July, 1983] © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 2101—2105 (1983) 2101

Self-diffusion and Melting in the Plastic Phases of Neopentane as Studied by NMR Relaxation at High Pressures

Sadamu Takeda, (the late) Gen Soda, and Hideaki Chihara*
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received December 2, 1982)

Proton spin-lattice relaxation time T_1 in the plastic phase of 2,2-dimethylpropane (neopentane) was measured at 10 MHz up to 170 MPa between 192.7 and 308.2 K. T_1 near the melting point is determined by self-diffusion. The enthalpy and volume of activation of this motion suggest that self-diffusion occurs through a single vacancy mechanism. The correlation time of self-diffusion at the melting point (T_f) is $(3.2 \pm 0.5) \times 10^{-7}$ s irrespective of external pressure. The diffusion rate is a function only of T_f/T, *i.e.* the law of corresponding states holds. The feature of activation properties of self-diffusion is strongly correlated with the melting phenomenon. The melting curve of the phase diagram was also determined and a possibility of existence of another plastic phase was found above 40 MPa.

Molecular motions in plastic crystals (ODIC, the orientationally disordered crystals) have been studied by a variety of experimental methods.[1] These crystals are characterized by a small entropy of fusion (less than 21 J K^{-1} mol^{-1}) and existence of a phase transition below which the crystal becomes brittle. In general, overall rotation of a molecule is highly excited in the plastic phase and even self-diffusion is seen by the NMR and other methods below the melting point in many plastic crystals.[2] There is an empirical law that the correlation time of self-diffusion becomes about 10^{-7} s at the melting temperature in different plastic crystals.[2] It leads us to believe that on-set of self-diffusion acts as a dynamical trigger of the melting phenomenon in these crystals. A large amount of experimental data have already been accumulated about the self-diffusion in plastic crystals but most of them are the results under ordinary pressure. It is the purpose of the present study to make a "corresponding state" type of analysis of the melting from the self-diffusion data on 2,2-dimethylpropane (neopentane) obtained under different pressures.

Neopentane is a typical compound having a plastic crystalline phase and a relatively large amount of experimental information is now available. The plastic phase of neopentane has the f.c.c. structure (a= 8.82 Å)[3,4] containing four molecules a unit cell. The melting and transition temperatures are 256.5 and 140.5 K, respectively, and their associated entropy changes are 12.0 and 18.7 J K^{-1} mol^{-1}.[5] The state of molecular motion in the plastic and brittle crystalline phases are fairly well understood by the NMR[6–10] and other methods.[11–13] Thus, it is generally substantiated that overall molecular tumbling is highly excited in the plastic phase with an activation enthalpy of 4.2 kJ mol^{-1}, while the activation enthalpy for self-diffusion was reported to be between 25 and 34 kJ mol^{-1}.[6,8,9]

The pressure dependence of molecular motion in the plastic neopentane has also been reported by Allen *et al.*[7] However, they dealt only with a limited temperature range. Therefore, we now extended the measurements of proton spin-lattice relaxation time of the plastic phase of neopentane under pressure up to the melting point and also determined its melting curve. The results were then analyzed to derive motional parameters related to self-diffusion and melting.

Experimental

High Pressure Vessel and Pressure Measurement. The high pressure vessel used in this experiment was a clamped type which is essentially the same as the one that has been reported elsewhere.[14] The seal materials were fluoride rubber, Teflon, and lead metal, which constitute a conventional Bridgeman-type pressure seal. The design of the electrical leads from the interior of the pressure vessel to the outside is similar to that used by Terry and Ruoff,[15] with a heat shrinkable Teflon tube (NSTube-910-2, Nitto Denko, Japan) and epoxy putty XD580 (Japan CIBA GEIGY) used for the seal materials.[14]

The pressure-transmitting medium is the sample itself and its pressure was measured by means of a "manganin gage" whose resistance was determined by the four-terminal method. The gage was calibrated for temperature- and pressure-coefficients. First, the pressure coefficient was determined at 293 K with reference to the standard Heise gage up to 200 MPa. Secondly, the temperature coefficient was determined at the ambient pressure between 175 and 330 K. The pressure coefficient also depends on temperature but it is reported that the effect is small; if we put $\Delta = \{R(P) - R(0)\}/R(0)$, the value of $(\mathrm{d}\Delta/\mathrm{d}T)/\Delta$ is less than 3×10^{-4} K^{-1}.[16–18] Therefore, we used $\Delta/P = 2.442 \times 10^{-5}$ (MPa)$^{-1}$ (at 293 K) throughout the temperature range studied in the present work (192 K to 308 K). The temperature coefficient of the resistance of manganin is not very small at low temperatures, *e.g.* 2×10^{-4} K^{-1} at 200 K, and this required a good precision of temperature measurement and control. The temperature of the specimen could be controled to within ±1/30 K and it was measured by several Chromel-P-Constantan thermocouples attached on the outside periphery of the vessel. The overall uncertainty in the pressure determination was about ±2.5 MPa.

Preparation of the Sample and T_1 Measurement. A sample of neopentane of commercial origin (Takachiho Kagakukogyo, Co.) was dried over Molecular Sieves 3A, 4A, and 5A in vacuum, purified by repeated vacuum distillation, and degassed by several freeze-pump-thaw cycles. The specimen was then distilled into the high pressure vessel through an adapter which connected the pressure vessel to the purification line.[14] The final purity of the specimen was better than 99.8 mol% by gas chromatography. The specimen was compressed at room temperature by use of a hydraulic press and the T_1 measurements were made under conditions of effectively constant volume.

Proton spin-lattice relaxation time (T_1) was measured using 90° train$-\tau-$90° pulse sequences at an operating frequency of 10.0 MHz. A series of T_1 values under pressure were measured by varying the temperature after the specimen had been compressed at room temperature. The temperatures at which the T_1 measurement was performed were fixed within ±0.1 K throughout the different series. Because the pressure inside the vessel changed when the specimen temperature changed, the primary experimental results of the different series were reorganized to show the pressure dependence of T_1 at a constant temperature.

It should be noted that the materials used to pressure-seal of the vessel did not contaminate the specimen as far as the T_1 values were concerned; we obtained completely reversible and reproducible results within the experimental uncertainty for the 10-d old sample held in the vessel as well as for a virgin specimen.

Results and Discussion

Self-diffusion and Its Activation Properties. The representative pressure dependence of the proton spin-lattice relaxation time in the plastic phase of neopentane at various temperatures are shown in Fig. 1. The plots for the measurements at seven additional intermediate temperatures (308.2, 293.2, 272.4, 252.5, 233.8, 214.0, and 192.7 K) fall between the curves but for the sake of clarity they were not included in this figure. The two motional processes, molecular rotation and self-diffusion, have been discussed from the continuous wave and pulsed NMR experiments in the plastic phase.[6–10]

There is a maximum in T_1 when it is plotted as a function of pressure for a constant temperature. This has been clearly demonstrated by Allen *et al.*[9] and its high-pressure side corresponds to the region where molecular tumbling is the dominant mechanism of the spin-lattice relaxation. The present study is essentially restricted to the low-pressure side of the T_1 maximum where self-diffusion mainly governs the relaxation rate. Where comparison is possible, our results are in reasonable agreement with the results of Allen *et al.* (who used 24.4 MHz for measurements).[9] Therefore, we will deal only with self-diffusion in this paper.

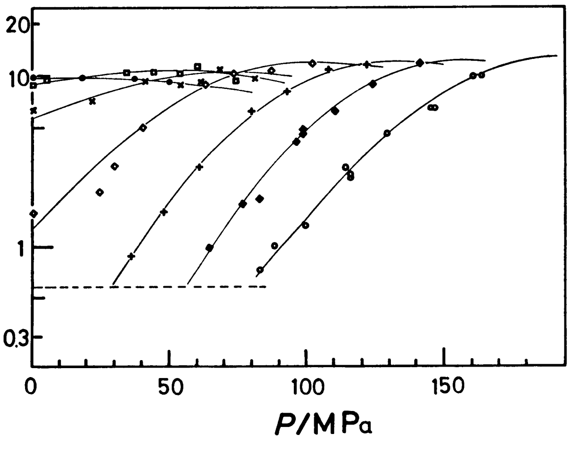

Fig. 1. Pressure dependence of the proton spin-lattice relaxation time at different temperatures; ○ 297.4 K, ◆ 281.0 K, + 263.6 K, ◇ 242.9 K, × 223.9 K, □ 214.0 K, ● 202.5 K. The dashed line shows the alignment of the melting points.

We assume the Arrhenius type of activation process for self-diffusion,

$$\tau_{\mathrm{SD}} = A\exp(\Delta G^*/RT) = \tau^0_{\mathrm{SD}}\exp(\Delta H^*/RT), \quad (1)$$

where τ_{SD} is the correlation time of self-diffusion and ΔG^*, the Gibbs energy of activation, is defined by

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

or

$$\Delta G^* = \Delta E^* + P\Delta V^* - T\Delta S^*. \quad (2)$$

Then, the activation volume ΔV^* and the activation enthalpy ΔH^* can be derived from the equations,[19]

$$\Delta V^* = RT\{\partial(\ln\tau_{\mathrm{SD}})/\partial P\}_T, \quad (3)$$

$$\Delta H^* = R\{\partial(\ln\tau_{\mathrm{SD}})/\partial(1/T)\}_P, \quad (4)$$

where the activation entropy ΔS^* has been assumed to be constant over the present temperature and pressure region.[19] Because what we observed is the low temperature branch ($\omega_0\tau_{\mathrm{SD}}\gg1$) of the T_1 curve due to self-diffusion, τ_{SD} is proportional to $T_{1\,\mathrm{SD}}$, where $T_{1\,\mathrm{SD}}$ is the relaxation time due to self-diffusion. Thus, τ_{SD} in Eqs. 3 and 4 can be replaced by $T_{1\,\mathrm{SD}}$ because the change of intermolecular dipole-dipole interaction can be safely ignored in the present pressure range.[9] One can obtain $T_{1\,\mathrm{SD}}$ from the equation,

$$T_1{}^{-1}{}_{\mathrm{obsd}} = T_1{}^{-1}{}_{\mathrm{SD}} + T_1{}^{-1}{}_{\mathrm{RO}}, \quad (5)$$

where $T_1{}^{-1}{}_{\mathrm{obsd}}$ is the observed spin-lattice relaxation rate (Fig. 1) and $T_1{}^{-1}{}_{\mathrm{RO}}$ is the spin-lattice relaxation rate due to molecular reorientation. Now, we try to separate the two contributions in Eq. 5. The second term of Eq. 5 was evaluated in the following way. Since the slope of $T_{1\,\mathrm{obsd}}$ on the high pressure side of the maximum (Fig. 1) agrees with the slope as determined by Allen *et al.* where comparison is possible, we used their slope so that smooth extrapolation of our T_1 curve to high pressure may be made. This extrapolation enables us to estimate $T_1{}^{-1}{}_{\mathrm{RO}}$ from the high-pressure branch of the $T_1{}^{-1}{}_{\mathrm{obsd}}$ curve.

The activation volume ΔV^* was then derived from linear plots of $\ln(T_{1\,\mathrm{SD}})$ against P at different temperatures. The activation volume ΔV^* (Fig. 2) thus derived was 133±18 cm^3 mol^{-1} between 252.5 and

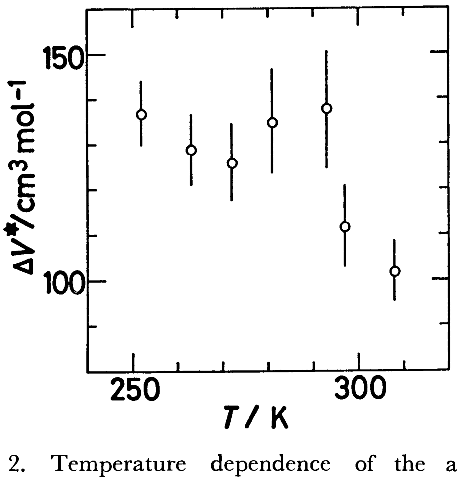

Fig. 2. Temperature dependence of the activation volume of self-diffusion.

293.2 K. The result is nearly equal to that obtained by Allen *et al.*[9] The two points above 297.4 K in Fig. 2 lie much lower than the other points; this may indicate possible existence of another phase transition as will be discussed below. The ratio of ΔV^* to the molecular volume V_m, which was determined to be 102 cm^3 mol^{-1} at 220 K from X-ray experiments,[3,4] is about 1.3. Because each of the formation and migration volume of a vacancy is not considered to be equal to V_m, the comparison of ΔV^* with V_m does not have a definite meaning. But the fact, $\Delta V^*/V_m = 1.3$, probably suggests that the self-diffusion in plastic neopentane is mainly controled by a single vacancy.

The feature of single-vacancy diffusion in plastic neopentane is assisted by the value of activation enthalpy ΔH^*. The plot in Fig. 1 can be rearranged to show the temperature dependence of T_1 at constant pressure. Through a similar procedure to the derivation of ΔV^*, the activation enthalpy ΔH^* of self-diffusion was calculated by use of Eq. 4 from the $\ln(T_{1\,\mathrm{SD}})$ *vs.* $1/T$ plot. Unfortunately, large errors involved in the determination of ΔH^* did not permit to determine its temperature coefficient but the average value of ΔH^* was 43.5±8.4 kJ mol^{-1} between 0.1 and 80 MPa which is somewhat larger than the value reported by Stejeskal *et al.*,[6] Roeder and Douglass,[8] and Allen *et al.*[9] The activation enthalpy ΔH^* is the sum of enthalpy of vacancy formation and enthalpy of migration,[20] each of which is usually considered to be nearly equal to the heat of sublimation L_s if self-diffusion proceeds *via* single vacancy mechanism.[2,21,22] In the case of neopentane, the ratio of ΔH^* to L_s[23] is

$$\Delta H^*/L_s = 43.5\ \mathrm{kJ\ mol^{-1}}/23.4\ \mathrm{kJ\ mol^{-1}} = 1.9 \tag{6}$$

at an ordinary pressure, which fact therefore suggests that self-diffusion in plastic neopentane is also controled by a single vacancy.

Phase Diagram. The melting point of neopentane under pressure was determined from the point where $\mathrm{d}P/\mathrm{d}T$ changed its slope. It was also seen by a discontinuous change in T_1. The results are shown in Fig. 3. The equilibrium curve must follow the Clapeyron-Clausius equation,

$$\mathrm{d}T_f/\mathrm{d}P = \Delta V_f T_f/\Delta H_f, \tag{7}$$

where ΔH_f is the enthalpy of fusion and ΔV_f is the change in molecular volume at T_f, the melting temperature. By substituting the appropriate values to ΔH_f (3.09 kJ mol^{-1}),[5] ΔV_f (7×10^{-6} m^3 mol^{-1}),[24] and T_f (256.5 K),[5] one obtains $\mathrm{d}P/\mathrm{d}T_f = 1.7$ MPa K^{-1}. The value found from Fig. 3 is 1.8 MPa K^{-1}, being consistent with Eq. 7.

There is possibility for existence of another solid phase which we designate Phase I′ between the plastic f.c.c. solid and the liquid phases above 40 MPa. It was inferred from a break in the curve of pressure *vs.* temperature at a prefixed volume. This curve is also shown in Fig. 3 as a dotted curve. According to Art-Ming Chen and Kai-Chow Chan who measured the density at 50 MPa at different temperatures, the density linearly decreases up to 273.5 K but it is smaller by about 3.2% at 286.3 K than may be predicted from a linear extrapolation. This also supports existence of a new Phase I′. It is difficult to speculate about the nature of Phase I′ or the new transition at this point, but there is no discernible change in the T_1 values on going from the f.c.c. phase to Phase I′. Also the fact that the melting curve of Fig. 3 is almost linear suggests that changes in physical properties at the new transition point will be small.

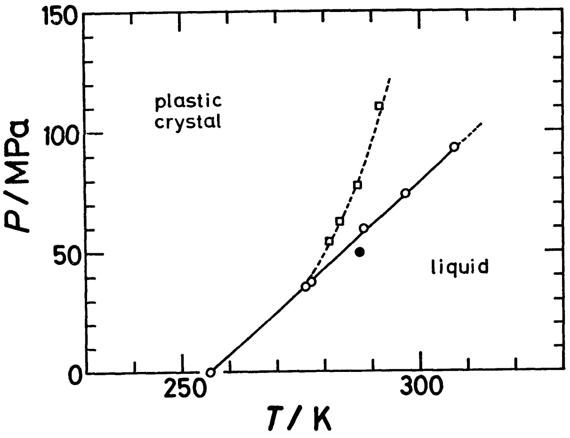

Fig. 3. Phase diagram of neopentane. Solid line shows the melting curve (○), while dashed line indicates a new transition line (see text). Full circle (●) is the melting point at 50 MPa determined by Art-Ming Chen and Kai-Chow Chain.[24]

The two points in Fig. 2 above 297.4 K correspond to the region where Phase I′ is stable. It is interesting to note that ΔV^* is smaller in Phase I′ than in Phase I (f.c.c.).

Corresponding State. If $\log(T_{1\,\mathrm{SD}})$ is plotted against T_f/T, one obtains a good straight line irrespective of the pressure. This is illustrated for some selected pressures in Fig. 4. The fact that they all fall on a single straight line indicates that the law of corresponding states holds for the spin-lattice relaxation time at least to within the bounds of scatter of points in Fig. 4. In other words, the diffusion rate is also a function of T_f/T only, since the correlation time τ_{SD} is related to $T_{1\,\mathrm{SD}}$ in the present case through

$$T_1{}^{-1}{}_{\mathrm{SD}} = 2.29\gamma^2 M_2(\omega_0{}^2\tau_{\mathrm{SD}})^{-1}, \tag{8}$$

which is derived using Torrey's correlation functions[25–27] for random walk in a f.c.c. lattice, where M_2 is the part of intermolecular second moment that is modulated by self-diffusion.

The threshold value of τ_{SD} at the melting point may be calculated from Eq. 8 using $M_2 = 1.1$ G^2 obtained at the ambient pressure.[7,10] It is $(3.2\pm0.5)\times10^{-7}$ s at T_f although T_f varies from 256.5 K (at 0.1 MPa) to 306 K (at 90 MPa). It seems that the threshold value of τ_{SD} is not only independent of pressure but it is a kind of constant of plastic crystal because most of the plastic crystals ever examined melt when the threshold value of τ_{SD} reaches a value of about 10^{-7} s.[2,28]

The linear relation of Fig. 4 shows that τ_{SD} is em-

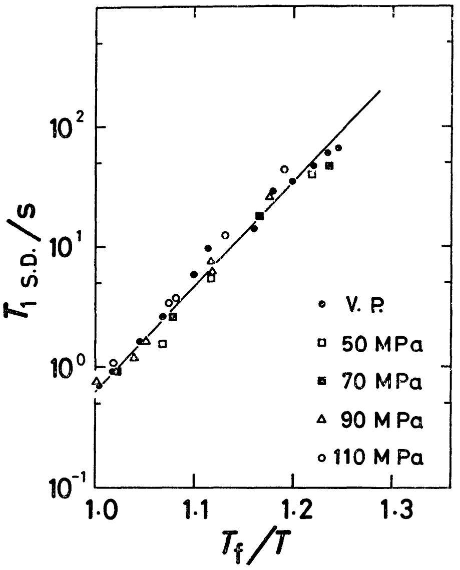

Fig. 4. Spin-lattice relaxation time due to self-diffusion ($T_{1\,\mathrm{SD}}$) is plotted against the reduced temperature T_f/T, where T_f is the melting temperature at each pressure. V.P. means the vapor pressure of the sample itself.

pirically given by

$$\tau_{\mathrm{SD}} = \tau^0_{\mathrm{SD}}\exp\{b(T_f/T)\}, \tag{9}$$

where b is 20.2±2.6 for neopentane. If one substitutes Eq. 9 to Eqs. 3 and 4, b is shown to be related to the enthalpy and volume of activation for self-diffusion through the formulas

$$\Delta H^* = bRT_f \tag{10}$$

and

$$\Delta V^* = bR(\mathrm{d}T_f/\mathrm{d}P). \tag{11}$$

By substituting Eqs. 10 and 11 into the Clapeyron-Clausius equation (Eq. 7), we obtain

$$\Delta V^*/\Delta H^* = \Delta V_f/\Delta H_f. \tag{12}$$

If we use the values observed in the present experiment, *i.e.* $\Delta V^*=133\pm17\ \mathrm{cm^3\,mol^{-1}}$ and $\Delta H^*=43.5\pm8.4\ \mathrm{kJ\,mol^{-1}}$, we obtain $\Delta V^*/\Delta H^*=3.3\pm1.1\ \mathrm{cm^3\,(kJ)^{-1}}$ which is in reasonable agreement with the value $\Delta V_f/\Delta H_f=2.3\ \mathrm{cm^3\,(kJ)^{-1}}$ where $\Delta V_f=7\ \mathrm{cm^3\,mol^{-1}}$[24] and $\Delta H_f=3.093\pm0.001\ \mathrm{kJ\,mol^{-1}}$.[5] Equation 12 which is an almost exact consequence of the relation (9) shows that the activation process for diffusion is in a way related to the melting process.

The activation energy ΔE^* of diffusion is the sum of the energy of formation (E_f) of a vacancy and its migration (E_m). Cauchman and Reynolds[29] derived a relation between the energy of migration of a vacancy (E_m) and the melting temperature (T_f),

$$E_m = \frac{K_1}{D}\left(\frac{k}{\hbar}\right)^2 T_f, \tag{13}$$

where K_1 and D are constants determined primarily by geometry of the lattice. By combining Eq. 13 with the formula for E_f due to Glyde,[30] we obtain a relation between ΔE^* and T_f similar to Eq. 13,

$$\begin{aligned}\Delta E^* &= E_m + E_f\\ &= \left(\frac{k}{\hbar}\right)^2\left(\frac{K_1+K_2}{D}\right)T_f\\ &= CT_f,\end{aligned} \tag{14}$$

where K_2 is also a constant. Because the contribution of the $P\Delta V^*$ term to the activation enthalpy, $\Delta H^*=\Delta E^*+P\Delta V^*$, is small (less than 1%), the comparison between Eq. 10 and Eq. 14 is possible. The constant b in Eq. 9 must therefore depend on the properties of the lattice in which diffusion takes place. In many plastic crystals, the value of b ($=C/R$) in Eq. 9 is also about 20[31] and similar values of C/R were also found for many metals. This fact is very suggestive but the theory is only of qualitative nature and does not warrant any quantitative calculation.

Finally, it is perhaps significant to note that the straight line of Fig. 4 covers both situations of melting of Phase I and Phase I′. This is related to the fact that we failed to detect any change in T_1 on going from Phase I to Phase I′. Probably, Phase I′ is also a plastic crystal which has a similar property to that of Phase I (f.c.c.).

The authors would like to express their gratitude to Dr. Akifumi Onodera for help provided in the calibration of the pressure gage (manganin gage).

References

1) "The plastically crystalline state, orientationally disordered crystals," ed by J. N. Sherwood, John Wiley & Sons, New York (1979).

2) J. M. Chezeau and J. H. Strange, *Phys. Repts.*, **53**, 1 (1979), and references cited therein.

3) A. H. Mones and B. Post, *J. Chem. Phys.*, **20**, 755 (1952).

4) R. Rudman and B. Post, *Mol. Cryst.*, **5**, 95 (1968).

5) H. Enokido, T. Shinoda, and Y. Mashiko, *Bull. Chem. Soc. Jpn.*, **42**, 84 (1969).

6) E. O. Stejskal, D. E. Woessnor, T. C. Farrar, and H. S. Gutowsky, *J. Chem. Phys.*, **31**, 55 (1959).

7) J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1965 (1953).

8) S. B. W. Roeder and D. C. Douglass, *J. Chem. Phys.*, **52**, 5525 (1970).

9) W. C. Allen, N. Liu, and J. Jonas, *J. Chem. Phys.*, **63**, 3312 (1975).

10) S. Takeda, G. Soda, and H. Chihara, *Mol. Phys.*, **47**, 501 (1982).

11) R. E. Lechner, *Solid State Commun.*, **10**, 1247 (1972).

12) R. C. Livingston, W. G. Rothschild, and J. J. Rush, *J. Chem. Phys.*, **59**, 2498 (1973).

13) C. Steenbergen and L. A. de Graaf, *Physica*, **96B**, 1 (1979).

14) T. Hasebe, G. Soda, and H. Chihara, *Bull. Chem. Soc. Jpn.*, **54**, 2583 (1981).

15) R. E. Terry and A. L. Ruoff, *Rev. Sci. Instr.*, **43**, 1379 (1972).

16) S. Yamamoto, *Bull. Natl. Res. Lab. Metrol.*, **24**, 23 (1972).

17) S. Yamamoto, *Bull. Natl. Res. Lab. Metrol.*, **25**, 1 (1972).

18) G. Fujii, N. Mori, H. Nagano, and S. Minomura, *Cryog. Eng.*, **4**, 226 (1969).

19) S. M. Ross and J. H. Strange, *J. Chem. Phys.*, **68**, 3078 (1978).

20) A. V. Chadwick and H. R. Glyde, "Rare gas solids," ed by M. L. Klein and T. A. Venable, Academic Press, New York and London (1977), Vol. II, Chap. 19, p. 1151.

21) J. N. Sherwood, "Surface and defect properties of solids, Specialist periodical reports," The Chemical Society, London (1973), Vol. 2, p. 250.

22) R. Folland, R. C. Jackson, J. H. Strange, and A. V. Chadwick, *J. Phys. Chem. Solids*, **34**, 1713 (1973).

23) S. M. Breitling, A. D. Jones, and H. Boyd, *J. Chem. Phys.*, **54**, 3959 (1971).

24) H. Art-Ming Chen and R. Kai-Chow Chan, *Can. J. Chem.*, **51**, 2141 (1973).

25) H. C. Torrey, *Phys. Rev.*, **92**, 962 (1953).

26) H. C. Torrey, *Phys. Rev.*, **96**, 690 (1954).

27) H. A. Resing and H. C. Torrey, *Phys. Rev.*, **131**, 110 (1973).

28) H. Chihara and N. Nakamura, *Mol. Cryst. Liq. Cryst.*, **41**, 21 (1977).

29) P. R. Couchman and C. L. Reynolds, Jr., *Philos. Mag.*, **34**, 327 (1976).

30) H. R. Glyde, *J. Phys. Chem. Solids.*, **28**, 2061 (1967).

31) N. Boden, *Chem. Phys. Lett.*, **46**, 141 (1977).