Experimental Observation of Anomalous Ordering in a Landau-Peierls System

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The smectic-A phase of a liquid crystal is characterized by a one-dimensional mass density wave in a three-dimensional liquid. High-resolution x ray measurements in the smectic-A phase of octyloxycyanobenzylidene (8OCB) show that the order-parameter scattering does not exhibit normal Bragg line profiles but rather corresponds to a power-law singularity of the form $(q_{\parallel}-q_0)^{-2}$, with $q_{\parallel}$ being the longitudinal wave-vector component. Also, the transverse line profile is anomalous.

A classic problem discussed by Peierls[1] in 1934 and Landau[2] in 1937 is whether in nature bodies can exist for which the density functions depend not on three, but only on one or two, coordinates. It has, of course, been convincingly demonstrated theoretically and, to a certain extent, experimentally that idealized one-dimensional spin systems do not possess an ordered phase at finite temperatures.[3] A closely related problem is that of the establishment of a 1D (one-dimensional) density wave in a 3D liquid medium. As first demonstrated by Landau,[2] in this case the mean-square fluctuations diverge logarithmically with the size of the sample thence destroying the long-range order (LRO). A similar logarithmic divergence occurs for 2D continuous-symmetry problems such as the 2D XY model[4] and 2D crystals.[5] In contrast to the 1D spin systems, it is believed both for the 2D XY model and for the 1D density-wave system that there is a second-order transition at finite temperatures to a state with long-range correlations but without LRO in the conventional sense.

The 1D density-wave system is, in fact, realized in nature in the form of a smectic-A liquid crystal. Following Landau, consider a liquid with density function $\rho=\rho(z)$ with $\rho=$ const along the x and y axes; we take as the displacement field along z (parallel to the liquid-crystal director) $u(\vec{r})=\sum_{\vec{q}} u_{\vec{q}} e^{i\vec{q}\cdot\vec{r}}$. It is then straightforward to show that in the harmonic approximation the change in free energy due to excitation of modes $u_{\vec{q}}$ is, to lowest order,

$$\Delta F=\tfrac{1}{2}\textstyle\sum_{\vec{q}}|u_{\vec{q}}|^2(Bq_{\parallel}^2+Kq_{\perp}^4), \tag{1}$$

and therefore from the equipartition theorem the mean-square fluctuation amplitude is

$$\langle u^2\rangle \sim T\int dq_{\parallel}\, d(q_{\perp}^2)/[Bq_{\parallel}^2+K(q_{\perp}^2)^2]. \tag{2}$$

This integral is easily seen to diverge logarithmically as $\vec{q}\to 0$. The analogy with the 2D models is also evident from Eq. (2), Landau and Peierls therefore concluded that such physical systems are unstable at all finite temperatures. Long-range order in the conventional sense should therefore not be possible and correspondingly the Bragg scattering from the smectic-A planes (of separation d) is expected to be anomalous.

The consequences for the expected scattering around the position $(0,0,q_0=2\pi/d)$ in the smectic-A phase may be calculated straightforwardly in the harmonic approximation[6] [Eq. (1)]. In this case, one finds that in the smectic phase the instantaneous correlations exhibit an anisotropic power-law dependence on the molecular separation. On Fourier transforming for an infinite sample in zero field, the x-ray profiles are predicted to follow

$$\begin{aligned} &I(0,0,q_{\parallel})\sim(q_{\parallel}-q_0)^{-2+x}, \quad q_{\perp}=0,\\ &I(q_{\perp},0,q_0)\sim q_{\perp}^{-4+2x}, \quad q_{\parallel}=q_0, \end{aligned} \tag{3}$$

with $x=(q_0^2/8\pi)kT(BK)^{-1/2}$. We should emphasize that, with x rays, one measures the instantaneous correlations so that Eq. (3) represents quasielastic rather than true elastic scattering. Analogous results have been obtained for the 2D harmonic crystal.[5] Clearly the harmonic approximation will break down near the smectic-A–nematic transition temperature T_c; however, there is currently no theory for the behavior near T_c. The logarithmic singularity of Eq. (2) is removed by both finite-size effects and by an applied magnetic field.[7] Experimentally, this means that in addition to the quasielastic scattering described by Eq. (3), one should observe true Bragg scattering at $(0,0,q_0)$. However, for a typical experimental arrangement this component may be unobservably small, especially near T_c.[8] In spite of the enormous theoretical effort, especially in the 2D systems, these anomalous scattering effects have not yet been observed directly in any

real physical system.

In this Letter we report a high-resolution x-ray study of the mass-density fluctuation spectra in the smectic-A phase of the liquid crystal octyloxycyanobenzylidene (8OCB). This liquid crystal has a second-order nematic–smectic-A transition at $T_c = 65.925$°C. The smectic-A ordering manifests itself in the x-ray spectrum as a peak at the position $\vec{\tau} = (0, 0, q_0)$, where $q_0 \simeq 0.197$ Å^{-1}. The salient result of our experiment is that in the smectic-A phase this peak in fact does not correspond to conventional Bragg scattering but rather may be described as a power law of the form $(q_{\parallel} - q_0)^{-\alpha}$, with $\alpha = 2.0 \pm 0.1$ as expected from Eq. (3). The line profile versus $q_{\perp}$, the wave-vector component perpendicular to the director, also indicates a power-law singularity with exponent ~4 for $T_c - T > 1$ K; however, the mosaicity of the crystal prohibits a detailed analysis.

The experiments were carried out on a two-crystal x-ray spectrometer using Cu $K\alpha$ radiation from a Rigaku 12-kW rotating-anode source. The experimental arrangement is shown schematically in the upper part of Fig. 1. Using germanium-single-crystal techniques it is possible to measure the liquid-crystal mass-density fluctuation spectrum with an instrumental spatial resolution expressed as half-widths at half-maximum (HWHM) of 4.3×10^{-4} Å^{-1} in the longitudinal direction, $< 2 \times 10^{-5}$ Å^{-1} in the transverse direction, and of 0.9×10^{-2} Å^{-1} in the direction perpendicular to the scattering plane. The liquid crystal was contained in a flat rectangular vessel 12 mm $\times$ 12 mm $\times$ 1.5 mm with 0.25-mm beryllium windows. An applied magnetic field of 500 G provided alignment of the director and hence of the smectic planes. Only the center 1×3 mm^2 was illuminated with x rays. The liquid-crystal holder was mounted in the center of a two-stage servo-controlled oven; typically, the temperature was constant to within (1×10^{-3})°C during an x-ray scan.

We now discuss the experimental results. The nematic–smectic-A phase transition, which is second order, occurs at 65.925°C. Below this temperature the longitudinal HWHM is nearly temperature independent with a value of 4.9×10^{-4} Å^{-1}, ~10% larger than the width expected for an ideal Bragg peak. The transverse width is ~0.002 Å^{-1} just below T_c and, in general, it increases gradually with decreasing T. This limiting transverse width is very much larger than the transverse instrumental width and therefore represents a macroscopic misorientation of the smectic planes in different regions of the sample. In crystallographic language this is simply the mosaicity.

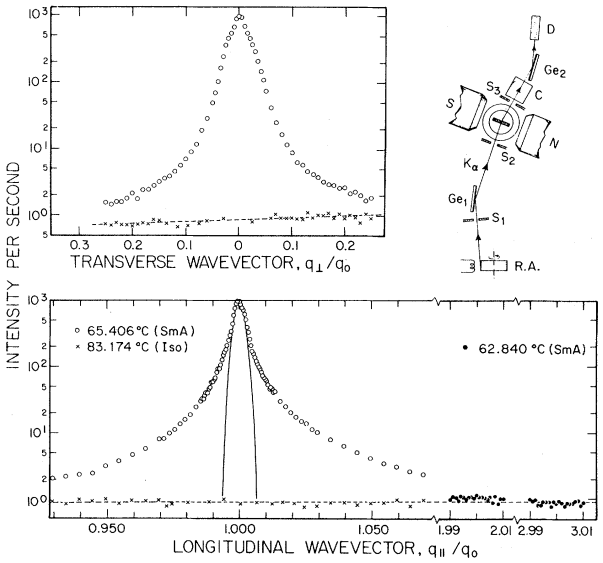

FIG. 1. Upper right, Cu $K\alpha$ X rays are generated in the rotating anode (RA). Bragg scattering from the two Ge crystals Ge_1 and Ge_2 determines the scattering angle to within 32 sec of arc. A single-domain liquid crystal is obtained by the magnetic field (500 G). The vertical divergences are determined by the source height and slit S_2 before the sample, and by a Soller collimator (10 min FWHM) with horizontal slits after the sample. Upper left, intensity profile of a transverse scan. Note the logarithmic intensity scale. Bottom, intensity profile of a longitudinal scan. A conventional Bragg peak would look like the solid curve with thermal diffuse wings below the background level. Scans through $(0, 0, 2q_0)$ and $(0, 0, 3q_0)$ indicate that the mass-density wave is purely sinusoidal.

The experimental results at $T = 65.407$°C, that is 0.52°C below T_c, are shown on a semilogarithmic scale in Fig. 1. It is immediately apparent that the observed scattering has a variety of unusual features compared with conventional Bragg scattering in a solid. Firstly we note that a strong peak occurs at $(0, 0, q_0)$ but that there is no evidence for a peak at either $(0, 0, 2q_0)$ or $(0, 0, 3q_0)$ on a relative intensity scale of 10^{-4}. Thus within this accuracy the smectic-A phase of 8OCB corresponds to a pure-sine-wave modulation of the density. Similar results were obtained previously in N-p-cyanobenzylidene-p-octyloxyaniline (CBOOA).[9]

Let us now consider the line profiles at $(0, 0, q_0)$. The solid curve at the center of the longitu-

dinal scan [scanning $\vec{q}$ along $(0,0,q_{\parallel})$] gives the instrumental resolution function; this corresponds to the expected line shape for Bragg scattering. In a crystalline solid there would also be $(q_{\parallel}-q_0)^{-2}$ thermal diffuse wings. However, our resolution ellipsoid has a volume of 2×10^{-10} Å^3 and thermal diffuse scattering is spread over a typical Brillouin-zone volume of ~0.2 Å^3. Even allowing for mosaicity, it is very conservative to estimate that thermal diffuse scattering in a crystal with conventional long-range order would never exceed 10^{-3} of the Bragg-peak intensity for our experimental conditions. We also verified this theoretical estimate by unsuccessful attempts to observe thermal diffuse scattering from graphite and squaric acid. It is evident therefore that the measured line profile differs in a fundamental fashion from that in a solid. The transverse scan, that is scanning $q_{\perp}$ with $\vec{q}=(q_{\perp},0,q_{\parallel}=q_0)$, is shown in the upper part of Fig. 1. Here the HWHM is 3.5×10^{-3} Å^{-1} due to the mosaic effect. Again we observe rather long tails similar to those in the longitudinal scan but dropping off more rapidly with $q_{\perp}$.

In order to illustrate the explicit q dependence of the scattering we show in Fig. 2 the scattering in log-log form for $T=64.606$°C ($t=|T/T_c-1|=4\times10^{-3}$), 65.407°C ($t=1.5\times10^{-3}$) and 65.704°C ($t=6.5\times10^{-4}$). By inspection, the longitudinal wings are approximately described by the form $(q_{\parallel}-q_0)^{-\alpha}$ with α near 2. The transverse wings are not as clean due to the mosaicity of the sample but, in terms of an effective power law $q_{\perp}^{-\beta}$, the exponent β decreases from around 4 at $t=4\times10^{-3}$ to around 2.5 at $t=6.5\times10^{-4}$. The mosaicity affects the $q_{\perp}$ scans to first order and the $q_{\parallel}$ linewidths only in second order; because of this we carried out a detailed quantitative analysis of the wings of only the longitudinal scans. Both the instrumental resolution and the mosaic spread (~1° HWHM from the $q_{\perp}$ scans) were used in deconvolution of the data. The parallel line profile could be fitted by $(q_{\parallel}-q_0)^{-\alpha}$ up to ~50% of the peak height; however, the quality of fit was affected by the precise mathematical form assumed for the mosaic spread. This did not occur if only data up to 10% of the peak height were used; least-squares fits yielded the solid lines with exponents shown in Fig. 2. At $T=64.606$°C, that is 1.3°C below T_c, the line shapes correspond closely to the predictions of the harmonic theory. Using Eq. (3) with values of B and K deduced from light scattering[10] we estimate $x\sim0.1$; thus the deviation from the $q_{\parallel}^2, q_{\perp}^4$ behavior should be as small

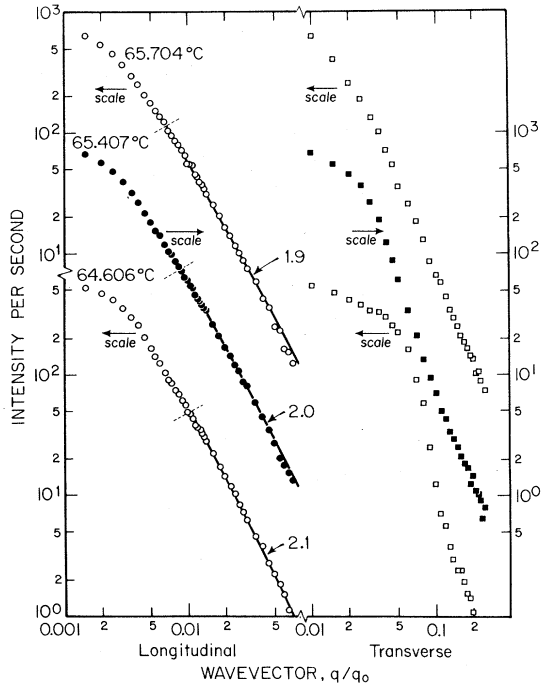

FIG. 2. The wings of longitudinal (left) and transverse (right) scans shown in double log plots. Open signatures, left ordinates; filled signatures, right ordinate. The increasing mosaicity with decreasing temperature is clearly seen in the transverse scans. The solid lines are the results of least-squares fits to power-law singularities, including both instrumental resolution and mosaic corrections as discussed in the text.

as observed. The longitudinal exponent α appears to decrease slightly on approaching T_c as anticipated from Eq. (3); however, the errors (±0.1 for each α) are such that we cannot be sure this is a real effect. In the absence of a theory which includes critical fluctuations, quantitative analysis of data near T_c is not particularly meaningful. However, our data indicate that the phase transition manifests itself in the x-ray scattering chiefly as a decrease in the exponent β for the transverse wings. It may be this represents the increasing importance of a $q_{\perp}^2$ term in the transverse wings; this would be consistent with behavior on the nematic side of the transition.[9] We may also note that our sample size is ~10^8 Å and the magnetic coherence length is ~6×10^5 Å in a field of 500 G. A Bragg peak due to these effects would not be observable with our resolution of 4.3×10^{-4} Å^{-1}. As we have discussed previously the relative intensity of the wings is so large we may conclude that any true Bragg component is

negligible compared with that in systems with conventional long-range order.

Thus our experiments have revealed that smectic-*A* liquid crystals provide an example of an anomalous dimensionality Landau-Peierls system which can be fruitfully studied experimentally, and the unusual form anticipated for the two-particle correlation functions in such systems has been directly verified. Most theoretical effort to date has been concentrated on the 2D *XY* model. The theory for smectic-*A* liquid crystals, especially near T_c, is relatively undeveloped and a significant theoretical effort is called for. On the experimental side, it should be possible to ameliorate the mosaic problems to obtain more accurate line shapes throughout the smectic phase.

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Extension of Equilibrium Formation Criteria to Metastable Microalloys

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Metastable microalloys of 25 metallic elements with beryllium have been prepared by ion implantation. The injected atoms have been found to occupy one of three sites available in the solvent lattice. A modified Landau-Ginsburg expansion using bulk alloy variables proposed by Miedema is completely successful in predicting the observed metastable-site preferences and indicates a broader applicability of these variables than was heretofore anticipated.

Defects in metals have been studied for the most part indirectly, and only in a few cases (e.g., "fast" interstitials[1,2]) are systematic quantitative data available. By and large, the solubility (or lack thereof) of one element in another and the choice of crystal structure of compounds are determined by energy differences which are small. This is particularly true for a defect or impurity where formation energies are largely canceled by lattice relaxation. Direct prediction of alloy properties from first-principles quantum-mechanical calculations may therefore not be meaningful.

The practical approach to this problem has therefore evolved as a search for appropriate elemental configuration variables with which known data (phase diagrams, crystal structures, etc.) can be systematized, thereby providing a predictive algorithm. The classic example of this schematic-coordinate-space method is that of Darken and Gurry[3] whose categorization of elements by electronegativity and atomic radius was partially successful in describing intermetallic-alloy solubilities. Similarly, Mooser and Pearson[4] achieved reasonable success in separating different observed crystal structures for a