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Brillouin Scattering in the Isotropic Phase of Nematic Liquid Crystals under High Pressure

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Brillouin scattering in the isotropic phase of the liquid crystals (MBBA and EBBA) was investigated under high pressure up to 3.3×10^3 kg/cm^2. The pressure variations of the sound velocities were recorded. It was found that the sound velocities did not change linearly against pressure. This effect is due to the pressure dependences of density and adiabatic compressibility. No pretransitional effect in sound velocity in the neighborhood of the nematic-isotropic transition point has been found, suggesting that the hypersonic sound wave does not couple to the molecular fluctuation even under high pressure. The adiabatic compressibilities and the molar sound velocities were calculated, and the molecular packing in the isotropic phase is discussed.

1 INTRODUCTION

Thermotropic liquid crystals have several states of mesophases between the crystal and the isotropic phases. The mechanism of these serial phase transitions has not been explained universally. As to the nematic-isotropic phase transition (N-I), some experimental results (e.g., light scattering intensity,[1] specific heat,[2] thermal expansion coefficient,[3] etc.[4]) show pretransitional phenomena near the N-I transition temperature. These results in the nematic and the isotropic phase can be well described with Maier-Saupe theory[5] and Landau-de Gennes model,[6] respectively. To investigate the mechanism of the phase transition associated with the molecular orientational fluctuation, studies of the dynamic critical behavior are desirable. The most popular means to investigate the dynamic properties are ultrasonic measurement and Brillouin scattering.

Ultrasonic measurements[7–9] of the nematic liquid crystals have been carried out crossing the N-I transition point, which indicated the pretransitional

phenomena in sound velocity and acoustic attenuation. The degree of the pre-transitional effects decreased as frequency increased. These temperature and frequency dispersions could be well described by a single relaxation process at temperature far from the clearing point and multi relaxation processes in the vicinity of the clearing point.

However, rather few investigations of Brillouin scattering in liquid crystals have been made. The reason for this seems due to the strong central component that covers the weak Brillouin doublet. As yet, no pretransitional effect in hypersonic sound velocity and attenuation near the critical point has been observed in Brillouin scattering of the liquid crystals. Steger and Litster,[10] Clark and Liao[11] for MBBA, Nordland[12] for cholesteryl 2-(2-ethoxy-ethoxy) ethyl carbonate (CEC), and several investigators[13-15] for other liquid crystals have found no anomalous change in hypersonic sound velocity near the clearing point. Only Durand and Liao[16] for CEC reported the sound velocity change by approximately 5% in the critical region. However, it is understood that this effect is due to the induced scattering loss of domain structure rather than structural relaxation associated with the phase transition. These observations were performed at atmospheric pressure, but Brillouin scattering under high pressure has not been carried out yet.

In the case of the materials whose intermolecular force is weak, such as liquid cyrstals, the thermodynamic parameters are changeable by the application of relatively low pressure. Therefore, investigations under high pressure are valid for the more universal interpretation of the phase transition. Some kinds of experimental results (DTA,[17] volume measurement,[18] NMR,[19] etc.[20]) have been published. But, acoustic properties under high pressure have not been reported. To elucidate whether hypersonic sound velocities under high pressure show the pre-transitional effects or not and to clarify the acoustic properties, we measured Brillouin scattering of *n-p*-methoxy-benzylidene *p-n*-butylaniline (MBBA) and *n-p*-ethoxy-benzyliden *p-n*-butylaniline (EBBA) in the isotropic phase for pressure range up to 3.3×10^3 kg/cm^2.

2 EXPERIMENTAL

2.1 Apparatus

Figure 1 shows a schematic diagram of the optical system. Radiation from the argon ion laser (NEC model GLS-3200) operating in the single mode at 5145 Å was used as a light source and the laser power was kept to 50 mW with the optical feedback circuit to avoid local heating and sample damage. This laser beam was first passed through Glan-Tompson prism (10^{-4} extinction ratio) for the perfect linear polarized light perpendicular to the scattering plane, and then focused on the sample in the optical vessel.

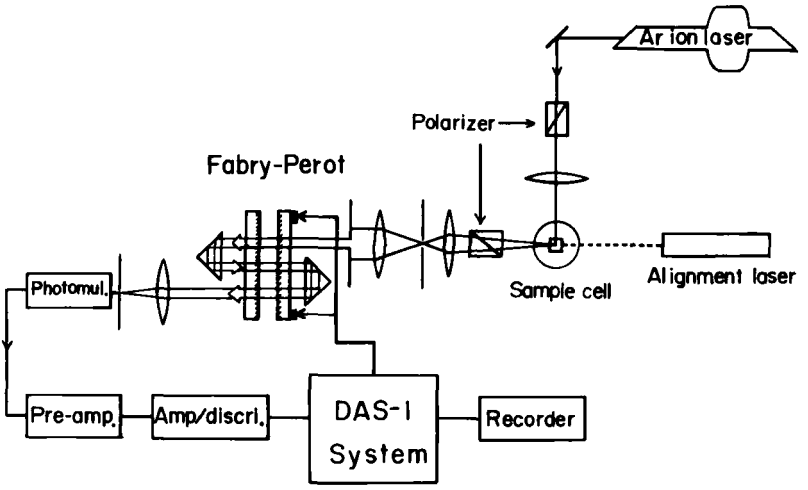

FIGURE 1 A schematic diagram of Brillouin scattering system with right angle geometry.

The light scattered through right angle was analyzed by a Glan-Tompson prism for polarization, and then by a triple-pass piezoelectrically scanned Fabry-Perot (FP) interferometer which consists of the two flat etalons ($\lambda/200$) whose reflectivity is 98% at 5145 Å. One of the etalons is scanned piezoelectrically by the ramp voltage supplied from DAS-1 system (Burleigh Co.).[21] The scattered beam was returned twice by the two corner cubes, and detected by a photomultiplier tube (Hamamatsu Ele. Co. R-649). The photon pulses were counted and accumulated in each memory of the multichannel analyzer (MCA, which consists of 1024 channels) in DAS-1 system.

Interferometer alignment, laser frequency drift and F-P cavity drift problems limit the instrumental factors. This DAS-1 system is equiped with an automatic drift stabilizer and finesse optimizer, so it is possible to scan for a long time while compensating peak drift and maintaining perfect parallel alignment of the two flat etalons. Furthermore, it allows extended data acquisition time for the selected regions of the spectrum (enhanced SNR in that region), so that the data acquisition time can be reduced. Typical accumulation time was about 15 min.

In the isotropic phase of liquid crystals, because of the high degree of molecular orientational fluctuation, the Rayleigh component is extremely intense and the Landau-Placzek ratio is as much as $10^3 \sim 10^4$ ($1 \sim 10$ for normal liquids). So the multi-pass technique[22] is indispensable in observing the Brillouin peaks of liquid crystals. The enormous improvement can be attained by the triple-pass system, as illustrated in Figure 2. In the case of single-pass system, overspreading Raileigh tails cover the weak Brillouin peaks. But triple-pass

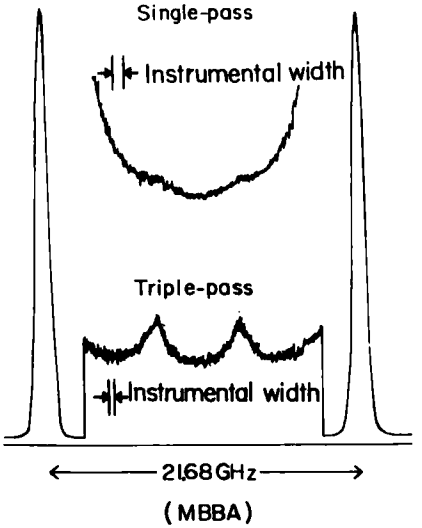

FIGURE 2 Superiority of the triple-pass system. The finesse of single-pass and triple-pass are about 24 and 50, respectively.

system enables one to investigate the Brillouin components because of the higher finesse. All measurements were performed with the triple-pass system.

2.2 Substances

Highly purified MBBA and EBBA samples were purchased from Fuji Shikiso Co. and their clearing temperatures were 44.5°C and 79.9°C for the best samples, respectively. Therefore, these samples were used without further chemical purifications. All liquids were filtered through 2000 Å membrane filters at least five times to remove the parastic scattering by dusts.

2.3 Optical Vessel

A glass-made piston cylinder (8mm in diameter and 20mm in length) was used as a sample cell and set in the high pressure optical vessel which has two sapphire windows and is usable up to 6×10^3 kg/cm^2. Details are described elsewhere.[23] Silicone oil (Toshiba TSF 451 10 c.s.) was used as the thermal and pressure transmitting fluid, and the temperature was controlled within 0.5°C. There have been no contamination with silicone oil up to 3×10^3 kg/cm^2.

3 RESULTS AND DISCUSSION

3.1 Sound Velocity

The spectrum of Brillouin scattering has two components shifted on either side of the exciting frequency ω_o by the frequency of the thermal phonon

$$\Omega = \pm(2\omega_0 n\, v1/c) \sin(\theta/2)$$

where n is the refractive index, c is the light velocity in vacuum, v is the sound veocity, and θ is the angle between the directions of incident and scattered radiation. To obtain the sound velocity, measurements of Brillouin shifts Ω and refractive index n are indispensable. Measurements of Brillouin shifts were performed at seven constant temperatures in MBBA and EBBA with increasing pressure up to the I-N transition points. Several raw spectra obtained in the isotropic phase of EBBA are given in Figure 3. Because of combination use of the triple-pass and the DAS-1 system, SNR was sufficient to determine the precise sound velocity within an accuracy of 1%. As the I-N transition point was approached, the Rayleigh intensity increased, the Brillouin peaks became weak and broad, and the Brillouin shifts increased with increasing pressure. The refractive indices of liquid crystals have been scarcely investigated under high pressure as yet. Horn[24] has reported those of MBBA and 5CB only in the nematic phase, but not in the isotropic phase. However, it is well known that the density is related to the refractive index by the following equation[25,26]

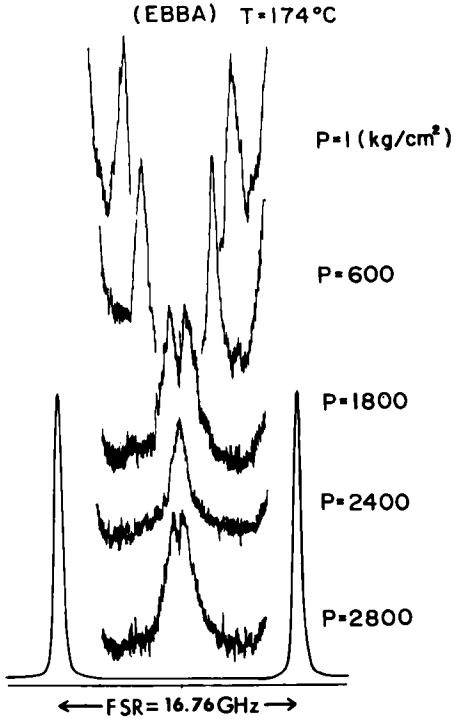

FIGURE 3 Several raw Brillouin spectra in EBBA under high pressure. The typical accumulation times at 1 and 2800 (kg/cm^2) were about 10 and 40 min., respectively.

$$R = \frac{M}{\rho}\frac{n^2 - 1}{n^2 + 1}$$

where ρ is the density, M is the molecular weight, n is the refractive index, and R is, so-called, molar refraction and independent of pressure and temperature. The above relation has been confirmed experimentally.[26] Therefore, the data of specific volume permit one to calculate the refractive indices. The specific volumes for MBBA and EBBA under high pressure have been investigated by some authors,[27-30] but the pressure and temperature ranges were narrow and insufficient to our requirements. We measured the specific volumes for wider range using high pressure dilatometer. The results were in good agreement with those reported by Kuss.[30] The pressure variation of EBBA was slightly larger than that of MBBA. From these data, we calculated the refractive indices using above equation. The value of refractive indices at atmospheric pressure by Freiser *et al.*[31] and Prasad *et al.*[32] were used to calibrate the constant R. Figure 4 gives plots of the refractive indices v.s. pressure. The accuracy is estimated to be 0.005.

The sound velocities in the isotropic phase were evaluated using measured Brillouin shifts and refractive indices. The pressure variation of the sound velocities for MBBA and EBBA are plotted in Figures 5 and 6, respectively. The sound velocity did not change linearly against pressure. This behavior does not come from the extrinsic effects, such as the decomposition of the sample,

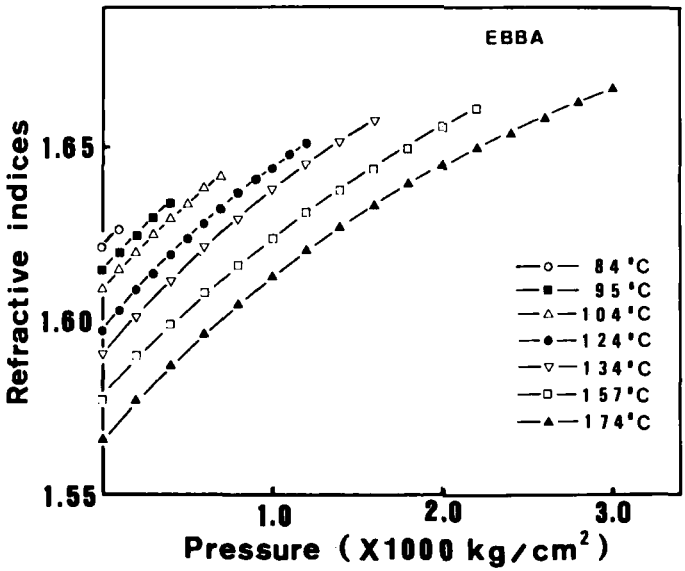

FIGURE 4 The plots of refractive indices v.s. pressure for EBBA at 5145 Å. These were calculated from the specific volume data.

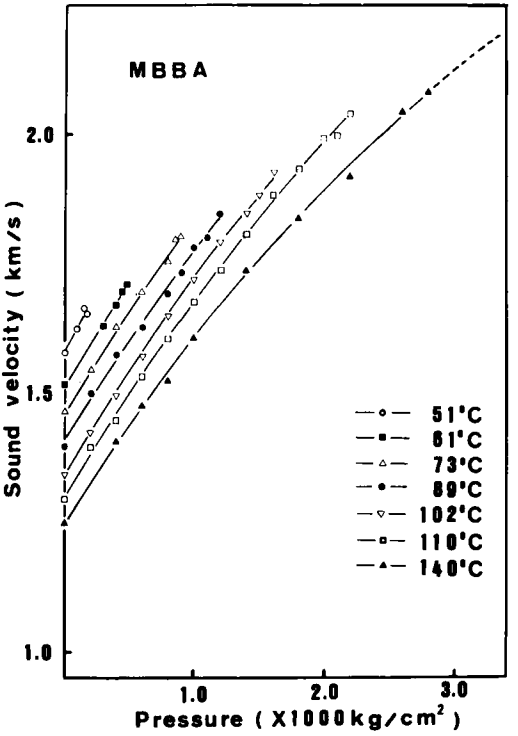

FIGURE 5 Pressure variation of the sound velocity for MBBA at different temperatures.

because the same results were obtained after one cycle. However, this seems not to be the pre-transitional effect we have expected, because the degree of nonlinearity did not change critically even in the vicinity of the transition points. These results are inconsistent with those of the ultransonic measurements.[25] Imura and Okano[33] have shown that the anomalous ultrasonic absorption and sound velocity in the isotropic phase just above the N-I transition point are associated with the critical fluctuation of the tensor order parameter. The free energy G may be expanded in powers of the order parameter.

$$G = G_0 + A\,(P, T)\,Q^2 + B\,Q^3 + \ldots$$

$$A\,(P, T) = a\,(P)\,(T - T^*)$$

Q is the tensor order parameter, T^* is the pseud second-order critical temperature and is slightly below the clearing temperature T_c. According to their theory, the coupling of sound wave and molecular orientational fluctuation can be achieved through the variation of the coefficient $A(P, T)$. The absorption

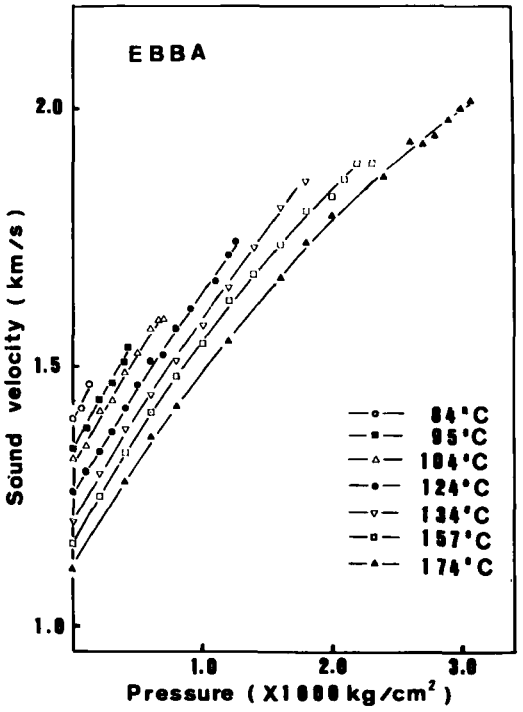

FIGURE 6 Pressure variation of the sound velocity for EBBA at different temperatures.

per wave length $\alpha\lambda$ and the velocity change $\Delta\nu$ are written as follows.

$$\alpha\lambda = \pi(\gamma_0 - 1)(C_p^0)^{-1} Im(\Delta C^*)$$
$$\Delta\nu = -\tfrac{1}{2}(\gamma_0 - 1)(C_p^0)^{-1} Re(\Delta C^*)$$
$$\Delta C^* = \frac{g k_B T^2}{32\pi}\left(\frac{a}{L}\right)^2\left(\frac{2L}{\omega\zeta}\right)^{1/2}(F_1(x) + iF_2(x))$$
$$F_1(x) = [x + (x^2+1)^{1/2}]^{-1/2}$$
$$F_2(x) = [x + (x^2+1)^{1/2}]^{1/2} - (2x)^{1/2}$$
$$x = \frac{\omega_0}{\omega}$$
$$\omega_0 = a(P)(T - T^*)/\zeta$$
$$\gamma_0 = C_p^0/C_v^0$$

where C_p^0 and C_v^0 are the heat capacity at constant pressure and at constant volume in the absence of the fluctuations, respectively. The constant g is assumed as $g \simeq 10$. L is the coefficient of the gradient term in the free energy expansion, and is taken to $L \simeq 0.4 \times 10^{-6}$ dyn. ζ is about 0.465 Poise. In taking the high frequency limit $\omega \sim 7.2 \times 10^9$ Hz, the change of sound velocity

and attenuation at the phase transition are expected 0.1% and 0.005, respectively. The limit of our resolving power prevents us to detect such slight anomalies. However, we have expected that if coefficient $a(P)$ would change dramatically by the application of pressure, the pre-transitional effect might become observable. Nevertheless, our results conclude that the coupling of the orientational fluctuation and the sound wave is too small for one to observe even under high pressure. This means that the pressure dependence of the coefficient $a(P)$ is not so large.

3.2 Molar Sound Velocity

The molar sound velocity $S = v^{1/3} M/\rho$, where v is sound velocity, M molecular weight, and ρ density, may be calculated by summing the increments for each atom in the molecule or alternatively chemical bonds in the molecule. One can predict the sound velocity correctly from a knowledge of the molecular structure. The average agreement between the observed and the summation value of molar sound velocities is usually within a few percent.[34,35] It can be observed that the molar sound velocity for MBBA is 3003 (102°C, 1bar), and is 3163 (104°C, 1bar) for EBBA. Though the only difference of the chemical structure is found in alkoxy group, the difference of the molar sound velocities is 160 and is smaller than the increment of molar sound velocity for —CH_2— bond, that is estimated 190. This is beyond our experimental error. It is supposed that the discrepancy of additivity rule of molar sound velocity comes from the difference of the molecular conformation. The same result is suggested by Raman scattering and NMR measurement.[36]

3.3 Adiabatic Compressibility

The adiabatic compressibility is another property of interest in the study of chemical structure by sound velocity measurements. From the sound velocity v and density ρ, the adiabatic compressibility K_s can be calculated by means of the equation $K_s = 1/v^2\rho$. The pressure variations of the adiabatic compressibility for MBBA and EBBA are shown in Figures 7 and 8, respectively. From the ultrasonic measurement, Bahadur and Chandra[37] have calculated the temperature variation of the adiabatic compressibility for EBBA at atmospheric pressure. Their value is in good agreement with us. It is supposed that there is no frequency dispersion for the adiabatic compressibility. The value of MBBA is smaller than that of EBBA, but has the similar variation against pressure. This fact suggests that the molecular packing of EBBA is more loose than that of MBBA. Our conclusion is consistent with other results. For example, Leadbetter[38] investigated the X-ray diffraction pattern and concluded that EBBA has a larger correlation length than MBBA. Furthermore, Specific volumes of MBBA and EBBA have been reported by Gulari and Chu

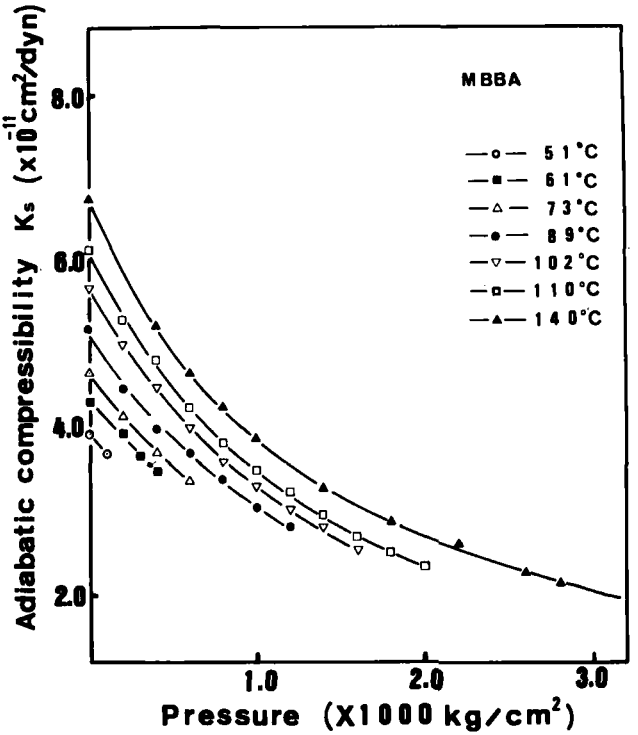

FIGURE 7 Pressure dependence of the adiabatic compressibility for MBBA.

(MBBA)[39] and Bahadur and Chandra (EBBA).[37] The difference of the molar volume calculated from their data at the same reduced temperature results in 23 cm^3/mol. This value is large enough for the addition of —CH_2— unit, which is estimated 14 ~ 18 cm^3/mol. These results are not contradictory to our conclusion.

4 SUMMARY

We measured Brillouin scattering of the nematic liquid crystals (MBBA and EBBA) under high pressure. The pre-transitional effects can not be observed near the transition regions. This means that the coupling of sound wave to the molecular fluctuation is small even under high pressure. The sound velocities calculated from Brillouin shifts and specific volumes did not change linearly against pressure. It is supposed that this is due to the pressure dependence of density and adiabatic compressibility. The adiabatic compressibility of EBBA is larger than that of MBBA. This fact suggests that molecular packing of EBBA is more loose than MBBA.

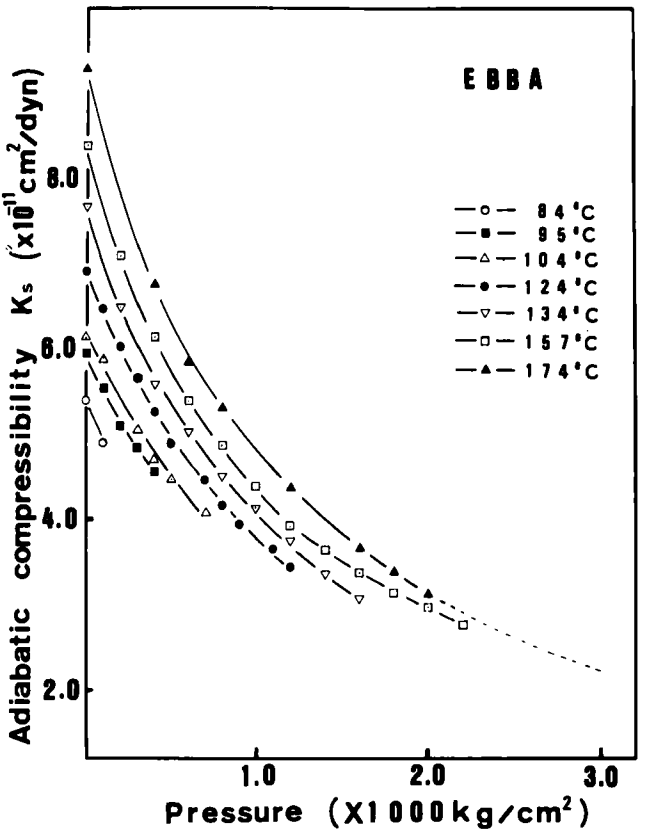

FIGURE 8 Pressure dependence of the adiabatic compressibility for EBBA.

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