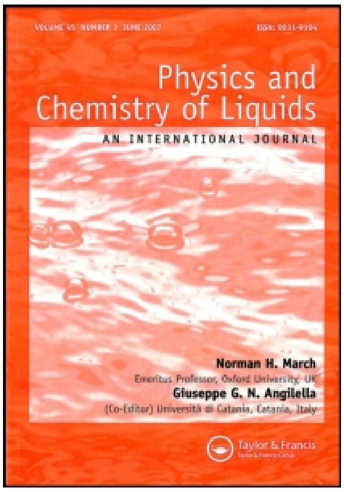

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Brillouin Scattering in Molten Antimony Trichloride

G. Maisano[a]; P. Migliardo[a]; F. Aliotta[b]; C. Vasi[b]; R. Triolo[c]
[a] Dipartimento di Fisica dell'Università and G.N.S.M. del C.N.R., Messina, ITALY [b] Instituto di Tecniche Spettroscopiche del C.N.R., Messina, ITALY [c] Istituto di Chimica Fisica dell'Università, Palermo, ITALY

To cite this Article Maisano, G. , Migliardo, P. , Aliotta, F. , Vasi, C. and Triolo, R.(1984) 'Brillouin Scattering in Molten Antimony Trichloride', Physics and Chemistry of Liquids, 13: 3, 231 — 240
To link to this Article: DOI: 10.1080/00319108408080781
URL: http://dx.doi.org/10.1080/00319108408080781

Phys. Chem. Liq., 1984, Vol. 13, pp. 231–240
0031-9104/84/1303-0231$18.50/0

Printed in the United Kingdom

Brillouin Scattering in Molten Antimony Trichloride

G. MAISANO and P. MIGLIARDO
Dipartimento di Fisica dell'Università and G.N.S.M. del C.N.R., 98100 Messina (ITALY)

and

F. ALIOTTA and C. VASI
Instituto di Tecniche Spettroscopiche del C.N.R., 98100 Messina (ITALY)

and

R. TRIOLO
Istituto di Chimica Fisica dell'Università, 90123 Palermo (ITALY)

(Received August 19, 1983)

Brillouin spectra in molten Antimony Trichloride are investigated for the first time. Measurements are performed both in the normal and in the supercooled region. The acoustic velocity and absorption, obtained by a refined method of analysis of the experimental data, as function of frequency and temperature, show a dispersion that is characteristic of associated liquids. This acoustic anomaly is interpreted in terms of a relaxation phenomenon in which the strong intermolecular forces are involved.

1 GENERAL CONSIDERATIONS

Recently the existence of cooperative phenomena in the dynamical[1,2] and statical[3,4] properties of liquid Antimony Tricloride, both in the normal and in the metastable (supercooled) regions, has been stressed. In the liquid state, this molten salt exhibits a structural arrangement that is far from being random. In fact, X-ray and neutron diffraction experiments,[3] near the melting point (73.4°C), and the subsequent theoretical interpretation on the basis of the RISM model[4] have shown that the melt has a chain structure in which the molecular unities (pyramidal $SbCl_3$) are strongly bonded via chlorine bridges. Furthermore, the existence of a van der Waals type interchain interaction has been confirmed. This bond connectivity could explain the anomalous chemical-physical properties (high dielectric constant,[5] low electrical conductivity and low autoionization constant[6]) of this peculiar system in which the long range coulombic forces seem to play a minor role. From this point of view, Antimony Trichloride looks like as an associated liquid[7] rather than a molten salt: it appears to be a structure dominated liquid.

Finally, it is a good solvent for both organic and inorganic compounds and this quality, together with the above mentioned ones, allowed some comparison with liquid H_2O.

The dynamical properties of $SbCl_3$ have been extensively studied by Raman spectroscopy, both near the solid-liquid transition[1] and in the supercooled region.[2] In particular, the isotropic Raman spectra show all the intermolecular stretching and bending modes of the pyramidal unities and the depolarized contribution shows a zero centered component (Rayleigh Wing) convoluted with a smoothed spectral contribution. The former was connected with a thermal activated process, with a characteristic energy value of about 2.4 Kcal./mol and a backward barrier height of 0.7 Kcal./mole, that can be associated with the breaking and making mechanism of chlorine intermolecular bonds. The latter was interpreted as due to a disorder induced Raman effective density of vibrational states $g^R_{\mathrm{eff}}(\omega)$, which is typical of many amorphous[8] and liquid[9] systems. This anisotropic spectral density envelopes the low frequency optical phonon modes of the crystal, so that the melt still maintains a memory of the ordered phase collective excitations.

In the present work the acoustic properties of the melt are investigated and are studied in some details by analyzing the system response to the time dependent stress by means of an ultrasonic probe and by studying the Fourier components of the density fluctuations correlation function by Brillouin scattering. The experiments are performed as a function of the temperature both in the normal and in the supercooled liquid phase.

We will show that, due to the high degree of cooperativity in the dynamic properties of the system, a dissipative bulk phenomenon, that is frequency and temperature dependent, is observed. A similar behaviour has also been reported in the literature for moderately supercooled liquids[10,11] and for low viscosity liquids with dependent structure effects,[12] in which strong interactions among molecules take place. In addition, it will be shown that the longitudinal relaxation time τ_L and the longitudinal relaxation modulus K_r, evaluated on the basis of visco-elastic theories,[13] give an activation energy of few Kcal./mol. which is connected with the finite mean life time of the chlorine bridges.

2 EXPERIMENTAL PROCEDURES AND HANDLING OF THE DATA

The high purity $SbCl_3$ was prepared by the same procedure elsewhere described[1] and was sealed, under low argon pressure, into a quartz optical cuvette (1.00×1.00 cm^2 of section). The purified, colourless melt of high optical quality was analyzed in the same cell for both ultrasonic and hypersonic measurements.

We used a specially built optical thermostat for the polarized list scattering (Brillouin) experiments with a temperature control within 0.002 °C in the investigated range $50 \leq T \leq 100$°C (Tm = 73.4°C).

We use a Tropel mod. 350 plane Fabry-Perot piezoelectrically scanned interferometer with a typical 90° scattering geometry.

The transferred wavevector $R = 4\pi/\lambda_0 \cdot n(T) \cdot \sin \theta/2$ values are 3.398 10^4 cm^{-1} at 98.7°C and 3.400 10^4 cm^{-1} at 40.1°C.A F.S.R. value of 8.0 Ghz was chosen as the best compromise between the Brillouin shift and the resolution. The measurements wave performed with a mean overall working finesse of 45. A single mode Ar^+ laser (Spectra Physics mod. 170) with a mean power of 800 mW at 5145 Å was used. The detection system consists of an RCA C-31034 cooled photomultiplier with a flat spectral response and a dark photoncount less than 10 photons/sec. The interferometer operations, as well as the collection and normalization of the experimental data, are controlled on-line by a Digital MINC 11/23 minicomputer. To obtain a good signal to noise ratio, many spectra (up to 10) were taken at each temperature and then automatically added taking into account possible zero-frequency drift. Furthermore, in order to reject all the unwanted contributions to the spectra (Raman, fluorescence and so on), an optical filter was inserted on the collection optics.

The ultrasonic experiments were performed with a standard MATEC pulse-echo apparatus. The X-cut quartz (transducer and receiver) of 5 Mhz fundamental frequency were bonded to the window of the same calibrated optical cuvette used for the Brillouin measurements. The cell was put into an air controlled thermostat with a temperature deviation of about 0.1°C. The apparatus was tested by performing some velocity measurements on pure water contained in a similar cuvette; the results were in very good agreement with the literature data.[14] The 15 Mhz velocity measurements accuracy is better than 1% while the same frequency absorption values are not processed because the additional losses at the various interfaces. Values of the density ρ and the refractive index n at the various temperatures, needed to calculate the acoustic quantities of interest, were taken from the literature.[15]

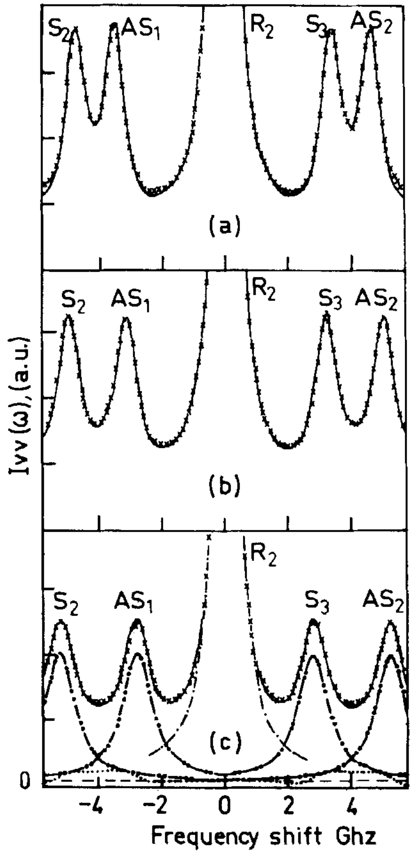

FIGURE 1 Brillouin Spectra of molten $SbCl_3$ at different temperatures. (a) $T = 98.7°C$; (b) $T = 75.2°C$; (c) $T = 50.4°C$; (S and AS refer Stokes and Antistokes component respect to the R central component) x: Exp. Points; ——— : Theoret. Fitting with EQ. (1); —·—·— : Rayleigh component; —··—··— : Symm. Brillouin components; .... : Asymm. Brillouin components.

As an example in Figure 1 we show three typical polarized spectra, taken at 98.7°C, 75.2°C and 50.4°C respectively; a theoretical fit (see the next section) is also shown.

3 DISCUSSION OF THE RESULTS AND CONCLUSIONS

The dynamical properties of a liquid systems are well described by the structure factor $S(k, \omega)$, which is defined as the Fourier transform of the density fluctuations time correlation function.[16] Using the usual hydrodynamic equations, the $S(k, \omega)$ proportional polarized spectrum can be written as:

$$I_{VV}(k, \omega) = \frac{A_R \cdot \Gamma_R(k)}{\omega^2 + \Gamma_R(k)} + \frac{A_B \cdot \Gamma_B(k)}{\{\omega - [\omega_0^2(k) - \Gamma_B^2(k)]^{1/2}\}^2 + \Gamma_B^2(k)}$$

$$+ \frac{A_B \cdot \Gamma_B(k)}{\{\omega + [\omega_0^2(k) - \Gamma_B^2(k)]^{1/2}\}^2 + \Gamma_B^2(k)} + \frac{\Gamma_B(k)}{[\omega_0^2(k) - \Gamma_B^2(k)]^{1/2}} \cdot \tag{1}$$

$$\cdot \left\{ \frac{\omega - [\omega_0(k) - \Gamma_B^2(k)]^{1/2}}{\Gamma_B^2(k) + \{\omega + [\omega_0^2(k) - \Gamma_B^2(k)]^{1/2}\}^2} - \frac{\omega - [\omega_0^2(k) - \Gamma_B^2(k)]^{1/2}}{\Gamma_B^2(k) + \{\omega - [\omega_0^2(k) - \Gamma_B^2(k)]^{1/2}\}^2} \right\}$$

where the first term represents the quasi-elastic contribution, the second the symmetrical lorentzian lines and the last two terms the asymmetric ones. Our data, deconvoluted from the instrumental resolution function, are fitted by Eq. 1. In order to obtain the better accuracy of the parameters the fitting was performed on three F.S.R. In this way we obtained the values of ω_0 and Γ_B from which the high frequency velocity V_0 and absorption α/f^2 can be calculated

These values are to be compared with analogous quantities founded by means of ultrasonic experiments. It is to be noticed that a direct comparison between ultrasonic measurements (that analyze the spatial damping of the sound wave) and Brillouin measurements (that refers to the temporal damping of thermal phonons) is not obvious.[18,19] In an ultrasonic experiment the driving frequency is imposed by the probe and it is a real quantity, while the wavevector turns out to be complex. Then, we can write:

$$V_u \equiv \frac{\omega}{\mathrm{Re}(k)} = V_0 \cdot \left[1 + \frac{\Gamma^2}{\omega^2}\right] \cdot \sec\left(\frac{1}{2}\mathrm{tg}^{-1}\frac{\Gamma}{\omega}\right) \tag{2}$$

where $V_0 = (K/\rho)^{1/2}$, K being the longitudinal modulus and Γ the damping parameter. On the contrary, in a Brillouin scattering experiments, the wavevector k is a real quantity, fixed by the experimental conditions, while ω is complex. In this case the following relation holds:

$$V_B \equiv \frac{\mathrm{Re}(\omega)}{k} = V_0 \cdot \left[1 - \frac{\Gamma^2}{4v_0^2 k^2}\right]^{1/2} \tag{3}$$

These circumstances have to be taken into account to avoid some nonphysical results. From our experiment we set the two probe independent quantities v_0 and α/f^2, which in a Brillouin experiment are related as:

$$v_0 = \frac{\omega_0}{k} \quad \text{and} \quad \frac{\alpha}{f^2} = \frac{2\pi\Gamma_B}{v_0 \cdot \omega_0^2} \tag{4}$$

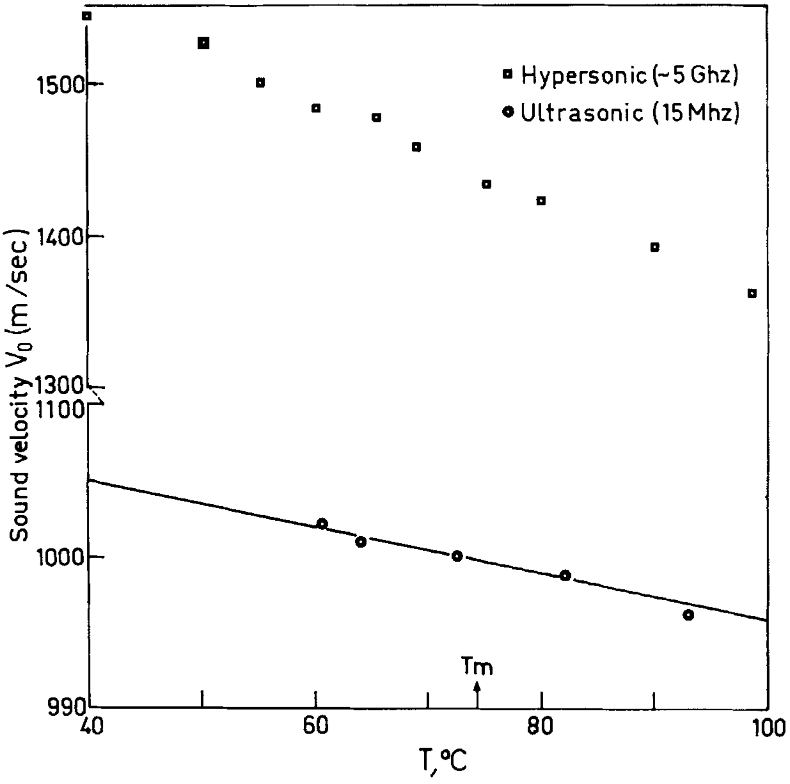

FIGURE 2 Sound velocity v_0 *vs* T. □: Hypersonic data; ○: Ultrasonic data; ——— linear best fit (see text).

In Figures 2 and 3 the velocity v_0 and the absorption α/f^2 are plotted as a function of the temperature. As far as the velocity data are concerned, the dispersive behaviour of v_0 is to be noticed. Furthermore the absorption values at high frequency are well above the "classical" value. The values of the non-relaxing, frequency independent, shear viscosity η_s, that enter in the classical expression are taken from literature.[6] We estimate an overall accuracy of the high frequency α/f^2 values of the order of 3%, while the error on the ultrasonic and hypersonic velocity is less than 1%. The values for the supercooled phase are extrapolated both by means of Arrhenius law and means of Fulcher-Tamman-Hess equation.[11] It has to be noticed that for $SbCl_3$ the ideal glass temperature T_0 of the V.F.H. equation takes the value of 210°K.

The structural effects are very important in our system, hence its acoustic behaviour can be connected to some relaxation phenomenon. These effects have a microscopic origin, because the finite time necessary for the restoring

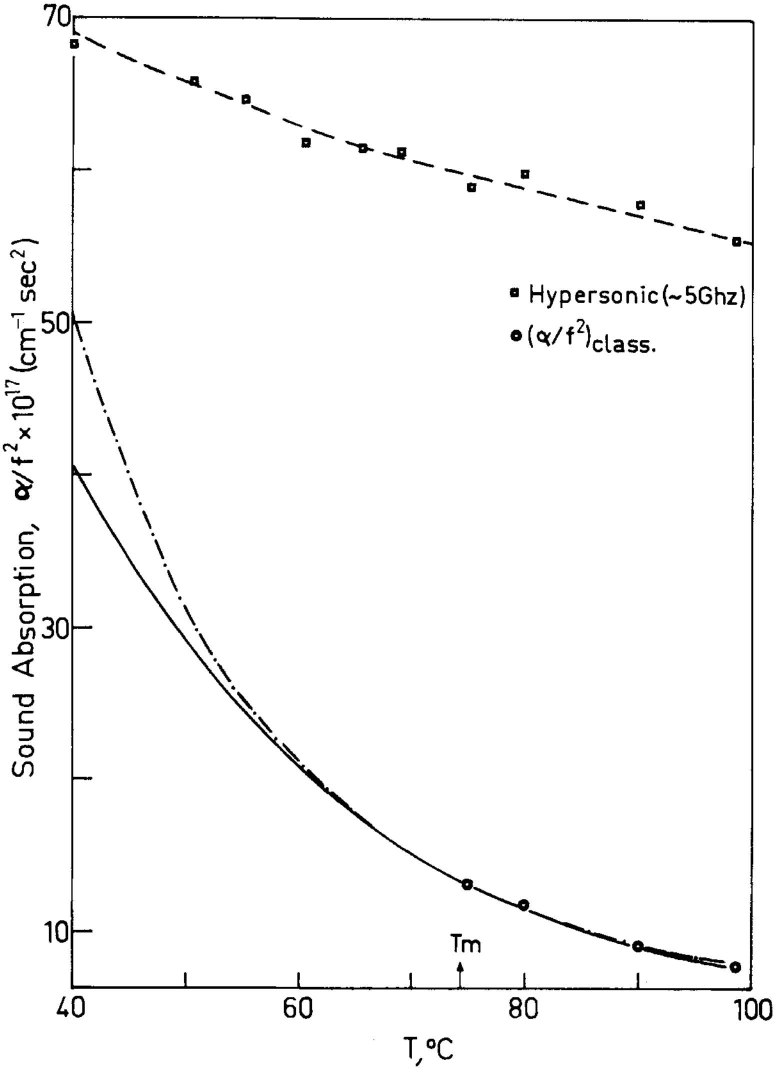

FIGURE 3 Sound absorption α/f^2 *vs* *T*. ☐: Hypersonic data. — — —: guide for eye; ○: $(\alpha/f^2)_{\text{class}}$; ————: $(\alpha/f^2)_{\text{class}}$ with η from Arrhenius law; —·—·—· with η_s from Tamman-Fulcher-Hess law.

forces to drive the system to a local equilibrium is altered by the pressure and temperature changes connected to the waves propagation. This phenomenon can be explained on the basis of the compressional relaxation or viscoelastic theories.[11,13] Accordingly, for a single relaxation process, we can write,

$$\frac{\alpha}{f^2} = \frac{2\pi^2}{\rho \cdot v_0^3} \cdot \left[K_r \cdot \frac{\tau_L}{1 + \omega^2 \cdot \tau_L^2} + \frac{4}{3}\eta_s \right] \tag{5}$$

$$v_0^2 = \frac{1}{\rho} \cdot \left[K_0 + K_r \cdot \frac{\omega^2 \tau_L}{1 + \omega^2 \tau_L^2} \right] \tag{6}$$

where K_r and τ_L are the relaxing part and the zero frequency value of the modulus. τ_L is the volume, or structural relaxation time. By combining the ultrasonic and the hypersonic results, the eqs. (5) and (6) give for τ_L:

$$\tau_L = \frac{\rho v_0^2 - K_0}{[\rho \cdot v_0^3/2\pi^2 \cdot (\alpha/f^2) - \frac{4}{3} \cdot \eta s] \cdot \omega^2} \tag{7}$$

In Eq. (7) the ultrasonic velocity values that enter in K_0 are obtained, as a function of the temperature, from the experimental data at 15 Mhz by means of a linear fit:

$$v_u = a - b \cdot T \tag{8}$$

where: $a = 153817$ cm./sec.

$b = 155.344$ cm./(sec.°K)

Finally, by inserting τ_L in Eq. (6), one can extract values of a function of the temperature. We are aware of the fact that some criticism could be raised about the assumption that structural processed in associated liquids follow an exponential decay law with a single relaxation time. Usually, in fact, this class of liquids relaxes with more complex laws.[20] Many theoretical models have been developed to explain this behaviour. In our case, the impossibility to obtain data on a more extended range of temperature in the supercooled region, in addition to the lack of information about the intermediate frequency values, did not allow us to perform a detailed analysis of the complex relaxational processes involved. Moreover, in order to gain information about the acoustic dispersion that are shown by the experimental results, we look at the temperature evolution of the relaxing modulus and of the relaxational longitudinal time τ_L.

From the plots of ln (K_r/τ) versus $1/T$, it is possible to obtain the difference of energy between the two states between which the system relaxes. The results are shown in Figure 4; the fitting from the law ln $(K_r/T) \sim \Delta G_0/RT$

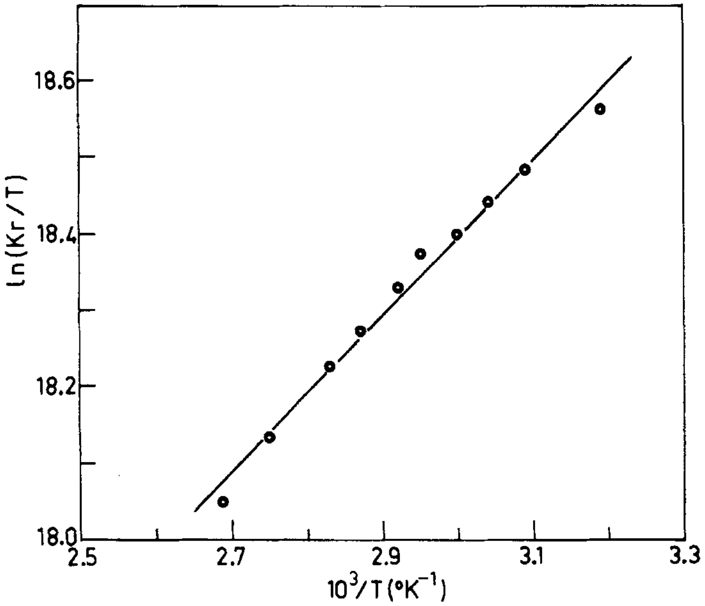

FIGURE 4 Arrhenius plot of the relaxation bulk modulus; O Exp. results; ——— : Theor. fit.

allows to obtain a value of 2.03 Kcal./mole for ΔG_0, that results independent from the extrapolation law for η_s in the supercooled region.

Values of the order of 0.2 nsec. are obtained for τ_L near the melting point and its temperature dependence gives an activation energy of 400 ÷ 500 cal./mole. If we assume a thermally activated process, this value represents the barrier energy for the reverse process and can be due to the strong intermolecular Antimony-Chlorine bridges.[4]

Surprisingly, this value together with the one of ΔG_0 obtained from the relaxing modulus K_r are in close agreement with those deduced by the analysis of the Rayleigh-wing in a previous work[2] where the quasi-elastic component of the molten $SbCl_3$ spectrum was correlated with an activated process of breaking and making chlorine bridges. On the basis of a "bond-lattice" model,[21] the two states in the liquid are characterized by the existence of intact bonds (state "on") and broken bonds (state "off").

In particular the above mentioned value of ΔG_0 can be interpreted as a fractional part of the vaporization energy.[13] On the other hand, in $SbCl_3$, the possibility to originate an "off" state need only the breaking of one of the three chlorine bridges. In this case, in fact, the possibility of an hindered rotation around the chain axis makes possible the hole formation and the subsequent volume variation in the melt.

We think that other measurements are needed to obtain more detailed information about this interesting liquid system (e.g. dielectric relaxation measurements). In fact a systematic study, in the intermediate frequency range between 10^6 Hz and 10^{10} Hz are in progress in our laboratory to better clarify the microscopic nature of the observed structural relaxation.

References

1. M. Fontana, G. Maisano, P. Migliardo, C. Vasi and F. Wanderlingh, *Opt. Acta*, **27**, 1087 (1980).
2. F. Aliotta, G. Maisano, N. Micali, P. Migliardo, C. Vasi, F. Wanderlingh, R. Triolo and G. P. Smith, *J. Chem. Phys.*, **76**, 3987 (1982), and references therein.
3. R. Triolo and A. H. Narten, *J. Chem. Phys.*, **69**, 3159 (1978).
4. E. Johnson, A. H. Narten, W. E. Thiessen and R. Triolo, *Faraday Discuss. Chem. Soc.*, **66**, 287 (1978).
5. L. Pazsitka and R. Bertran, *J. Electroanal. Chem.*, **28**, 119 (1970).
6. J. W. Mellor, *Inorganic and Theoretical Chemistry*, Longmans, London 1960, vol. 9, p. 468; see also P. Pascal, *Nouveau Traité de Chimie Minérale*, Masson et Cie, Paris, 1958, vol. XI, p. 562.
7. F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, **56**, 413 (1972).
8. See e.g. M. H. Brodsky *Light Scattering in Solids* edited by M. Cardona, Springer, Berlin, 1975, pp. 204–251.
9. F. Aliotta, M. P. Fontana, G. Maisano, P. Migliardo, C. Vasi and F. Wanderlingh, *J. de Physique*, **42**, 57 (1981).
10. G. D'Arrigo, *J. Chem. Phys.*, **75**, 921 (1981).
11. Most of the acoustical properties of supercooled liquids were reviewed by G. Harrison *The Dynamic Properties of Supercooled Liquids*, Acad. Press, London- N.Y., 1976, and references therein.
12. D. Sette, *Handbuch der Physik*, Springer-Verlag, Berlin, 1961, pp. 304–328.
13. T. A. Litovitz and C. M. Davis, *Physical Acoustics* edited by W. Mason, Academic Press, London-N.Y., 1965, vol. II-A, pp. 281–349.
14. V. A. Del Grosso and C. W. Mader, *J. Ac. Soc. Am.*, **52**, 1442 (1972).
15. Literature data (from ref. 6) are used for the density ρ with the same temperature dependence law used for extrapolating the data in the supercooled region. Furthermore the refractive index was calculated from the values of the density by means of the Lorentz-Lorenz equation.
16. See e.g. J. P. Boon and S. Yip, *Molecular Hydrodynamics* McGraw-Hill, N.Y. 1980, pp. 1–104.
17. C. J. Montrose, V. A. Solovyev and T. A. Litovitz, *J. Ac. Soc.*, Am. **43**, 131 (1980), and D. A. Pinnow, S. J. Candan, J. T. La Macchia and T. A. Litovitz, J. *Ac. Soc. Am.*, **43**, 131 (1968).
18. W. A. B. Evans and J. C. Powles, *J. Phys. A*, **7**, 1944 (1974).
19. R Mountain, *Rev. Mod. Phys.*, **38**, 205 (1966).
20. Th. Dorfmuller, H. Dux, G. Fytas and W. Mersch, *J. Chem. Phys.*, **71**, 366 (1979).
21. C. A. Angell, *J. Chem. Phys.*, **75**, 3698 (1971).