temperatures respectively. Computer-fitted curves are given by the full lines. The phonon parameters were obtained from these fittings. Statistical errors were calculated as given in Ref. 12.

The resolution function of the spectrometer was calculated by Monte Carlo simulation. Optimal experimental conditions were determined from these calculations.

As stated earlier phonon dispersion curves were measured in two directions, namely in the (301) and (112) direction for both room and nitrogen temperatures. The results are shown in Figures 5 and 6. The zone boundaries for these directions can be given as 0.3922 Å$^{-1}$ and 0.4171 Å$^{-1}$ respectively, at room temperature. Transversal and longitudinal acoustic and, in addition, optical branches were found in both directions. The presence of mixed modes at intersection points can be clearly seen. The measured phonon lines around such points were observed to be significantly broadened. Unfortunately phonon resonances at small momentum transfer values could not be measured due to technical difficulties. The known data for the optical branches at these low energies are also not good enough for comparison.[13]

One part of the inelastic scattering measurements was performed at high momentum transfers where the contribution of multi-phonon processes was very high. This is connected with the low Debye temperature of the PAF crystal. The statistical error of these data is correspondingly much higher.

## IV. CONCLUSIONS, DISCUSSION

The first conclusion from the experimental data is that well pronounced, relatively high intensity phonon resonances were measured on the small PAF single crystal. By comparing Figure 5 with Figure 6, one can see that no strong temperature dependence of the phonon dispersion relations can be observed. Some phonons are shifted toward higher enrgies with temperature and in other cases the temperature dependence is reversed.

The overall picture is similar to that of liquid crystalline PAA[6] including the intersections between the acoustic and the optical branches. This observation may indicate that similar "dispersion relations" can be expected in the liquid crystalline phase of PAF as well. The extension of present studies will cover the inelastic measurements in this latter phase. Calculations, based on first principles, are also under way to obtain, for comparison with the obtained experimental data, theoretical phonon dispersion relations.

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