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OPTICAL DETERMINATION OF SMECTIC A LAYER SPACING
IN FREELY SUSPENDED THIN FILMS

Charles Rosenblatt and Nabil M. Amer

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Applied Laser Spectroscopy Group
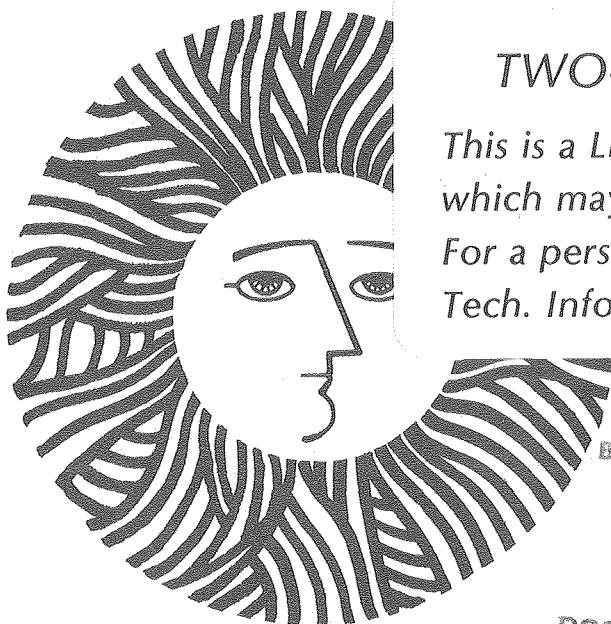Lawrence Berkeley Laboratory
University of California
Berkeley, CA   94720

ABSTRACT

Optical measurements of smectic A layer spacings in freely suspended thin films of three liquid crystals are reported. Although the measured spacings are close to those reported for the bulk, some anomalous behavior is noted. In addition, we report that the smectic A phase in the film can exist at unusually high temperatures.

Freely suspended liquid-crystal thin films offer a potentially powerful experimental tool for the investigation of the physics of two-dimensional systems. These films are quantized in one or more molecular layers, and can be readily created in the laboratory[1]. Many of their properties have been investigated by light scattering techniques[2,3], and recently the nature of molecular order in thick films (>30 molecular layers) has been determined by x-ray scattering[4]. Definitive x-ray measurements of thin films await further development of intense synchrotron-produced x-ray sources to compensate for the small scattering intensity.

We have employed a simple optical approach to deduce the layer spacing of smectic A thin films ($2 \leqslant N \leqslant 15$). Since these freely suspended films are much thinner than optical wavelengths, one can make use of optical interference effects to measure smectic layer spacings. Consider the case of a light beam incident on a thin uniform[5] slab of material. The reflectivity coefficients for electric fields in ($R_\parallel$) and perpendicular to ($R_\perp$) the plane of incidence are given by[6]

$$R_\parallel = \frac{(n_\parallel^2 \cos^2 i - \cos^2 r_\parallel)^2 \sin^2 a_\parallel}{4n_\parallel^2 \cos^2 i \cos^2 r_\parallel + (n_\parallel^2 \cos^2 i - \cos^2 r_\parallel)^2 \sin^2 a_\parallel} \qquad (1)$$

$$R_\perp = \frac{(\cos^2 i - n_\perp^2 \cos^2 r_\perp)^2 \sin^2 a_\perp}{4n_\perp^2 \cos^2 i \cos^2 r_\perp + (\cos^2 i - n_\perp^2 \cos^2 r_\perp)^2 \sin^2 a_\perp} \qquad (2)$$

where: i = angle of incidence

$r_\parallel$ ($r_\perp$) = angle of refraction for the parallel (perpendicular) mode

$n_\parallel$ ($n_\perp$) = index of refraction for the parallel (perpendicular) mode

$a_\parallel$ = $n_\parallel k h \cos r_\parallel$

$a_\perp$ = $n_\perp k h \cos r_\perp$

k = wavevector of light

h = thickness of film

The smectic A phase is birefringent and the optic axis lies perpendicular to the plane of the film (and therefore in the plane of incidence) (see Fig.1). $n_\perp$ is therefore independent of i and is equal to n_0, the ordinary component of the refractive index. However, for light polarized in the plane of incidence (parallel mode), $n_\parallel$ is given by the usual formulae

$$n_\parallel = \left[\frac{\sin^2 r_\parallel}{n_\varepsilon^2} + \frac{\cos^2 r_\parallel}{n_0^2} \right]^{-1/2} \qquad (3)$$

$$\text{and} \quad \sin r_\parallel = \frac{\sin i}{n_\parallel}, \qquad (4)$$

which easily simplify to yield a transcendental equation in the variable $n_\parallel$. Here n_ε is the extraordinary component of the refractive index. In principle, three independent measurements of $R_\parallel$ at three different angles i would yield n_0, n_ε, and the film thickness h . Such a measurement, in addition to yielding the film thickness (and hence layer spacing for a film of N layers),would provide useful information about the density of the film (through the symmetric component of the dielectric tensor) as well as the orientational order (through the assymetric component of the dielectric tensor). Nevertheless, small errors in such quantities as $R_\parallel$ and uncertainties in i strongly propagate in this technique, creating large errors in the quantities of interest; the errors are sufficiently large to render this measurement meaningless.

We have consequently opted for a somewhat less ambitious measurement, though nevertheless interesting. One measurement of $R_\parallel$ at a given angle yields a surface in (h, n_0, n_ε) space (cf. eq. 1); on the other hand, a measurement of $R_\perp$ at some angle i yields a line h vs. n_0. Hence, although we cannot extract absolute values of h and n_0, we can nevertheless gain some insight as to their behavior in thin films.

Three materials are investigated: octyloxy cyanobiphenyl (8OCB) butyloxybenzylidene octylaniline (40.8), and cyanobenzylidine octyloxyaniline (CBOOA). Films are drawn across a 6 mm square hole in a microscope cover slide and are housed in a small oven, with a temperature stability of ± 300 mk (see Fig. 1). The portholes for light passage are covered with microscope slides, tilted in the plane of incidence by 3.6° with respect to the film; this prevents light reflected by the glass window from interfering with light reflected from the film. Light from a 2 mW He-Ne laser first passes through a polarizer, a beam splitter, then into the oven, where the angle of incidence i is 20° (Angles of 8° and 30° were also checked, with no systematic variation in the results). Two identical photodiodes are used and are biased in parallel with the same voltage source. One photodiode monitors the reflected intensity and the other monitors the beam-split signal, and hence is calibrated to the incident intensity. $R_\perp$ is then taken as the ratio of the reflected intensity to the incident intensity, corrected for small voltage offsets, stray light, and the transmission of the reflected light through the glass window.

Thirty to forty films are drawn at a given temperature for each material studied. The measured reflectivities are quantized[1,2,3], taking on well-defined values corresponding to the number N of smectic layers; the scatter in data around any given value of $R_\perp$ is generally less than 1%. For thin enough films (N≤15) Eq. 2 reduces to $R_\perp \propto h^2$. Assuming that $h = a_0 N$, where a_0 is a constant layer spacing, one can associate a value of N with each $R_\perp$ such that $R_\perp \propto a_0^2 N^2$.

We also assume that the index of refraction n_0 is constant and independent of film thickness; thence, from Eq. 2, we calculate a film thickness for each measured $R_\perp$ and hence N. In

Fig. 2a we plot h vs. N, assuming $n_0 = 1.50$[7], the bulk value for 8OCB at

T = 67.3°C. Performing a least squares fit to the function $h = a_0 N + b$,

we obtain a = 31.1 $\pm$ 0.2, b = -1.4, and an rms error is 2.2. The very small

negative intercept is characteristic of all our results. Although it may

arise from real physical effects (such as slightly thinned outer layers

because of the assymetric environment near the surface), it can also be due

to a changing value of n_0 which is a function of N. This effect may be seen

more easily in Figure 2b, where we have plotted h/N vs. N. Although the

scatter is about $\pm$ 0.2 angstroms, it can be seen that values of h/N for

N $\leqslant$ 4 are generally less than those for larger N. If, however, one assumes

that n_0 were 1.49 for N $\leqslant$ 4 (rather than 1.5), the effect would be to increase

h/N to values more closely resembling those of the thicker films, i.e.,

about 31.0 angstroms. In other words, n_0 may be slightly reduced in thinner

films. With the present technique, however, one cannot ascertain whether a

thickness-dependent refractive index is due to orientational or density

considerations, if in fact there is a refractive-index effect at all.

In Figures 3a, 3b, and 3c we plot layer spacing vs n_0[7-10] for the

materials 8OCB, 40.8, and CBOOA respectively. We have assumed that n_0 is

constant as a function of N and therefore the layer spacing shown is the

slope of the h vs. N line, as in Fig. 2a. If one assumes, however, that n_0

is N-dependent (cf. Fig. 2b) and that a_0 is simply h/N, then values of a_0

would be reduced by 0.1 to 0.2 angstroms in thicker films from those reported

in Fig. 3,for a constant n_0. In thinner films the correction would be slightly

greater. Since the error bars for a_0 are $\pm$ 0.5 angstroms, these corrections

fall within experimental error. (In addition to scatter, errors arise from a

small uncertainty in angle i and from local variations in the transmission

coefficient through the oven's glass window.)

We have also investigated the temperature dependence of the layer spacing. For 8OCB and 40.8 there appears to be no systematic temperature-dependent behavior of h vs. N_O in the films. In CBOOA, however, there appears to be a weak but systematic increase in a_O as a function of temperature. The data shown in figure 4c are for T = 82.3°C. Assuming a fixed n_O, a_O decreases by approximately 0.2 angstroms at T = 74.5°C and increases from that shown by 0.2 angstroms at T = 85.3 C. It is interesting to note that this is the first reported case of a smectic A film existing at temperatures which would normally be nematic in bulk; earlier measurements[3] on the chiral material decyloxybenzylidene-p′-amino-2-methylbutylcinnamate (DOBAMBC) have shown the existence in films of the chiral smectic C phase at temperatures in which the bulk is in the smectic A phase.

In figure 3 asteriks show the approximate bulk behavior in the smectic A phase at T= 64°C for 8OCB,[7,11] T = 60°C in 408,[4,8] and T = 80°C in CBOOA.[9,10,12] Although the bulk data lie very close to the a_O vs. n_O lines, the measured values of a_O are nevertheless consistently smaller than their corresponding bulk values, assuming n_O is identical in film and bulk. Such an effect might arise from an assymetric surface potential or the smeared-out nature of the film's surface. On the other hand one can also view the data from the standpoint of a_O being the same in both bulk and films with n_O in films being smaller than in bulk. Such an effect can arise from a decreased density in films as films tend to maintain the chemical potential of the bulk reservoir in the presence of a surface tension. It was shown[2] in smectic C films that the density is independent of N; however, the density effect needed to account for our results are very small and would fall well within the error bars of the earlier experiment. A decreased n_O can also be due to orientational effects.

Reflectively measurements alone cannot answer all these questions. However, our approach, in conjunction with future x-ray and light scattering experiments, should enable the elucidation of the nature of orientational ordering, possible

density effects, and of the transition from two to three dimensionality in these films.

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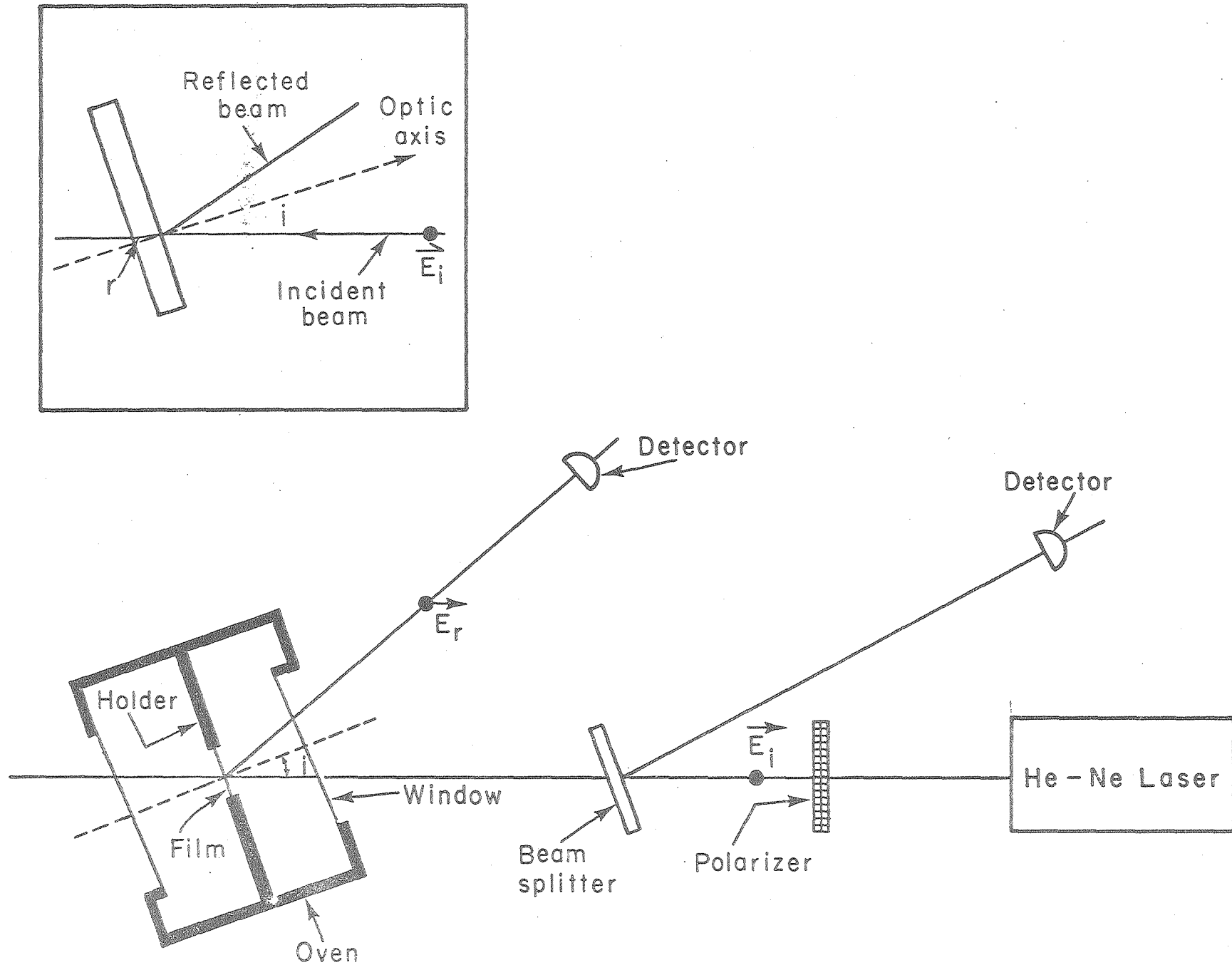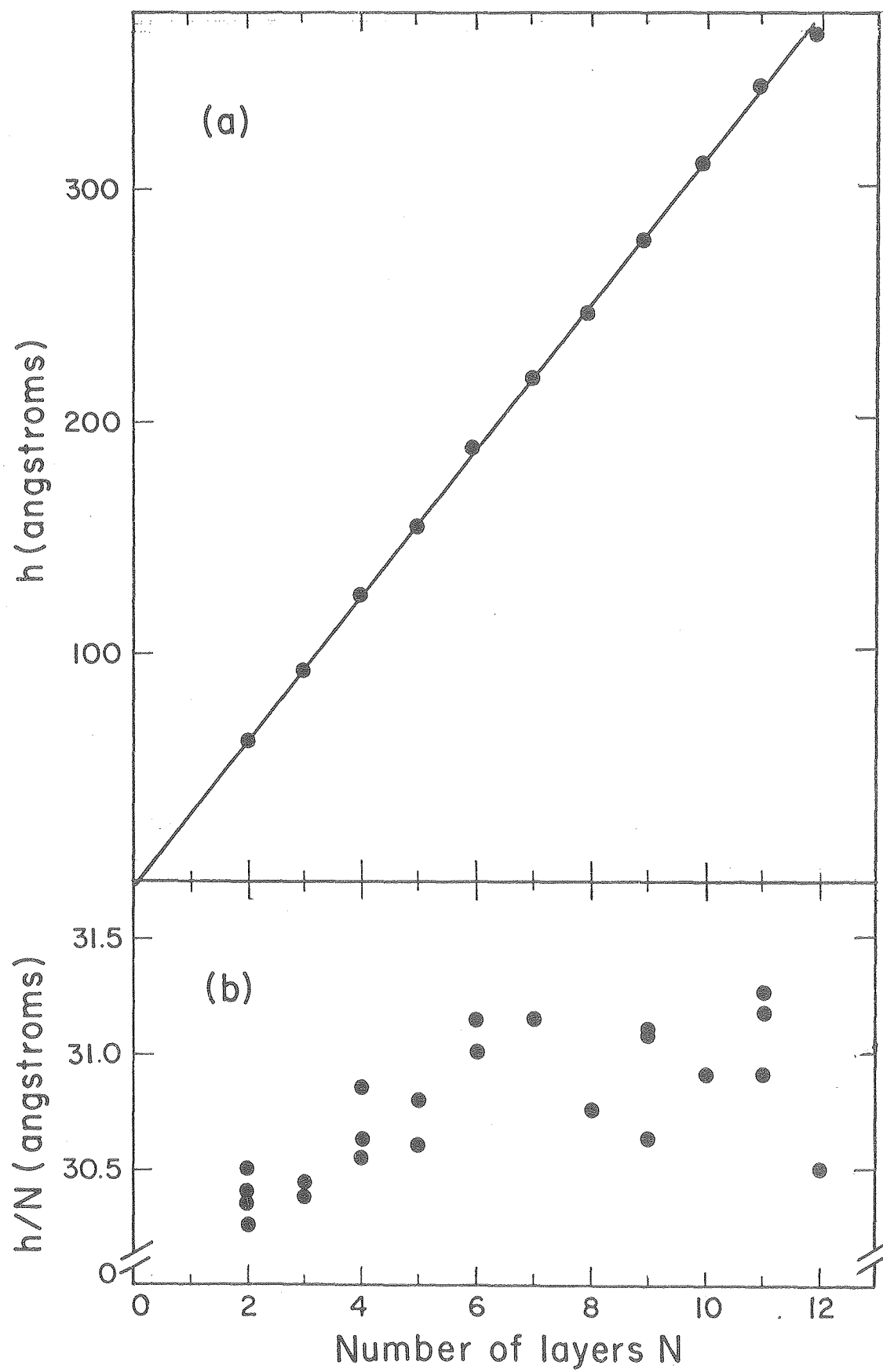12) R. Ribotta, J. Physique Colloq., 37, C3-149 (1976).

Figure Captions

Figure 1 - Optical arrangement

Figure 2 - a) Film thickness vs. N in 80CB at 65.5°C assuming $n_o=1.50$. Line is least squares fit to data points. Error bars are approximately ±1%.
b) h/N vs. N for some material.

Figure 3 - Layer spacing a_o as obtained in figure 2a vs ordinary refractive index n_o for three materials. Error bars are shown. Asterisks represent bulk data, where values of a_o are obtained from X-ray experiments.
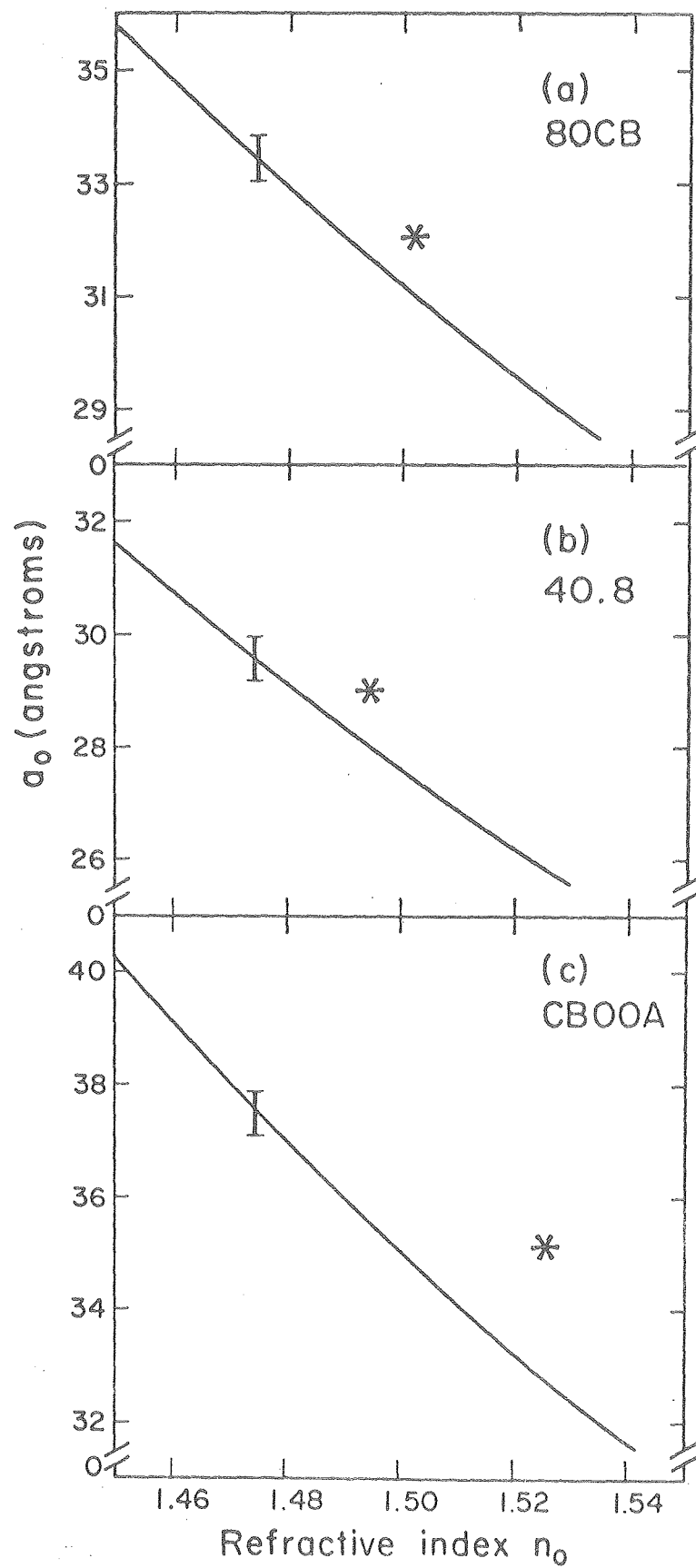
(Fig. 1)

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(Fig. 2)

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(Fig. 3)