Thermal properties of two low viscosity silicon oils as functions of temperature and pressure

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The thermal conductivity and the specific heat capacity per unit volume have been measured for two low viscosity grades of Dow Corning® 200 fluid (polydimethyl siloxane) in the range 110 to 350 K and under pressures up to 2.0 GPa (20 kbar). Both the quantities studied are found to increase with increasing pressure in the liquid phase. From the measured data the phase diagrams are obtained. The 5 mm²/s (5 cSt) grade fluid does not crystallize, but undergoes a glass transition at 1.0 GPa at room temperature. The 1 mm²/s (1 cSt) grade has a more complicated phase diagram with a partly crystalline phase at low temperatures and pressures and two glass transitions at high temperatures and pressures.

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I. INTRODUCTION

The original motivation behind this work was to find a chemically inert pressure transmitting medium with good electrical insulating properties. While many liquids are in common use as pressure transmitting media in high pressure experiments, all have some definite drawbacks. The light alcohols, and notably ethanol-methanol mixtures,[1] are hydrostatic up to quite high pressures but suffer from relatively low electrical resistivities, mainly due to their hygroscopic properties. Also, they tend to attack commonly used adhesives, such as epoxy. Light hydrocarbons, such as the pentanes, have good insulating properties and are useful up to high pressures, but are somewhat awkward to handle due to their low boiling points and the fact that they easily wet most surfaces. A third group of media, light mineral oils, have excellent electrical and water-repellent properties but usually freeze at relatively low pressures (below 1 GPa).

In this work we have investigated the phase diagrams of two silicone fluids. We have chosen to investigate the thermal conductivity and the specific heat capacity of the material, since this gives us both useful data on the thermal properties of the material under pressure and also clear indications of the state of the sample, whether it be liquid, glassy, or crystalline.

II. EXPERIMENTAL DETAILS

The liquids investigated are Dow Corning® 200 fluids with kinematic viscosities 1 mm²/s (1 cSt) and 5 mm²/s (5 cSt), respectively. Similar silicones are available from other manufacturers under other trade names, such as Midland Silicones MS200, ICI Silicone FIII, and General Electric SF-96.

These liquids are linear polydimethyl siloxanes with the general chemical formula $(CH_3)_3SiO-[(CH_3)_2SiO]_n-(CH_3)_3Si$. The molecules consist of a silicon-oxygen "backbone", to which are attached two methyl groups at each silicon atom. The siloxane chain is chemically very stable, and thus these liquids are chemically inert and excellent electrical insulators. Furthermore, they are characterized by high boiling points and low melting points. Most physical properties, such as viscosity, are little affected by temperature changes. This is generally attributed to a tendency for the linear siloxane chain to coil itself up as a short helix at low temperature.[2] Thus, at low temperature the molecules are compact and can easily move, while at high temperature the chains are stretched out and entangled, offsetting the effect of the increase in thermal energy.

DC200 fluid is obtainable in many grades, characterized by their kinematic viscosity, which at room temperature varies between 0.65 and 1×10^5 mm²/s. None of these, with the possible exception of the lowest viscosity fluid, is a pure polydimethyl siloxane oligomer. Instead, any DC200 fluid contains siloxane chains with widely varying lengths. The approximate mean molecular weight can, however, be calculated from the viscosity or other physical properties.[3–5] We have chosen to investigate the 1 and 5 mm²/s grades, since these, according to the manufacturer, had the lowest freezing points of those grades available to us and, at the same time, boiling points well above 100 °C.

The high pressure measurements were all carried out in a 45-mm-diam piston and cylinder vessel, which could be cooled by freon and/or liquid nitrogen down to 100 K or electrically heated to well above room temperature. Measurements of the thermal conductivity λ and the specific heat capacity per unit volume ρc_p, where ρ is the density of the sample, were made using an improved version of the transient hot wire method described earlier.[6] In all cases, temperature was measured with Chromel-Alumel thermocouples, while the pressure was calculated from the piston load using an empirical friction correction.

III. EXPERIMENTAL RESULTS

The pressure dependence of λ and ρc_p at room temperature was first measured up to 1 GPa for two samples of the 5 mm²/s grade fluid. For the second sample measurements were also made as functions of temperature between 110 and 375 K at 1.0 and 0.21 GPa. Also, a final pressure run was made up to 2 GPa and back to atmospheric pressure at 250 K.

The results obtained in these experiments are shown in Figs. 1–3. Figure 1 shows λ and ρc_p as functions of pressure P up to 2 GPa at 250 K. The peak in λ and the simultaneous
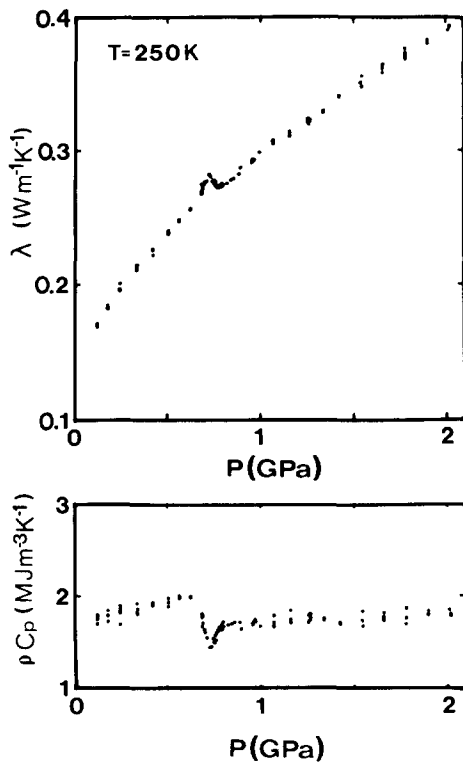
FIG. 1. Pressure dependence of λ and ρc_p for 5 mm²/s 200 fluid at 250 K.

step in ρc_p at 0.73 GPa are characteristic signs of a glass transition in the material.[7,8] Neither the peak nor the deep minimum in ρc_p are real effects but are, instead, experimental artifacts believed to be the results of structural relaxations in the material having characteristic times comparable to the heat pulse duration. Any crystallization would have shown up as a large peak in ρc_p and a step in λ, but no such features are observed. As would be expected, the pressure dependence of λ is larger in the liquid than in the glassy state. Also, while λ as a function of P is almost linear in P above the glass transition, it is strongly nonlinear below, re-
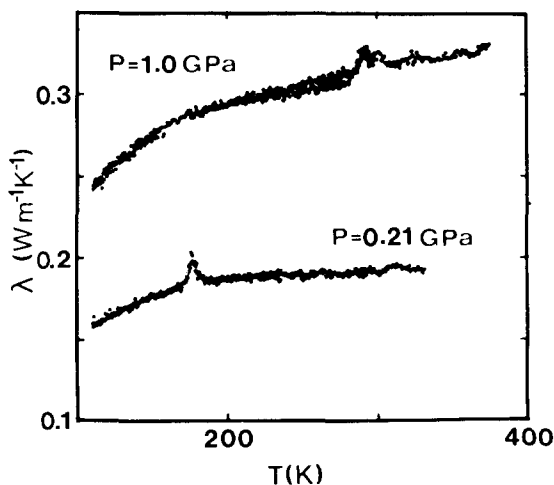

FIG. 2. Thermal conductivity as a function of T at 1.0 and 0.21 GPa for 5 mm²/s 200 fluid. At 1 GPa results are shown for both increasing and decreasing T.
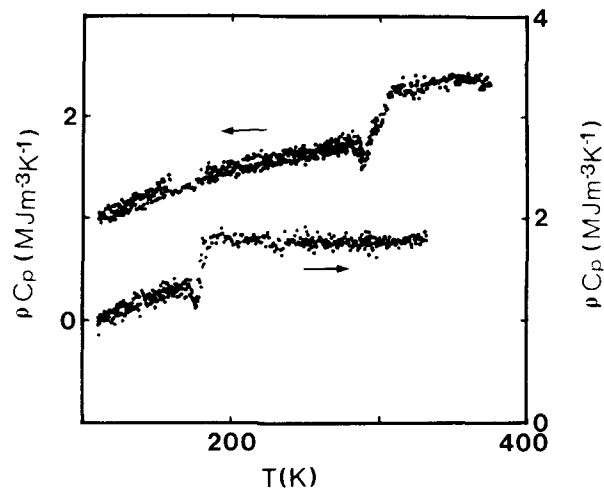

FIG. 3. Specific heat capacity per unit volume for 5 mm²/s 200 fluid as a function of T. Upper curve (left-hand scale) at 1.0 GPa, lower curve (right-hand scale) at 0.21 GPa.

flecting the strong pressure dependence of the compressibility of silicone fluids.[9] The specific heat capacity per unit volume increases with P in the liquid, but is approximately constant in the glass.

Figure 2 shows λ as a function of T at 1.02 and 0.21 GPa. As before, no crystallization is observed, and the curves λ (T) conform very well with those generally observed for glass forming liquids and polymers[8,10] with no change in the absolute value of λ at the glass transition temperature T_g. The corresponding data for ρc_p are shown in Fig. 3.

The absolute value of λ at 300 K and atmospheric pressure was found by extrapolation to be $\lambda = 0.142$ W/m K, with a weak negative temperature dependence. The pressure dependence of λ at 300 K in the liquid state could be well described by the expression λ (P) $= 0.142(1 + 1.51 P - 0.35 P^2)$ W/m K, with P in GPa. Above 300 K we found the pressure coefficient to increase with T at approximately the same rate as the compressibility.[11] In the glass phase we found an approximately linear pressure dependence, which at 250 K can be written λ (P) $= 0.20(1 + 0.49 P)$ W/m K. At lower pressures and temperatures the pressure coefficient is larger due to the higher compressibility in the material, and in the range 110–170 K and 0.2–1.0 GPa (see Fig. 2) we calculate a mean pressure coefficient of about 0.79 GPa.$^{-1}$

For ρc_p at 300 K and atmospheric pressure we found $\rho c_p = 1.5$ MJ/m³ K, with the pressure dependence in the liquid given by $\rho c_p(P) = 1.5$ $(1 + 0.67$ $P - 0.27$ $P^2)$ MJ/ m³ K up to $P = 0.9$ GPa. As can be seen from Fig. 1, the pressure dependence of this quantity is much smaller in the glass phase. At 250 K, ρc_p increases by only about five percent from 1 to 2 GPa. Since there are no data available for the compressibility of this particular grade of 200 fluid at high pressure, the pressure dependence of c_p alone has not been calculated. However, it seems reasonable to assume that c_p decreases with increasing pressure, at least in the glass phase. Finally, Fig. 4 shows the phase diagram obtained in this experiment.

At room temperature the results for the 1 mm²/s grade material differ only quantitatively from those shown above,
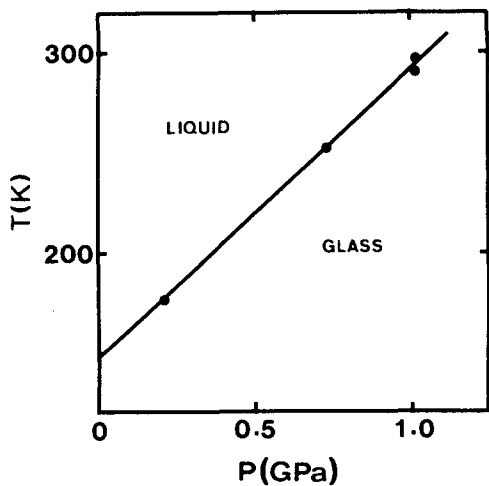
FIG. 4. Phase diagram for 5 mm²/s 200 fluid. Points denote experimental results.

FIG. 6. Temperature dependence of λ at 0.12 GPa for 1 mm²/s 200 fluid. Note the compressed λ scale.

with a smooth pressure dependence of both λ and ρc_p up to the glass transition at about 1.4 GPa. Figure 5 shows the temperature dependence of λ between 110 and 300 K at 1.0 GPa. The only unusual feature is the double peak at T_g; this also showed up as a double step in the ρc_p data. Lowering the pressure to 0.12 GPa, we then swept the temperature down to 110 K and back to 300. At this pressure, the liquid was found to crystallize at slightly below 200 K. This was indicated both by the characteristic behavior of λ and ρc_p at the transition and by a peak in a recording of temperature versus time in the sample. The crystallization was not complete, however, as could be seen by a glass transition occurring at about 180 K (Fig. 6). Melting was rather sluggish and seemed to continue over a large temperature interval and to give a double peak in λ (dashed lines in the figure).

To obtain further data on the phase diagram of the material we then studied a second sample by taking it through glass transition and crystallization/melting along several isobars and isotherms. The phase diagram found is shown in Fig. 7. In the figure, the triangles indicate the P-T coordinates of the upper glass transition peak found in the experi-
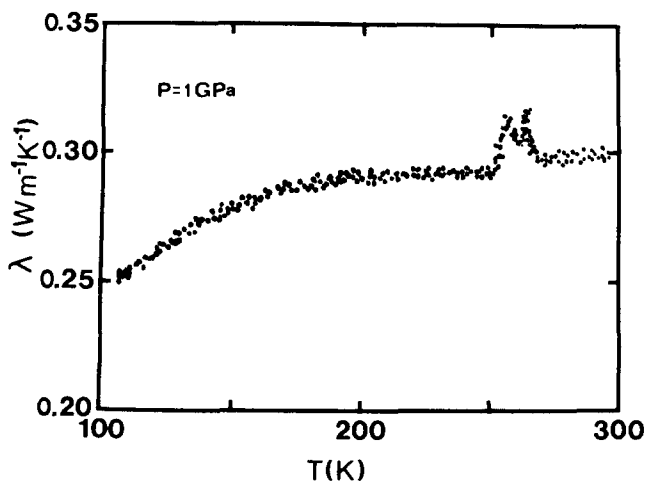
ments. The dashed line parallel to the glass-liquid boundary indicates the position of the lower glass transition peak. The squares indicate crystallization, while the circles indicate melting points. Thus, at 0.25 GPa the liquid could be supercooled to about 208 K before crystallization occurred; the resulting crystals were then stable up to the melting point at about 245 K. The amount of supercooling needed to crystallize the liquid increases with increasing pressure. At times, a second crystallization occurred on heating the already crystalline material within the range of metastability of the liquid phase. No crystallization could be obtained above 250 K at the cooling (and heating) rate of 0.5 K/min used. In Table I we give interpolated data for T_g and T_m at some selected pressures.

At 300 K, λ in the liquid state can be described by $\lambda(P) = 0.124\,(1 + 1.93\,P - 0.50\,P^2)$ W/m K, with P less than 1.3 GPa. The pressure dependence is stronger than for the higher viscosity grade material, as should be expected for a more compressible substance.[9,11] Above the glass transition λ is well described by the linear function $\lambda(P) = 0.20\,(1 + 0.52\,P)$ W/m K. The specific heat per unit volume in

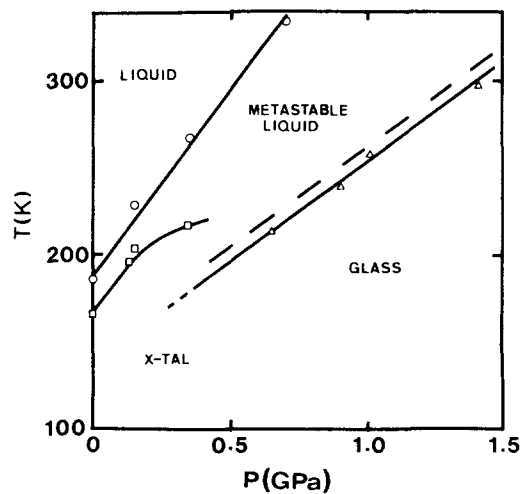FIG. 5. Temperature dependence of λ at 1.0 GPa for 1 mm²/s 200 fluid.

FIG. 7. Phase diagram for 1 mm²/s 200 fluid. See text for an explanation of symbols.

TABLE I. Interpolated values of the glass transition temperature T_g and the melting point T_m under pressure for Dow Corning® 200 fluid. Asterisk (*) denotes extrapolated value.

Pressure (GPa)	5 mm²/s grade T_g (K)	1 mm²/s grade T_m (K)	T_g (K)
0	147*	185	145*
0.25	183	245	⋯
0.50	219	294	199
0.75	254	331	226
1.00	290	⋯	253
1.25	⋯	⋯	280
1.50	⋯	⋯	307

the liquid state can not be well described by a single quadratic expression. There is a strong nonlinear pressure dependence below 0.5 GPa, but an almost linear dependence above. The absolute value at atmospheric pressure is again $\rho c_p = 1.5$ MJ/m³ K, with a mean pressure coefficient up to 1 GPa of approximately 0.35 GPa^{-1}.

No data are given for the material in the crystalline phase, since the degree of crystallinity, and thus also λ and ρc_p, varied strongly with the crystallization temperature and pressure. From the temperature dependence[10] of λ, we have estimated that the average volume crystallinity of our samples was usually about 25%.

IV. DISCUSSION

The thermal conductivity of polydimethyl siloxanes has been measured previously by other workers at both atmospheric[12] and elevated[13] pressures. Jamieson and Cartwright[12] found that, for all viscosity grades, λ could be described to within ± 4% by the expression

$$\lambda = \lambda_{50} + a(t - 50),$$

where

$$\lambda_{50} = 0.157[1 - 4.52/(\nu + 11.45)] \text{ W/m K},$$

$$a = (-5.2 \times 10^{-4} + 2.5 \times 10^{-6} \lambda_{50}) \text{ W/m K}^2.$$

In these expressions t denotes the temperature in °C, λ_{50} is the thermal conductivity at 50°C, and ν is the kinematic viscosity in cSt (or mm²/s) at 25 °C. The results for λ at 300 K are then 0.112 and 0.126 W/m K for the 1 and 5 mm²/s grades, respectively. Nemzer and Pugach[13] have investigated the pressure dependence of λ up to 0.2 GPa between 20 and 200 °C for three polydimethyl siloxanes with viscosities 5, 100, and 400 mm²/s. The results for the first of these can be directly compared to our results. With P in GPa we find for λ $(P)\lambda$ (0.2)/λ (0) = 1.29, to be compared with their result λ (0.2)/λ (0) = 1.32. The absolute value of λ at atmospheric pressure is given as 0.123 W/m K, in good agreement with Jamieson and Cartwright.[12]

The difference between our results at atmospheric pressure and those given above is surprisingly large. However, most of this difference is probably explained by the fact that our zero pressure results are in fact extrapolations of our high pressure measurements. Since most of the problems encountered when using hot wire methods are caused by convection in the liquid, we have made no measurements below

0.1 GPa. Since the viscosity increases very fast with pressure,[14] we believe that convection errors are negligible at high pressures. At 0.2 GPa, our results for λ in the 5 mm²/s grade fluid are only about 6% higher than those of Nemzer and Pugach,[13] while at atmospheric pressure the difference is 15%. Also, the compressibility of the material is known to be very large at low pressures.[9,11] It thus seems that λ increases very strongly with pressure near atmospheric pressure and that our quadratic expression for λ in terms of P is unable to take this into account.

The general features of the phase diagrams for the two materials are in good agreement with the mesurements by Bridgman,[9,14,15] who investigated the compressibility,[9] viscosity,[14] and phase diagrams[15] of several pure dimethyl siloxane oligomers. He found[9] that only the dimer could be brought to freeze under pressure in the range up to 4 GPa, while, surprisingly, all the higher molecular weight liquids seemed to stay in the liquid phase (there is no change in volume at the glass transition). Later,[15] he was able to crystallize several of these liquids under pressure by supercooling the pressure cells and to study the pressure dependence of T_m. Although the 200 fluids investigated by us are, of course, no pure oligomers, the average pressure derivative $dT_m/dP \simeq 210$ K/GPa found by us for the 1 mm²/s grade fluid is in very good agreement with the value 200 K/GPa found by Bridgman for the pure trimer, which should have a molecular weight similar to the mean molecular weight of our sample.[5]

The glass transition of polydimethyl siloxanes has not, to our knowledge, been studied previously under pressure. At atmospheric pressure, however, both crystallizations and glass transitions have been found by dielectric,[16] acoustic,[17] and calorimetric[18] measurements. Usually it is found[16,18] that, on cooling, there is a crystallization at about 170–200 K, followed by a glass transiton below 150 K. On heating, the glass transition is followed by melting of the crystal at T_m, which is usually 20–40 K above the crystallization temperature. The exact values for T_g and T_m depend on molecular weight and cooling and heating rates. In both thermal[18] and dielectric[16] measurements the melting usually takes place in a two-step process, giving two peaks in a thermogram or two steps in a curve of dielectric loss versus T. Double glass transitions are also sometimes observed.[18]

Our measurements on the 5 mm²/s grade fluid under pressure did not show any trace of crystallization. This is in agreement with the observations by Bridgman[9] that high molecular weight polydimethyl siloxanes do not crystallize under pressure. This is probably due to the inability of the long molecular chains to rearrange themselves into a regular array on the short time scale of the experiment (several hours). Instead, the supercooled liquid vitrifies at sufficiently high pressures. We did not investigate the phase boundary at atmospheric pressure; however, a linear extrapolation of our results to zero pressure indicates a value of T_g of 147 K. This is almost identical to the T_g found by Cowie and McEwen[19] for polydimethyl siloxanes of very high molecular weight, using differential scanning calorimetry and thermomechanical analysis. However, it should be noted that the phase boundary usually is not a straight line, but curves

away from the T axis, and also that the present method usually[7,8] gives a value of T_g that is several K higher than that found by semistationary methods. This indicates that our value of 147 K for T_g at zero pressure corresponds more nearly to a differential scanning calorimetry value of 135–140 K, which is in good agreement with that found by Cowie and McEwen[19] for materials of similar molecular weight.

At high temperatures and pressures the 1 mm²/s grade fluid always showed two glass transitions, as shown in Figs. 5 and 7. However, at lower P and T, crystallization always occurred before T_g, and in this region only one glass transition was observed. It can be noted that a linear extrapolation of the upper glass transition to zero pressure would give $T_g = 145$ K, which is in good agreement with literature values[19] of 123 K (for the pure trimer), allowing for the effects discussed above and the fact that this material is more compressible[9] at lower pressures and thus should be expected to have a less linear behavior of $T_g(P)$. At atmospheric pressure, double glass transitions are rarely seen in polydimethyl siloxanes, but are common in polydiethyl or polydipropyl siloxanes.[20] The fact that both crystallization and glass transitions are observed in the same material can be explained in many ways: One possibility is that part of the liquid crystallizes, while the rest forms a liquid glass forming matrix around the crystallites. Another is that the 200 fluid is a mixture of several viscosity grades, and that the low molecular weight component crystallizes at low temperature, leaving a fluid component of higher molecular weight to vitrify at still lower T. This is, however, unlikely, since fractionated,[18] almost pure oligomers show the same behavior. There is also a possibility that the crystallization is an ordering of the molecules, while the glass transition at low temperature is a freezing of the side chain movements. Furthermore, it has been suggested[17] that there is no actual crystallization, but only a coiling of the molecules into a more compact helical form, which subsequently would promote the formation of small crystallites. From our experiment we conclude that crystallization only occurs at low pressures, while at high pressures the decreased mobility of the molecules results in the formation of a glass. The mechanism responsible for the glass transition at atmospheric pressure, however, is independent of pressure, resulting in a double glass transition being observed at high pressures. We suggest that this picture is compatible with both the first and the third model above. However, it is tempting to associate the glass transition mechanism to the side chains, since longer side chains always give two glass transitions.[20] It should also be noted that we noted small indications of a second glass peak in some of the measurements on the 5 mm²/s fluid (see Fig. 2).

The double peak at T_m observed in the experiment (Fig. 6) is a common feature of many polymers. In the present material this has been attributed[18] to reorganization of metastable crystals after partial melting. Due to limitations inherent in the method, our temperature resolution is too poor

to allow us to investigate the properties of the material between the two "melting points". It is possible that there is a narrow region of a second crystalline phase close to the melting point. Since the molecules of the crystalline material are known to be coiled up into a compact, helical form, it could even be speculated that this phase could be similar to the viscous crystalline phase observed in polydiethyl siloxanes[21] or the plastic crystalline phase common among linear hydrocarbons.[22]

Finally we note, from a technical point of view, that the 1 mm²/s grade fluid seems to be a promising candidate as a pressure medium at temperatures above 250 K and for pressures up to 1.3 GPa at room temperature and above. It has excellent electrical and water-repellent properties and a boiling point of 425 K. On the negative side, we can note a rather high compressibility[9] and a strong dependence of viscosity on pressure.[14]

ACKNOWLEDGMENT

[1] G. J. Piermarini, S. Block, and J. D. Barnett, J. Appl. Phys. **44**, 5377 (1973).
[2] J. Ames, J. Sci. Instrum **35** 1 (1958).
[3] P. Sen and A. P. Patro, Nuovo Cim. B **59**, 12 (1969).
[4] A. Weissler, J. Am. Chem. Soc. **71**, 93 (1949).
[5] J. L. Hunter, T. B. Lewis, and C. J. Montrose, J. Acoust. Soc. Am. **35**, 481 (1963).
[6] O. Sandberg, P. Andersson, and G. Bäckström, J. Phys. E **10**, 474 (1977).
[7] O. Sandberg, P. Andersson, and G. Bäckström, in *Proceedings of the 7th Symposium on Thermophysical Properties*, edited by A. Cezairliyan, (ASME, New York, 1977), p. 181.
[8] O. Sandberg, "Thermal Properties of Organic Glass Formers Under Pressures" Ph.D. thesis, Umeå University, 1980 (unpublished).
[9] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **77**, 129 (1949).
[10] D. W. van Krevelen, *Properties of Polymers* (Elsevier, Amsterdam, 1972).
[11] R. N. Richtenthaler, D. D. Liu, and J. M. Prausnitz, Macromolecules **11**, 192 (1978).
[12] D. T. Jamieson and G. Cartwright, "Thermal Conductivity of Silicone Oils," NEL Report No. 646, Glasgow, 1977.
[13] V. G. Nemzer and V. V. Pugach, Teploenergetika Issue 5, 90 (1977).
[14] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **77**, 117 (1949).
[15] P. W. Bridgman, J. Chem. Phys. **19**, 203 (1951).
[16] R. M. Hakim, R. G. Olivier, and H. St-Onge, IEEE Trans. Electr. Insul. EI-12, 360 (1977).
[17] A. G. Beattie, J. Appl. Phys. **43**, 1448 (1972).
[18] C. L. Lee, O. K. Johannson, O. L. Flaningam, and P. Hahn, Polymer Preprints **10**, 1311 (1969).
[19] J. M. G. Cowie and I. J. McEwen, Polymer **14**, 423 (1973).
[20] C. L. Lee, O. K. Johannson, O. L. Flaningam, and P. Hahn, Polymer Preprints **10**, 1319 (1969).
[21] J. M. Pochan, M. F. Frois, A. O. Goedde, C. L. Beatty, and D. F. Pochan, *Liquid Crystals*, edited by F. D. Saeva (Dekker, New York, 1979), p. 411.
[22] N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals* (Oxford University, Oxford, 1978), p. 667.