fluence of the perturbing lattice potential, has been studied theoretically by Watson *et al.*[16] According to their theory, it is linearly related to both q_{latt} and the density of electronic states at the Fermi energy. Therefore this "overshielding" effect should be most important for the transition metals with a high density of d states at the Fermi level, and they predicted it to be of the order of $-100q_{\text{latt}}$ for the case of Re. Recently another strong indication has been found for a dominant contribution of the conduction electrons to the EFG in cadmium metal, measured by the time-differential perturbed angular-correlation technique.[17] The EFG found is considerably larger than the direct lattice contribution and shows a temperature dependence opposite to the one expected from the lattice expansion.

Presently very few experimental data are available for the EFG's (including their signs) in hexagonal d transition metals. With the high resolution of the 6.2-keV γ resonance of ^{181}Ta more such data may hopefully be obtained in the near future.

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Light-Scattering Study of the Dynamical Behavior of Ordering just above the Phase Transition to a Cholesteric Liquid Crystal*

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Rayleigh light scattering was observed with photon-counting techniques in the isotropic phase of cholesteryl 2-(2-ethoxyethoxy) ethyl carbonate just above the transition temperature to a cholesteric liquid crystal. Both the temperature and wave-vector dependences of linewidth and intensity were measured. The data are in good agreement with the dynamical behavior of short-range order described by an extension of the Landau–de Gennes theory. Bragg-interference fringes due to sizable cholesteric-type ordering were observed in the isotropic phase near the transition point.

Experiments[1-3] just above the transition temperature of the phase transition from an isotropic to nematic liquid crystal have shown the existence of pretransitional ordering phenomena in the isotropic phase. The correlation length in nematic pretransitional ordering remains so small that its effect on the intensity and width of the Rayleigh scattered peak remains negligible.

This Letter reports experimental results on Rayleigh scattering in a cholesteric material

CEEEC [cholesteryl 2-(2-ethoxyethoxy) ethyl carbonate] in a range of about 3°C above the transition temperature. The results are markedly different from the behavior near a nematic transition, and have the following characteristics: (1) The half width at half-intensity of the Rayleigh line is typically in the 10^3-Hz range. (2) Both the Rayleigh width and its inverse intensity show a T-T^* dependence, where T^* is the second-order phase-transition temperature if the first-order one is absent. (3) They also exhibit a $1+\xi^2q^2$ dependence, where ξ is the correlation length and q is the scattering wave vector. (4) Scattered light close to the forward direction exhibits Bragg-like interference fringes which are first observed at 0.68°C above T^*. (5) The Rayleigh line shape is a single Lorentzian above $T_{\rm BF}$—the temperature at which the Bragg fringes appear. Deviation from Lorentzian shape gradually increases as the temperature drops below $T_{\rm BF}$. (6) $T_c - T^* \leq 0.109$°C, where T_c is the first-order transition temperature at which the complete phase change takes place. Such weak first-order behavior is compatible with the smallness of the latent heat of transition.[4]

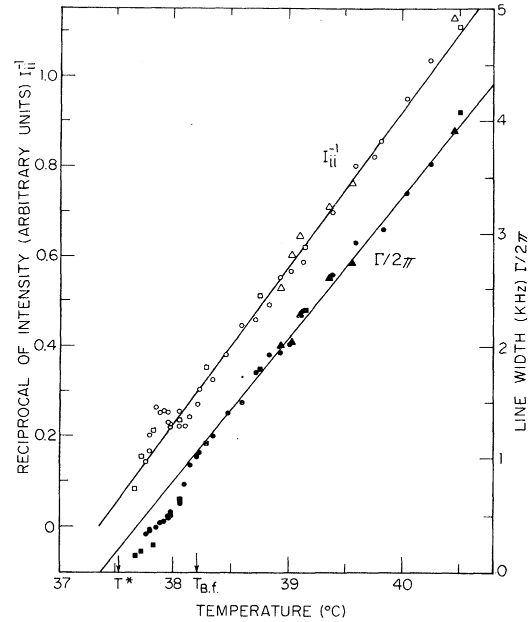

FIG. 1. Half-width Γ of the Lorentzian spectrum (lower curve) and reciprocal scattered intensity I_{ii}^{-1} (upper curve), plotted as functions of temperature for CEEEC in the isotropic phase. The solid lines are fits to the data by Eq. (3) for Γ and Eq. (4) for I_{ii}^{-1}. The scattering angle is 90°; both the polarizer and analyzer are normal to the scattering plane. The three different symbols (square, circles, and triangles) are data points taken two months apart from one another.

Clipped photon-counting techniques are used for the Rayleigh scattering experiment. The correlation in scattered photon arrival times, as measured by photomultiplier output pulses caused by individual photoelectrons, is analyzed by a digital autocorrelator which has a time resolution of 10^{-7} sec/channel. The photon counting tube is ITT model FW-130. The dark count is about 3 counts/sec at room temperature, whereas the signal is typically 10^2-10^4 counts/sec. A 65-mW He-Ne laser is used as the light source. The scattering cell is enclosed in a closely fitted aluminum cylinder with its temperature stabilized to better than ±0.001°C (±0.0006° typical) by a feedback servo-control system. Such stability is achieved by surrounding the complete unit in a second enclosure with its temperature maintained constant to within ±0.02°C. The sample temperature is measured by a platinum resistance thermometer. The sample was purchased from Eastman Kodak. It is filtered (using a 0.2 μm Millipore filter) and pumped under a 10^{-6}-Torr vacuum for one day to remove all gaseous content. This degassing procedure includes repeatedly freezing and warming the sample. Finally the sample is sealed in the scattering cell under 1 atm pressure of He gas. After such treatment, the transition temperature of the sample is found to be 7.2°C higher, and shows no sign of change over a period of many months.[5]

The temperature dependences of the Rayleigh linewidth and intensity are shown in Fig. 1. Above 38.236°C, the line shape is Lorentzian; below that, a gradual deviation takes place. The linewidth is smaller than 4.1×10^3 Hz at 3°C above T^*, which by extrapolation is found to be 37.53°C.

The Rayleigh linewidth measurements as a function of q^2 are shown in Fig. 2. One can recognize that the slopes of the three straight lines at different temperatures are about the same.

A diffuse Bragg fringe first appears at $T_{\rm BF}$ = 38.209°C and about 33.5° from the forward direction. At slightly lower temperatures as many as three fringes are observed at relative angles satisfying the higher-order Bragg conditions. As the temperature is further lowered, the contrast of the Bragg fringe increases and reaches its peak at T = 37.922°C, then decreases with the temperature. The primary fringe has moved outwards through an angle of 1.40° at T = 37.765°C. The linewidth measured at lower laser beam in-

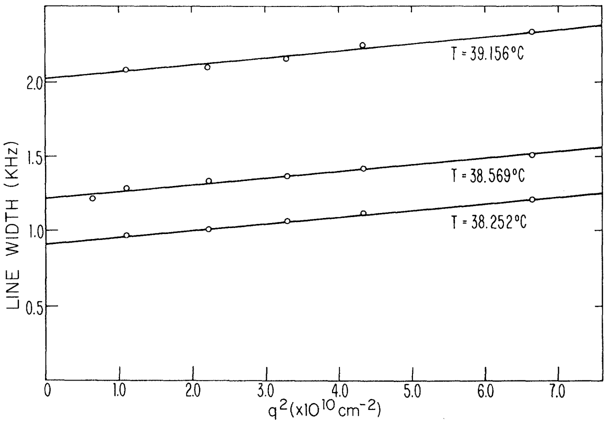

FIG. 2. q dependence of the linewidth Γ, measured at three different temperatures above T_{BF}. The experimental points are fitted by Eq. (3) (the solid lines).

tensity shows that the heating effect due to the laser power is not serious.

To interpret the experimental data, both the models suggested by de Gennes for nematic and cholesteric materials in their isotropic phases are used. Their corresponding Landau free-energy densities have the following forms[6]:

$$F_N = F_0 + \tfrac{1}{2} A Q_{ij} Q_{ij} + \tfrac{1}{2} L_1 (\nabla_k Q_{ij})(\nabla_k Q_{ij}) + \tfrac{1}{2} L_2 (\nabla_i Q_{ij})(\nabla_k Q_{kj}), \tag{1a}$$

$$F_C = F_N + L_1 q_0 Q_{ij} (\nabla \times \tilde{Q})_{ij}, \tag{1b}$$

(summed on repeated indices) where the subscripts N and C represent nematic and cholesteric, respectively. $\tilde{Q}$ is a symmetric traceless second-rank tensor, representing the local orientational order of the molecules; $A = a(T - T^*)$ according to the mean field theory, and a is a constant; L_1 and L_2 are elastic constants in the isotropic phase, and they are assumed to be temperature independent. This is verified experimentally by the constancy of the slopes of the lines in Fig. 2. q_0 is just $2\pi/P$, and P is the characteristic spiral pitch of a cholesteric liquid; F_0 is the isotropic part of the free energy and is independent of temperature.

It is proposed that above T_{BF} an isotropic cholesteric material behaves as a quasinematic liquid in its isotropic phases and thus Eq. (1a) should be used. However, the spatial derivatives of the order parameter Q, which are small for nematic materials, are very important in the cholesteric case. When the ordering parameter ξ (the correlation length) becomes comparable with the pitch P of the helical ordering, the dominant terms in the free energy take the form in Eq. (1b). This occurs at the temperature T_{BF} which marks the experimental observation of Bragg diffraction fringes.

The power spectrum of the scattered light may be expressed in terms of the spatial and temporal correlations of the order parameter Q in the standard manner.[6,7] For the case that both the incident and the scattered polarizations are normal to the scattering plane, one finds

$$S_{ii}(\omega, q) \propto (\omega^2 + \Gamma^2)^{-1}, \quad T > T_{BF}. \tag{2}$$

The index i represents the laboratory coordinates $i = x, y$. The half-width Γ of the Lorentizian spectrum is

$$\Gamma = (A/\nu)(1 + \xi^2 q^2). \tag{3}$$

The correlation length ξ is defined as $\xi \equiv (L_1/A)^{1/2}$. ν is the self-relaxation parameter of Q and it has the dimension of viscosity. In obtaining Eq. (2) it has been assumed that $L_1 \approx L_2$.

The integrated scattered intensity is inversely proportional to Γ, as follows from Eqs. (2) and (3),

$$I_{ii}^{-1}(q) \propto A(1 + \xi^2 q^2), \quad T > T_{BF}. \tag{4}$$

The experimental results shown in Figs. 1 and 2 are well described by Eqs. (3) and (4) above T_{BF}. The temperature dependence of the ordering parameter $\xi(T)$ can then be derived from both the theoretical expressions (3) and (4) and the available experimental data for Γ and I_{ii}. It is plotted in Fig. 3. The factors a/ν and L_1/ν have the values 7.93×10^3 sec^{-1} °C^{-1} and 2.93×10^{-8} sec^{-1} cm^2, respectively.

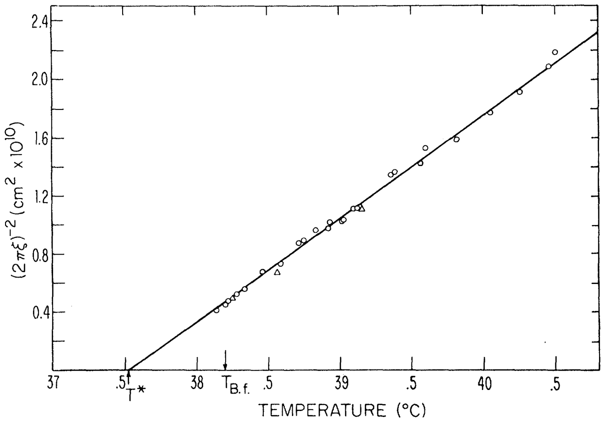

FIG. 3. Reciprocal of the correlation length squared, plotted versus temperature. It is constructed from the data points in Figs. 1 and 2 and fitted with a $T - T^*$ linear law.

For $T \lesssim T_{\rm BF}$, Eq. (1b) has to be used as suggested by de Gennes.[6] The line shape becomes non-Lorentzian, and in particular the I_{xy} component of the scattered light exhibits an interesting form,

$$I_{xy}(q) \propto (1+\xi^2q^2)[A(1+\xi^2q^2+2\xi^2q_0q)(1+\xi^2q^2-2\xi^2q_0q)]^{-1}. \tag{5}$$

The detailed discussion of Eq. (5) has been given by de Gennes.[6] One important feature is a diffuse Bragg-like interference pattern which should appear at $q \approx q_0$, as $\xi q_0 \rightarrow \frac{1}{2}$. If one takes the value of ξ at $T_{\rm BF}$ ($\simeq$38.209°C) from Fig. 3 and multiplies it by the value of q_0 ($\approx q$ for scattering angle $\theta \approx 33.5°$), one finds that $\xi q_0 = 0.2$ experimentally, which is 40% of the predicted value.

Deviation from $T-T^*$ dependence below 38.148 °C in the Γ and I_{ii}^{-1} data is possibly caused by three factors: (1) nonexponential decay of the fluctuations due to intermode couplings; (2) a composited (non-Lorentzian) line shape caused by multiple scattering; (3) the breakdown of the mean field approximation. As the correlation length ξ is approximately the size of the wavelength λ of the probing radiation, multiple scattering becomes very serious. The free energy described by Eq. (1) can only predict a second-order phase transition at a temperature T^* at which the local ordering will diverge. However, before the local order can grow very large, terms having higher order than Q^2 can no longer be ignored in the free-energy expansion. Consequently a first-order transition will be imposed by those terms at a temperature T_c slightly higher than T^*. de Gennes[6] has pointed out that this should occur before ξq_0 reaches unity. The upper bound of T_c for CEEEC is determined by the nontransmittance point of the laser beam through this 5-mm-long sample path and is found to be $T_c \leqslant 37.639$°C. At this temperature it is found that $\xi q_0 = 0.52$ from the measurements. This small difference, $T_c - T^* \leqslant 0.109$°C, makes it possible to observe the q dependence in Γ and I_{ii}^{-1} (the latter is not presented in this Letter, but has the same general behavior as Γ) as well as Bragg fringes.

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[7] The details of the formalism of the theory and calculations will be reported in a separate publication. Only results which are relevant to the measurements reported in this Letter will be quoted.