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NMR Determination of Phase Diagrams in Crystals with Orientational Disorder

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Pulsed nmr techniques have been used to determine the melting curves of cyclohexane and hexamethyldisilane (HMDS) and the brittle-to-plastic solid state transition in HMDS over a pressure range to 2.8 k bar. Inherent pressure hysteresis at both melting and solid–solid transitions is attributed to a "superpressing" phenomenon analogous to supercooling. The solid–solid transition in HMDS exhibits a "region of indifference" attributed to a distribution of local pressures within the polycrystalline sample. The nmr technique has the advantage that the proportion of different phases present in a sample may be determined.

INTRODUCTION

As part of a nuclear magnetic resonance (nmr) investigation into the effects of hydrostatic pressure on molecular motion in plastic crystals,[1] a pulsed nmr technique has been used to monitor phase changes as a function of temperature and pressure in two such polycrystalline materials, cyclohexane (C_6H_{12}) and hexamethyldisilane (HMDS, $(CH_3)_3SiSi(CH_3)_3$). This method exploits the discontinuities in nuclear spin relaxation times which occur at phase transitions. The well known abrupt increase in spin–spin relaxation time T_2 (or sudden narrowing of the nmr line) which takes place on melting provides a convenient means of determining the melting point.[2] Previous studies of plastic crystals have shown that the spin-lattice relaxation time, T_1, often increases abruptly by several orders of magnitude across the solid–solid phase transition from the low temperature (brittle) phase II to the plastic phase I. This phenomenon may be used to locate the transition

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point precisely. The proportion of the two phases co-existing during a transition may also be determined. The phase diagrams of few plastic crystals have been studied as yet. A comprehensive list of melting curve determinations prior to 1963 has been compiled by Babb, and contains only about six plastic crystals. Recently Würflinger[3] has studied a number of these materials using differential thermal analysis. A more conventional technique that has also been employed detects the volume change at the transition.[4,5] The melting curve of cyclohexane has been measured by both of these methods,[3,5,6] and our measurements on this material provide a useful comparison of techniques. As far as we are aware, the phase diagram of HMDS was unknown previous to this study.

EXPERIMENTAL

The system of pressure production and measurement has already been described,[1] together with the temperature controller. Samples were loaded under vacuum into glass cells sealed by a mercury reservoir which transmitted the pressure. The arrangement provided known hydrostatic pressures up to 2.8 k bar.† The low temperature limit of the system was set by the freezing point of mercury at the pressure of operation. The upper temperature limit was 380 K which was determined by the stability of the epoxy resin used in the probe construction.

Reagent grade cyclohexane was purified by fractional distillation, after which only one impurity (methyl cyclopentane at a concentration of 30 p.p.m.) was detected by V.P.C. techniques. The HMDS sample was also well characterized with an impurity level of less than 50 p.p.m. hexamethyldisiloxane and xylene.

Melting point determinations were most conveniently carried out under isothermal conditions. At each temperature, and under a pressure which was slightly greater than the melting pressure, the spin-echo amplitudes resulting from a Meiboom–Gill pulse sequence[7] were seen to exhibit a characteristic exponential decay with a time constant, T_2, of a few milliseconds. As the pressure was slowly reduced the echo pattern changed as the sample melted to a much more gradual decay, typical of a mobile liquid, with T_2 equal to a few seconds. At the transition the echo amplitude decay showed a double exponential behaviour corresponding to a solid and a liquid component, but the transition was sharp in that the two components co-existed in equilibrium at one pressure only for each temperature. The

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† 1 k bar = 10^5 Pa.

solid II–solid I transition in HMDS was determined in an analogous manner. With the sample in phase II the pressure was slowly (and isothermally) reduced until a sudden increase in T_1 appeared at the change to the plastic phase. The spin-lattice relaxation curve was also a combination of two exponential relaxation rates at the transition, the intensity of each depending on the amount of each phase present.

RESULTS AND DISCUSSION

The melting curve obtained for cyclohexane is shown in Figure 1. As expected for a pure sample, no premelting effects were observed and the precision of the method was determined by the accuracy of reading the pressure gauge, the uncertainty being estimated as ± 7 bar. Figure 1 also shows the results obtained recently by Würflinger[3] by the DTA method. These results are the most comprehensive to date and agree with and extend the previous volumetric measurements.[5,6,8] Our nmr measurements are in excellent agreement with the determination of Würflinger. Also shown in Figure 1 are points obtained using the Simon equation

$$\left[\frac{T_F}{T_0}\right]^c = \frac{P}{a} + 1$$

which was fitted by Babb[8] to the early data of Deffet.[6] This data extended only to 1 k bar, but the extrapolation using Babb's parameters for the melting

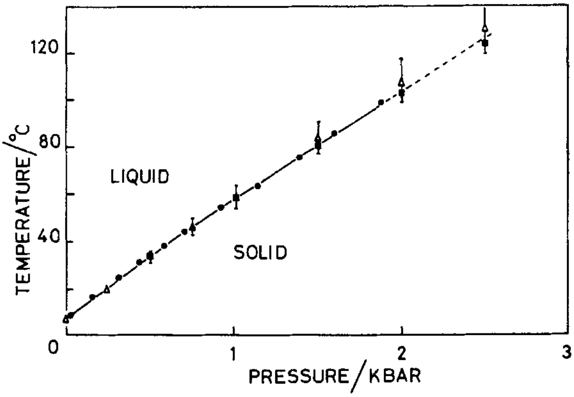

FIGURE 1 Melting curve of cyclohexane. ● Determined by nmr T_2 measurements. ■ Determination by Würflinger[3] using DTA. △ From Simon equation fitted by Babb[8] to data of Deffet.[6]

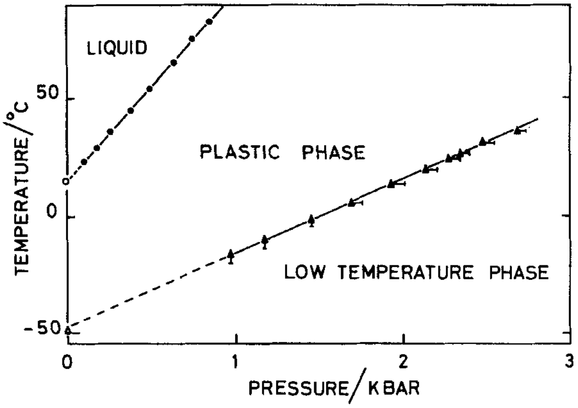

FIGURE 2 Phase diagram of hexamethyldisilane. ● Liquid–Solid I transitions determined by nmr T_2 measurements. ▲ Solid I (Plastic)–Solid II (Brittle) transitions determined by nmr T_1 measurements. △ Solid I–Solid II transition at atmospheric pressure.[9]

point at zero pressure, $T_0 = 279.7$ K, and constants $a = 3640 \pm 175$ bars and $c = 1.42 \pm 0.06$ are reasonably close to the measured values of the melting temperature T_F at pressures P up to 2.5 k bar. The predicted curvature in T_F vs P at high pressure is also confirmed.

The phase diagram obtained for HMDS is shown in Figure 2. The variation of the melting temperature with pressure was determined and again a sharp transition was observed with no pre-melting effects. The extrapolation of the results to atmospheric pressure gives a melting point of 288 K in good agreement with the accepted value[9] of 287.7 K.

In both cyclohexane and HMDS a pressure hysteresis was observed in the melting point, higher values of the melting pressure P_f being obtained on compression than on decompression measurements at the same temperature. The values obtained on isothermal decompression are believed to be the true melting point values and are the quantities shown in the figures. The metastable persistance of the liquid at pressures greater than the melting pressure is presumably analogous to the phenomenon of supercooling, and is therefore termed "superpressing".

The solid I–solid II transition curve obtained for HMDS is also shown in Figure 2. An inherent pressure hysteresis was also observed for this transition and this is again attributed to a superpressing effect. It has already been reported[10] that, at atmospheric pressure, the plastic phase could be supercooled by at least 10 K. However, even on a decompression cycle, the transition was not sharp, a two component spin-lattice relaxation curve being observed over a pressure range of about 70 bars. The amplitude of the signal corresponding to phase I gradually increased at the expense of that corresponding to phase II indicating that the proportion of each phase present in the sample changed with pressure in an apparently reproducible manner. The mixed phases also appeared to be in equilibrium as the proportion of each phase present was time independent when pressure and temperature were held constant for periods of several hours. The ranges of pressure for which two phases were observed to be present under decompression are indicated by the horizontal bars in Figure 2. An alternative procedure in which the phase transition was observed for increasing temperature under isobaric conditions was also employed. The temperature range over which the two phases were observed to be present is indicated on Figure 2 by a vertical bar line. The previously determined value for the transition temperature at atmospheric pressure[9] is also included in Figure 2 and is seen to be in good agreement with a linear extrapolation of the high pressure transition curve.

The apparent co-existence of the two phases in the region of the solid–solid transition might be due to a distribution in either pressure or temperature over the sample. However, the presence of a temperature gradient over the sample would also be expected to confer a finite width to the melting point determinations. It would also result in a temperature range being associated with the solid–solid transition under atmospheric pressure and no such behaviour has been observed. It therefore seems that a distribution of local pressures must exist within the sample in phase II, arising from random orientations of the crystallites, although in that case the apparent "width" of the transition might be expected to increase with external pressure. Bridgman[4] noted that pressure induced solid–solid transitions of finite width occur in a variety of materials. He named the pressure range over which the transition will not run, although the two phases are in contact, the "region of indifference" and has shown that it corresponds to an infinitely small transition velocity. Since the nmr technique can distinguish clearly the proportion of the two different phases present at one time, and a measurement can be made very quickly (in about 1 sec), keeping pressure and temperature constant, it offers a very useful method of investigating the kinetics of such transitions.

The nmr relaxation time method of investigating the pressure and temperature dependence of phase transitions was found to be a reliable and convenient one for the study of plastic crystals. Since the changes in relaxation time associated with both solid–liquid and solid–solid transitions are usually considerably more than an order of magnitude, the accuracy of the determination of a transition point depends only on the accuracy of the measurement of pressure and temperature. Measurements are made under equilibrium conditions, in contrast to dynamic methods such as D.T.A. and progress through a transition can be made extremely slow. Since the number of (resonant) nuclei in each phase may be detected by nmr two phase systems which correspond to very small regions of each phase, may be distinguished and transition velocities could be investigated. The nmr method could prove particularly useful in transitions where the volume change or heat of transition is small or is otherwise difficult to detect provided that a significant change in molecular motion occurs at the transition.

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