yields a factor of -2 (-1 from Wick's theorem, and 2 from both possible orientations). Thus each fermion diagram yields the same contribution as the corresponding GLW diagram for $n=-2$, provided we choose $\epsilon_k = k^2 + r_0$. Since the interaction trivially vanishes in (2), the perturbed partition function is equal to the unperturbed one, for the GLW as well as for the fermion problem.

The proof extends to the two-point correlation function, as well as to the case of long-range or nonlocal interactions. However, as expected, the one-to-one correspondence between the fermion and GLW diagrams breaks down for the vertex function: Indeed, fermion diagrams involve a minus sign not only for closed loops, but also for each crossing of open loops when there are four external legs or more, in contradistinction to GLW diagrams.

We conclude with a few remarks. In the general solution[4] for $d=1$ and n arbitrary, the critical point $r_0=0$, $n=-2$ appears as a triple point in the plane r_0, n. However, in the renormalization-group approach[2] around $d=4$, nothing special happens at $n=-2$ to the coupling constant $u_0(\epsilon)$ which generates the scaling behavior in perturbation theory. This supports the idea that critical indices as a function of n have no discontinuity between the physical region and the line $n=-2$. This line, on which exact results have been derived here, is thus a good starting line for extrapolation. From this point of view, expansions in powers of $n+2$ would prove as useful as those existing in $4-d$ and $1/n$.

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Measurement of Self-Diffusion in Liquid Crystals by a Multiple-Pulse NMR Method*

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A NMR technique, which consists of a superposition of (i) a Waugh-type multiple 90° rf pulse sequence removing dipolar interactions, (ii) a pulsed magnetic-field-gradient sequence, and (iii) a relatively slow Carr-Purcell train of 180° pulses is used to determine translational self-diffusion coefficients in liquid crystals where the classical NMR technique fails because of too short a T_2.

The most basic property of liquid crystals is that they flow while sustaining an orientationally ordered structure. Very little, however, is known on the nature of this process on a microscopic basis. This is at least partly due to a lack of suitable techniques which would allow a fast and accurate determination of the translational self-diffusion coefficients in these systems. The proton magnetic-resonance spin-echo method[1] would be ideally suited for such a purpose if it would work. This method can be successfully applied for the determination of self-diffusion coefficients only if the extra damping of the transverse nuclear magnetization due to the change in the Larmor frequency as a result of migration of the molecules across the inhomogeneous applied magnetic field is larger than the inherent damping due to spin-spin interactions (T_2). In liquid crystalline systems the dipolar broadening is not completely averaged out by molecular motion as in isotropic liquids, and therefore T_2 is so short that the classical NMR method fails.[2]

Doane and Parker[3] have partially removed dipolar interactions by working with an oriented

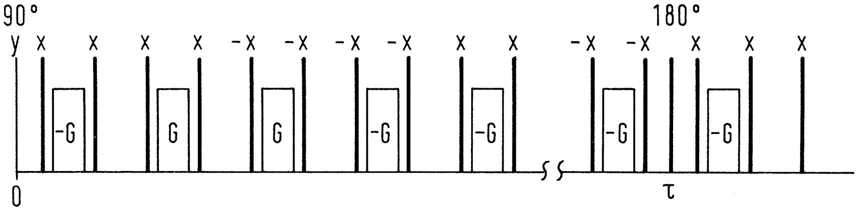

FIG. 1. Schematic diagram of rf $(y, x, 180°)$ and field-gradient (G) pulse sequences used for the determination of self-diffusion in liquid crystals. The y and x pulses are 90° pulses applied along the y and x directions in the rotating frame.

smectic liquid crystal at the magic angle $(\Theta = 55°)$. This method can be applied only in some special cases, and it does not represent a general solution of the problem.

In the present Letter we propose the use of a new technique which overcomes the above-mentioned difficulties and which allowed—as we believe—the first direct NMR determination of translational self-diffusion coefficients in nematic liquid crystals. The technique we used represents a superposition of a Waugh-type[3] multiple 90° rf pulse sequence, averaging out dipolar interactions, a pulsed linear magnetic-field-gradient sequence, and a relatively slow Carr-Purcell train of 180° rf pulses.

The detailed pulse sequence is shown in Fig. 1. For experimental convenience we used the simplest Waugh sequence,[4] which averages out dipolar interactions. It consists of a train of equally spaced 90° pulses which are shifted in phase with respect to the first 90° pulse by $\frac{1}{2}\pi$. The spacing between the first 90° pulse, applied along the y direction in the rotating frame, and the second 90° pulse, applied along the x direction, is $\frac{1}{2}t_0$, whereas the spacing between all other x pulses is t_0. Since four 90° pulses represent an identity transformation, $[\exp(-\frac{1}{2}i\pi I_x)]^4 = 1$, the cycle time t_c is $t_c = 4t_0$. To prevent an accumulation of phase errors and to make the experimental setup less critical, the phases of each second pulse cycle are reversed so that the Waugh sequence we used is $y, x, x, x, x, -x, -x, -x, -x$, etc.

It has been shown by Haeberten and Waugh[5] that if the cycle time t_c becomes small as compared with T_2, the spin system behaves over long times Nt_c—where N is the number of cycles—as if under the influence of an effective time-independent average Hamiltonian $\bar{\mathcal{H}}$ which can be expressed in terms of a rapidly converging series:

$$\bar{\mathcal{H}} = \sum_{l=0}^{\infty} \bar{\mathcal{H}}^{(l)}, \tag{1}$$

where

$$\bar{\mathcal{H}}^{(0)} = \sum_{i=1}^{K} A_i, \tag{2a}$$

$$\bar{\mathcal{H}}^{(1)} = \tfrac{1}{2}\sum_{i<j} [A_i, A_j], \tag{2b}$$

$$\bar{\mathcal{H}}^{(2)} = \tfrac{1}{12}\Big\{ \sum_{i<j} \big[(A_i - A_j), [A_i, A_j]\big] + 2\sum_{i<j<k} \big[A_i, [A_j, A_k]\big] + \big[[A_i, A_j], A_k\big]\Big\}, \tag{2c}$$

$$A_i = \frac{t_{i+1} - t_i}{t_c}\mathcal{H}(t), \quad t_i < t < t_{i+1}. \tag{3}$$

In deriving the above expressions it was assumed that the Hamiltonian $\mathcal{H}(t)$, as transformed by the rf pulses, is constant during the $\mathcal{H}$ intervals (t_i, t_{i+1}) of the cycle t_c. The results (2a)–(2c) can be most simply obtained from the theorem of Liapunov[6] in the theory of systems of linear differential equations with periodic coefficients.

The first y pulse transforms the spin Hamiltonian into the rotating frame, and the Waugh cycle of x pulses partially averages out the dipole-dipole interaction Hamiltonian $\mathcal{H}_D$. Though $\bar{\mathcal{H}}_D^{(0)}$ as given by (2a) and (3) is nonzero, it commutes with I_x, $[\bar{\mathcal{H}}_D^{(0)}, I_x] = 0$, so that in this order the dipolar contribution to the second moment term in the free induction decay vanishes. Since $\bar{\mathcal{H}}_D^{(1)} = 0$, it is only $\bar{\mathcal{H}}_D^{(2)}$ which gives a dipolar contribution to the decay of the precessing nuclear magnetization. The decay time is thus significantly lengthened. The above Waugh sequence, however, also averages out the static field-gradient term

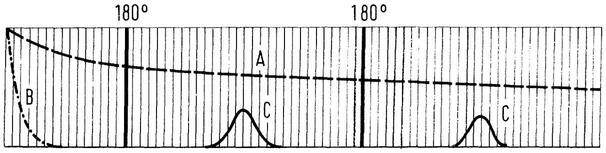

FIG. 2. "Waugh" signal envelope without (*A*) and with (*B*) applied field-gradient pulses. Echoes appear (*C*) when a slow Carr-Purcell train of 180° pulses is superimposed on the Waugh sequence in the presence of gradient pulses.

in the Hamiltonian. During the five intervals of the cycle, $0<t<\frac{1}{2}t_0$, $\frac{1}{2}t_0<t<\frac{3}{2}t_0$, $\frac{3}{2}t_0<t<\frac{5}{2}t_0$, $\frac{5}{2}t_0<t<\frac{7}{2}t_0$, $\frac{7}{2}t_0<t<4t_0$, the values of the field-gradient term are ΔI_z, ΔI_x, $-\Delta I_z$, $-\Delta I_x$, ΔI_z, respectively, and the average over the cycle vanishes. If, however, the field gradient is applied in pulses so that $\Delta=\omega-\omega_0$ is different from zero only in the second and fourth intervals and its sign in the fourth interval is just opposite to the one in the second interval, the effect of the field gradient does not average out.

The shortening of the decay time due to the presence of the pulsed field-gradient sequence is illustrated in Fig. 2. Here, the broken lines show the Waugh echo envelope without an applied field gradient; the dotted line shows the same envelope in the presence of the field gradient pulses. The loss of magnetization caused by the field gradient is, however, not irreversible. The magnetization can be recovered in the form of echoes which appear at times $(2n)\tau$ if a slow Carr-Purcell train of 180° pulses is applied at times $n\tau$, where τ is an integral multiple of the cycle time $t_c=Nt_0$.

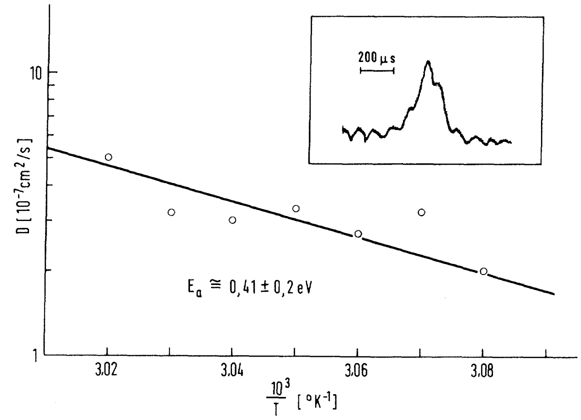

FIG. 3. Temperature dependence of the self-diffusion coefficient $D_{\parallel}$ in the smectic-*A* phase of 4-*n*-butoxybenziliden-4'-*n*-octylaniline. The inset shows the boxcar trace of the first echo the dependence of which on the width of the gradient pulses was used to determine $D_{\parallel}$.

The echo maxima are given by

$$m(2n\tau)=m(0)\exp[-2n\tau/T_2^{x}-\tfrac{1}{12}\gamma^2\delta^2\vec{G}\cdot\overleftrightarrow{D}\cdot\vec{G}(2n\tau)], \tag{4}$$

where δ is the total time the field gradient $\vec{G}=\operatorname{grad}H_z$ is on during the interval $(2n\tau)$ and $\overleftrightarrow{D}$ is the self-diffusion–constant tensor. The effective decay time T_2^{x} is limited by the second-order dipolar contribution $[\mathcal{H}_D^{(2)}]$, the mixed field-gradient–dipolar terms which, as well, occur in second order, and the spin-lattice relaxation time in the rotating frame, $T_{1\rho}$. By measuring the ratio between the spin-echo amplitudes with and without a field gradient, $m(G\neq0)/m(G=0)$, as a function of the width of the field-gradient pulses, the various components of $\overleftrightarrow{D}$ can be obtained.

As an example we measured partially deuterated MBBA (paramethoxybenzilidenebutylaniline) which is nematic at room temperature and where T_2 is of the order of 100 μsec. The value of t_0 we used is 25 μsec. The amplitude of the field-gradient pulses was about 50 G/cm and the gradient pulse width was varied between 5 and 14 μsec. Echoes could be still seen 60–100 msec after the first y pulse, demonstrating that T_2^{x} is of the order of $T_{1\rho}$ and hence much longer than T_2. From the dependence of the echo amplitudes on the widths of the gradient pulses, the component of the self-diffusion tensor parallel to the magnetic field, $D_{\parallel}$, is obtained at 21°C: $D_{\parallel}=(2\pm1)\times10^{-6}$ cm^2/sec. It is interesting that this value is significantly larger than the self-diffusion coefficient in the isotropic phase at 40°C.

The values of $D_{\parallel}$ were as well found to be surprisingly large in the rather viscous smectic-*A* phase of 4-*n*-butoxy-benziliden-4'-*n*-octylaniline (Fig. 3). The value of $D_{\parallel}=0.5\times10^{-6}$ cm^2/sec at 58°C is only 4 times smaller than that in the isotropic liquid phase at 82°C, where $D=2\times10^{-6}$ cm^2/sec.

The diffusion coefficient $D_{\parallel}$ was also measured within 1° below the nematic-solid transition point in MBBA, where the signal is not nematic anymore but not yet characteristic of a rigid solid. The value of the diffusion coefficient here is $D_{\parallel}=(2\pm0.5)\times10^{-8}$ cm^2/sec.

Using the same technique but a different set of gradient coils we measured $D_\perp$, i.e., the component of the diffusion tensor perpendicular to the static magnetic field. The results for nematic MBBA show that $D_\parallel > D_\perp$, but the error involved—which is mainly due to the calibration of the gradient—was relatively large. To avoid this we are constructing a new gradient-coil arrangement where the direction of the gradient can be changed by a simple rotation of the coils, keeping all other factors constant.

In conclusion we would like to point out that the above technique can be used not only for self-diffusion measurements in liquid crystals but also in many other systems where the classical NMR method fails because of a T_2 too short. The success of the method depends on whether the cycle time t_c—which is limited by the widths of the pulses and the recovery time of the sensing system—can be made smaller than T_2.

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Optical Transitions between Conduction Bands in Copper and Copper-Based Alloys*

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An anomalous shift of the onset of interconduction-band optical absorption in copper-aluminum alloys gives precise values for the direct and indirect energy band gaps, setting the upper-Q_+ band profile in pure copper in the Fermi-surface-neck region of $\boldsymbol{k}$ space. In addition, it establishes the range of validity of a direct-transitions model. A consistent pattern of behavior is suggested among copper-based alloys with polyvalent solutes.

A recent study of the optical properties of Cu-Al alloys[1] with Al concentrations greater than 2 at.% indicated that the threshold for interconduction-band (ICB) absorption had shifted from the direct to the indirect neck gap (see Fig. 1) by ~2 at.% Al. This suggested that the onset of indirect transitions (induced by impurity scattering) or the static smearing of states (due to disorder) could be studied in this alloy.

In this paper, we present new optical results for Cu-Al in the concentration range 0 to 2 at.% Al, which suggest that the ICB threshold remains governed by the direct neck gap up to 1.3 at.% Al and shifts to the indirect neck gap between 1.3 and 2 at.% Al. Extrapolations of the low- and high-concentration data thus provide the direct and indirect neck gaps as a function of concentration, supporting and possibly improving upon the recent photoemission revisions[2] of these gaps for the Cu case. Also, analysis of residual-resistivity data and available optical data for Cu-based alloys with different polyvalent solutes suggests that a shift of the ICB threshold is a previously overlooked general feature occurring in widely different ranges of concentration, but in the same range of conductivity mean free path (Λ). Although a scaling of optical effects with Λ is not necessarily an obvious expectation (as discussed below), it appears that if such a scaling law is postulated, it becomes possible to understand in a unified way the optical properties of the alloy series Cu-Zn, -Ga, -Ge, -As, in addition to Cu-Al.

Figure 2 shows new $\epsilon_2(\omega)$ curves for α-phase Cu-Al single crystals together with a high-resolution Cu $\epsilon_2(\omega)$. The latter curve shows more