Raman Scattering near the Tricritical Point in SbSI†

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Measurements of the temperature and pressure dependences of Raman and elastic light scattering were used to investigate the dynamics of the tricritical point in SbSi at $T \cong 235$°K and $P \cong 1.4$ kbar. The results are discussed in terms of a mean-field treatment of tricritical points.

There has been considerable interest in the question of the existence of "Curie critical," or tricritical, points (where the phase transition changes from first order to second order) in ferroelectric materials.[1-4] The existence of tricritical points has been demonstrated for He^3-He^4 mixtures,[5] magnetic systems,[6] and the structural transition in NH_4Cl[7] using density, magnetic field, and pressure, respectively, as external parameters. Electric fields and hydrostatic pressure have been used as external parameters in attempts to change the order of the transition in ferroelectrics. Recent measurements[8] of the electric field dependence of the transition in KH_2PO_4 indicated that the critical field is quite large (~6500 V/cm) and no tricritical point was observed. Similarly, the first-order nature of the transitions in $BaTiO_3$ and $PbTiO_3$ decreases with pressure[9] but, because the hydrostatic pressures required are higher than those readily available, no tricritical points have been observed in these materials. In this Letter I report measurements of the pressure and temperature dependences of Raman and elastic Rayleigh scattering in the ferroelectric SbSI which indicate that SbSI does indeed exhibit a tricritical point.

On the basis of early measurements[10] SbSI was reported to undergo a second-order transition at 233°K in addition to the first-order ferroelectric transition at 293°K. Volk, Gerzanich, and Fridkin[11] examined the pressure dependence of the dielectric properties of SbSI and reported a triple point, which also displayed critical behavior, at 233°K and 1.5 kbar; however, later measurements by Syrkin *et al.*[12] disputed these results. More recent attempts to observe the 233°K transition using Raman scattering, dielectric constant, and x-ray measurements revealed no indication of this transition,[4] and the search for a critical point using dielectric techniques was inconclusive.[4] The present measurements of the Raman spectra also do not reveal any indication of the 233°K transition; however, measurements of the pressure dependence of the Raman spectra indicate that the ferroelectric transition does indeed change from first to second order at what appears to be a pressure-induced tricritical point.

The ferroelectric transition in SbSI occurs at ~293°K at atmospheric pressure and is associated with a soft optic mode which is underdamped in the ferroelectric (FE) phase and Raman inactive in the paraelectric (PE) phase. Although by symmetry the transition is allowed to be second order (symmetry D_{2h} to C_{2v}), the transition is first order at atmospheric pressure. The transition temperature decreases very rapidly with pressure ($dT_c/dP \cong -40$°K/kbar); in fact, Samara[4] has shown that the transition can be completely suppressed for $P \gtrsim 9.5$ kbar.

Raman spectra taken at various pressures near the transition pressure P_c of 4.54 kbar at 119°K are illustrated in Fig. 1. Because SbSI is a semiconductor with a band gap near 6200 Å,[13] the data were taken with the 6764-Å line of a krypton laser. The experimental details have been discussed previously[14]; the pressure medium was either helium or nitrogen gas.

As P is decreased below P_c, the soft mode first appears at a shoulder on the laser line. On further decrease of P, the soft mode becomes underdamped with increasing frequency. From the data in Fig. 1, the transition appears to be continuous at this pressure. At lower pressures than shown in Fig. 1, the soft mode couples with an optic mode of the lattice near 32 cm^{-1}; another mode coupling occurs near 42 cm^{-1}. These mode couplings have previously been observed.[15]

It is very difficult to determine the order of a phase transition from the temperature (or pressure) dependence of the soft-mode frequency since the frequency cannot be followed to $\omega = 0$. I therefore measured the intensity of the $\omega = 0$

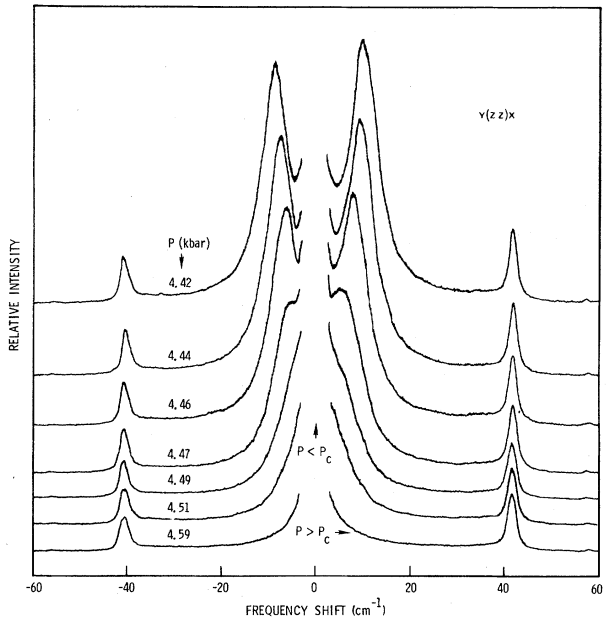

FIG. 1. Raman spectra of SbSI at various pressures very near P_c at 119.4°K.

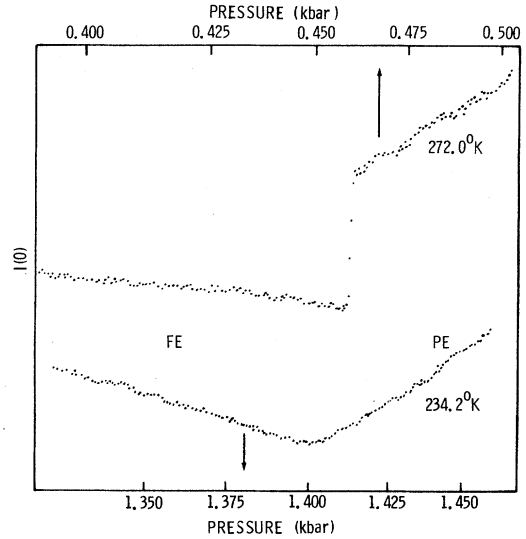

FIG. 2. $I(0)$ versus pressure for temperatures above and below the critical point.

scattering versus temperature and pressure. The pressure dependence of $I(0)$ is shown in Fig. 2 for two temperatures. Since the scattered light is collected from the bulk of the sample, the change in $I(0)$ is dominated by changes in the *transmitted* light rather than changes in the scattering coefficient; e.g., similar results are obtained if one monitors the intensity of a Raman-active phonon mode through the transition. (The large decrease in the transmitted intensity is similar to the behavior observed in Rayleigh-scattering measurements[16] near the tricritical point in NH_4Cl.)

First consider the curve at 272°K; as P_c is approached from the PE phase, $I(0)$ decreases as the order-parameter fluctuations increase. At P_c, $I(0)$ drops discontinuously as the crystal undergoes a first-order transition and domains form which scatter the incident and collected light. As the pressure is further decreased, the domain size increases and $I(0)$ increases. Completely analogous results are obtained as a function of temperature at constant pressure. In this temperature and pressure range the transition exhibits an appreciable hysteresis.

As the transition temperature is decreased with increase in pressure, the magnitude of the discontinuity of $I(0)$ and hysteresis in P_c (or T_c) decrease until $T \lesssim 235$°K where $I(0)$ changes continuously through the transition. This behavior is shown in the lower curve of Fig. 2 for $T = 234$°K. Here, $I(0)$ decreases smoothly as $P \to P_c$, attains a minimum value at $P = P_c$ with no discontinuity, and increases smoothly as one moves away from P_c. For $T \leq 235$°K I observe no hysteresis within experimental uncertainty (±0.002 kbar). The transition thus appears to be second order for $T \leq 235$°K and $P \geq 1.40$ kbar. Since the transition is unambiguously first order for $T > 235$°K, SbSI apparently exhibits a tricritical point at $T \cong 235$°K and $P \cong 1.40$ kbar.

Assuming that these observations indicate the existence of a tricritical point in SbSI, one can obtain a first approximation for the expected behavior from Landau's theory of continuous phase transitions. The free energy F can be written as

$$F = \tfrac{1}{2}A(T - T_c)P_s^2 + \tfrac{1}{4}BP_s^4 + \tfrac{1}{6}CP_s^6 + \ldots , \quad (1)$$

where P_s is the spontaneous polarization (order parameter), A is a constant, and B and C are taken to be slowly varying functions of temperature (or pressure). For $C > 0$, F describes a first-order transition if $B < 0$, a second-order transition if $B > 0$, and a tricritical point at $B = 0$. For a second-order transition, the stability conditions yield the inverse susceptibilities χ^{-1} as

$$\chi^{-1} = A(T - T_c), \quad T > T_c , \quad (2a)$$

$$\chi^{-1} = 2A(T_c - T), \quad T < T_c , \quad (2b)$$

while P_s has a temperature dependence of the

form

$$P_s \propto (T_c - T)^{1/2}. \quad (3)$$

Near a tricritical point T_t ($B=0$) these expressions become

$$\chi^{-1} = A(T - T_t), \quad T > T_t, \quad (4a)$$

$$\chi^{-1} = 4A(T_t - T), \quad T < T_t, \quad (4b)$$

with

$$P_s \propto (T_t - T)^{1/4}. \quad (5)$$

(Since temperature and pressure are equivalent variables, similar results are obtained as a function of P.) One therefore expects the exponent of the order parameter to change from $\frac{1}{2}$ to $\frac{1}{4}$. The exponent for the susceptibility, on the other hand, does not change; rather the slope ratio for χ^{-1} changes from 2 to 4. Since Raman scattering probes $\chi(\omega)$, this treatment predicts that the functional form of ω will not change, but that there will be a change in the slope of ω^2 versus T (or P) near the tricritical point.

The pressure dependence of the soft mode is illustrated in Fig. 3 for temperatures above and below 235°K. It should be noted that the line shape is not quite Lorentzian; I have therefore plotted the *peak* position because of the ambiguity in the line shape. The data follow an $\omega^2 \propto P$ dependence as expected, although there is some deviation near P_c. However, this deviation is probably an artifact of the asymmetric line shape and the increase in the ratio of the damping to the frequency as ω decreases. Furthermore, the slope decreases from $\omega^2 \cong 218(P_c - P)$ at 231°K to $\omega^2 \cong 125(P_c - P)$ at 119°K. Unfortunately, the soft mode is not Raman active for $T > T_c$ so that the slope ratio has not been directly measured; however, it is known that SbSI obeys a modified Curie-Weiss law of the form $\epsilon = C^*/(P - P_0)$ for $T > T_c$, where C^* is essentially pressure independent in this temperature range.[17] Since SbSI obeys an Lyddane-Sachs-Teller relation of the form $\omega^2\epsilon \cong$ const,[4] combining the above observations indicates that the slope ratio changes by ~1.75 as the temperature is decreased from slightly below T_t to well below T_t. In view of the uncertainties in this analysis, this is in reasonable agreement with the classical value of 2.

In conclusion, it appears that SbSI exhibits a tricritical point near $T = 235$°K and $P = 1.40$ kbar. These measurements are being extended to lower frequencies to investigate any interactions which may occur between the soft mode and the acoustic modes in the ferroelectric phase near this point. Measurements of the static dielectric properties, which unfortunately rely very heavily on the existence of good quality crystals, are needed near this point to determine if the behavior can be adequately described by a classical treatment, and more detailed investigations of the dynamics will

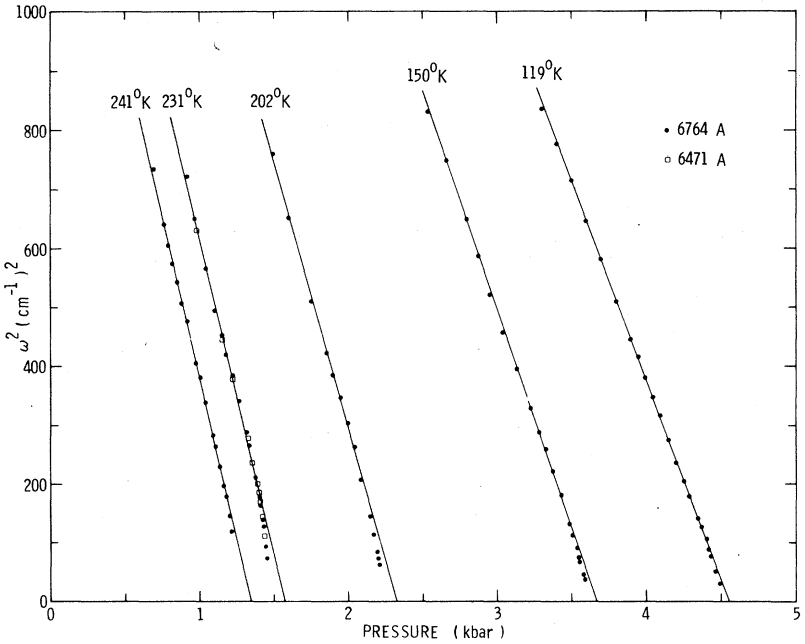

FIG. 3. Plot of ω_s^2 versus P for various temperatures.

require calculations of the line shape of the soft mode.

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Acoustic Brillouin-Zone Effect in a Cholesteric Liquid Crystal*

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Gaps in the acoustic attenuation for wave vectors satisfying the Bragg condition have been observed in a mixture of cholesteryl choloride and cholesteryl myristate.

We report here the first observation of an ultrasonic Brillouin-zone effect in a cholesteric liquid crystal. It has been shown by Parsons and Hayes,[1] on the basis of a modified Leslie model, that the Brillouin-zone effect should be observed when the component of the sound-propagation wave vector, $\vec{q}_s$, along the helix axis matches the zone spacing, $q_0=\pi/P$, where P is the pitch. This condition is given by the Bragg-like relation

$$2P\cos\theta=\lambda_s, \tag{1a}$$

or

$$q_s\cos\theta=q_0, \tag{1b}$$

where θ is the angle between the helix axis and the sound-propagation direction and λ_s is the sound wavelength. It was argued that since the viscosity tensor (rather than the elastic-constant tensor) is periodic, the effect would show up in the attenuation coefficient (rather than the phase velocity). Parsons and Hayes derived the following approximate expressions for the acoustic damping coefficient, Γ_q (in $\sec^{-1}$): for $q_s\cos\theta \ll q_0$ or $q_s\cos\theta \gg q_0$,

$$\Gamma_q=(q_s^2/2\rho_0)[(\alpha_4+\alpha_7)+\alpha_5\sin^2\theta+\tfrac{3}{8}\eta\sin^4\theta] \equiv \Gamma_{q0}; \tag{2a}$$

for $q_s\cos\theta \lesssim q_0$,

$$\Gamma_q=\Gamma_{q_0}-(\alpha_5/4\rho_0)\sin^2\theta(q_s^2+2q_0^2) -\tfrac{1}{8}(\eta/\rho_0)\sin^4\theta q_s^2; \tag{2b}$$