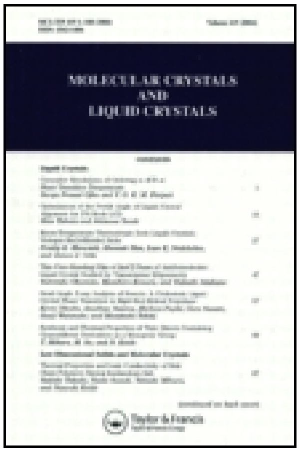
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 19 February 2013, At: 13:51
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Crystallographic Studies of Clathrate Hydrates. Part I

D. W. Davidson [a] , Y. P. Handa [a] , C. I. Ratcliffe [a] , J. A. Ripmeester [a] , J. S. Tse [a] , J. R. Dahn [a] , F. Lee [a] & L. D. Calvert [a]

[a] Division of Chemistry, National Research Council of Canada, Ottawa, Canada, K1A OR9

Version of record first published: 20 Apr 2011.

To cite this article: D. W. Davidson , Y. P. Handa , C. I. Ratcliffe , J. A. Ripmeester , J. S. Tse , J. R. Dahn , F. Lee & L. D. Calvert (1986): Crystallographic Studies of Clathrate Hydrates. Part I, Molecular Crystals and Liquid Crystals, 141:1-2, 141-149

To link to this article: http://dx.doi.org/10.1080/00268948608080205

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1986, Vol. 141, pp. 141-149
0026-8941/86/1412-0141/$15.00/0
© 1986 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:51 19 February 2013

Crystallographic Studies of Clathrate Hydrates. Part I.†

D. W. DAVIDSON, Y. P. HANDA, C. I. RATCLIFFE, J. A. RIPMEESTER, J. S. TSE, J. R. DAHN, F. LEE and L. D. CALVERT

Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A OR9

(*Received January 31, 1986*)

Low-temperature neutron and X-ray diffraction studies show the gas hydrates of oxygen and nitrogen to be structure II (Fd3m), as recently found also for the hydrates of the small argon and krypton molecules. New lattice parameters of three structure I and 14 structure II hydrates from powder X-ray diffraction at 170 K are reported. The thermal expansion coefficient of tetrahydrofuran hydrate was determined from X-ray diffraction at some 50 temperatures between 18 and 263 K and found to be three times as great as for ice near 100 K and 30% higher near 250 K. Lattice parameters of 40 type II clathrate hydrates are compared at 0°C and found to lie within 0.10 Å of 17.30 Å.

Keywords: clathrate hydrates, oxygen hydrate, nitrogen hydrate, X-ray diffraction, thermal expansivity

Some thirty years ago von Stackelberg and his students showed[1] that gas hydrates were clathrates and found that all 29 gas hydrates which they examined by X-ray powder diffraction formed cubic lattices of one or the other of two structures. Structure I had a unit cell 12 Å in size and was formed in 16 cases by relatively small guest molecules, while in 13 other cases larger molecules were encaged in a structure II lattice with a 17 Å unit cell.

Ten years later Jeffrey and his colleagues confirmed and refined[2] the two structures by single-crystal X-ray studies. A number of powder X-ray studies of individual hydrates have since been reported, to bring to 23 each the number of structure I and structure II lattice parameters to have been recorded for single guest species. Type II

---

†Issued as NRCC No. 25561.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:51 19 February 2013

hydrates were inevitably formed by molecules larger than about 5.8 Å in maximum van der Waals diameter. Only a few clathrate hydrates have been found to be of neither structure I nor II: dimethyl ether appears to form[3] (besides a type II hydrate) a hydrate which is probably isostructural with the tetragonal (4/mm) bromine hydrate,[4] while the structure[5] of the hydrate of *t*-butylamine is so far unique.

Thus the experience from crystallographic study of 49 of the 114 known clathrate hydrates suggests that, with few exceptions, each of the others may be realistically assigned to one of von Stackelberg's two structures on the basis of the size of the guest molecule. Such assignments have in fact often been supported by some knowledge of the compositions (6 to 8 water molecules per molecule of guest for type I and 17 for type II) and by the structurally-sensitive NMR and dielectric properties.[6,7]

Until very recently, however, there were no structural studies of the relatively unstable hydrates formed by molecules smaller than about 4.5 Å in diameter: argon, krypton, oxygen, carbon monoxide, nitrogen and methane. These hydrates are stable at 0°C only under high gas pressures but may be studied by diffraction methods if the samples are maintained at temperatures (e.g., 100 K) low enough to avoid decomposition. Low-temperature X-ray and neutron diffraction have unexpectedly shown[8] that structure II is the stabler form of argon and krypton hydrates, although (expectedly) methane hydrate is structure I.

We report here the results of crystallographic studies of oxygen and nitrogen hydrates and new X-ray lattice parameters, mostly from powder studies at 170 K, of 17 additional clathrate hydrates. We also make use of the measured thermal expansivity of tetrahydrofuran hydrate to compare at a common temperature the unit cell sizes of all 40 structure II hydrates for which diffraction data have now been reported.

EXPERIMENTAL METHODS

Oxygen and nitrogen hydrates

Oxygen deuteriohydrate for neutron diffraction study was prepared over a period of three days from out-gassed D_2O ice at about −30°C under a pressure of 238 atm of research purity (Air Products and Chemicals Inc.) oxygen gas. Elastic neutron scattering curves were recorded at 5.6 K as before[8] in the Chalk River Laboratories of Atomic Energy of Canada Limited. Further details are given else-

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:51 19 February 2013

where.[9] Nitrogen hydrate was prepared in a similar way at −20°C from finely powdered ice and 127 atm of nitrogen gas. This pressure is about 1.4 times as great as the minimum pressure required for hydrate stability at this temperature. After cooling to 77 K, the excess pressure was released, the pressure vessel opened, and nitrogen hydrate powder transferred to thin-walled capillary tubes which were then mounted in the X-ray diffractometer where they were held at about 100 K in a stream of cold nitrogen gas during recording of the diffraction pattern. Ice which condensed on the capillary was continually removed during the exposure period. Most other experimental details were the same as described for other hydrates in the next section.

X-ray diffraction of hydrates at 170 K

Of 18 hydrates examined, 16 were previously studied by solid-state NMR; they were prepared and annealed as already described.[6] A new hydrate of CF_3CH_2Cl was formed from an out-gassed mixture of the component liquids by alternately shaking and cooling to below 0°C. Some ice lines were present in the diffraction patterns of this hydrate and of 2-chloropropane hydrate. The hydrate of 1,3-dioxolane was prepared by freezing a solution of 1 mole in 17 moles of water.

Powder diffraction photographs were taken, mostly at 170 ± 10 K, with Zr-filtered Mo radiation (wave length 0.710688 Å) in a flat-plate camera previously described.[10] An internal Si standard[11] was used for some measurements but it was found to be more effective to use a Si specimen to calibrate the specimen to film distance. Films were measured and corrected for shrinkage as before.[12] Lattice parameters were determined and standard deviations estimated from least squares analysis of lines weighted according to their measurability. Films were measured twice. The number of lines measured varied between 10 and 28 according to the quality of the sample. Differences between observed and calculated values of 2θ averaged 0.05° and corresponded to a measuring accuracy of 0.05 mm.

Temperature-dependent diffraction of tetrahydrofuran hydrate

The expansivity of the structure II hydrate of THF was measured by recording the positions of three relatively strong lines in the X-ray powder diffraction pattern, corresponding to Miller indices 115 + 333, 135, and 066 + 228, at about 50 temperatures between 20 and 263 K.[13]

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:51 19 February 2013

The automatic powder diffractometer was equipped with a closed-loop liquid helium cryostat.

RESULTS

The neutron diffraction pattern at 5.6 K shows oxygen deuteriohydrate to be structure II (Fd3m), with a lattice parameter of 17.070 Å to within a standard deviation of 0.003 Å.

The X-ray diffraction pattern of nitrogen hydrate at 100 K likewise gives structure II. For twelve well-defined lines the lattice parameter is 17.11 Å, the standard deviation about 0.06 Å.

X-ray diffraction confirmed the NMR evidence[6] of formation of structure I (Pm3n) hydrates by sulfuryl fluoride (SO_2F_2), perchloryl fluoride (ClO_3F), and ethylene sulphide (thiirane). Lattice parameters at 170 K were 11.975, 11.985, and 12.00 Å, respectively, with standard deviations of about 0.01 Å.

Fourteen of the clathrate hydrates examined at 170 K proved to be structure II. Their lattice parameters are included in Table I ("this work"), along with values previously reported for hydrates of this structure. In two cases, cyclobutane and dimethyl sulphide, the hydrates were made from D_2O. In general the formation of structure II by these guest species was anticipated[6] from their NMR and dielectric properties. However, the hydrate of 1,1,1-trifluoroethane did not show the expected type II diffraction pattern and remains uncharacterized.

The results of the thermal expansivity measurements of THF hydrate[13] may be represented by

$$\Delta a/a_0 = -4.292 \times 10^{-4} + 1.4174 \times 10^{-5} T + 1.1747 \times 10^{-7} T^2 - 5.891 \times 10^{-11} T^3 \quad (1)$$

to an average deviation of about 4% between 18 and 250 K. Here a_0 is the lattice parameter at 25.2 K and $\Delta a = a(T) - a_0$. Values of the linear expansivity $d \ln a(T)/\mathrm{d}T$ at 100, 150, 200, and 250 K are 36, 45, 54 and 61 × 10^{-6} K^{-1}, respectively. These values are in good agreement with those recently reported by Roberts *et al.*[14] who found 28, 42, 52, and 62 × 10^{-6} K^{-1} at these temperatures from a push-rod dilatometric study of THF hydrate between 80 and 265 K. Since the corresponding values for hexagonal ice are respectively about 13, 25, 37 and 48 × 10^{-6} K^{-1}, the expansivity of this type II hydrate is uniformly larger than for ice, being about three times as great near 100 K and about 30% larger near 250 K.

Table I lists 60 values of the lattice parameter as measured for 40

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:51 19 February 2013

TABLE I

Values of the cubic lattice parameter of structure II hydrates

Guest molecule	$a(T)$/Å	$\pm E$/Å	T/K	Reference	$a(0°C)$/Å
Ar	17.07	0.04	100	8	17.22
Kr (D$_2$O)[a]	17.01	0.01	5.7	8	17.20
(D$_2$O)	17.01	0.05	100	8	17.16
	17.08	0.08	100	8	17.23
O$_2$ (D$_2$O)[a]	17.07	0.01	5.6	this work	17.26
N$_2$	17.11	0.06	100	this work	17.26
SF$_6$	17.21	0.10	273	1	17.21
SeF$_6$	17.14	0.01	170	this work	17.24
cyclopropane	17.07	0.02	110	23	17.21
cyclobutane (D$_2$O)	17.135	0.01	170	this work	17.24
methyl cyclopropane	17.175	0.01	170	this work	17.28
propane	17.40	0.10	273	1	17.40
isobutane	17.57	0.10	273	1	17.57
CH_2Cl_2	17.33	0.10	273	1	17.33
$CHCl_3$	17.33	0.10	273	1	17.33
CCl_4	17.29	0.03	170	this work	17.39
C_2H_5Cl	17.30	0.10	273	1	17.30
$CH_3CHClCH_3$	17.21	0.05	170	this work	17.31
$CH_3CF_2CH_3$	17.28	0.02	170	this work	17.38
CF_2Cl_2	17.37	0.10	273	1	17.37
	17.13	0.15	275	24	17.13
$CFCl_3$	17.29	0.10	273	1	17.29
CF_3CH_2Cl	17.14	0.03	170	this work	17.24
CH_3CF_2Cl	17.29	0.10	273	1	17.29
CH_3I	17.14	0.10	273	1	17.14
CF_3I	17.10	0.06	170	this work	17.20
dimethyl ether	17.27	0.11	123	25	17.40
	17.47	0.10	273	1	17.47
oxetane (trimethylene oxide)	17.095	0.006	135	12	17.22
	17.1	0.1	110	12	17.25
	17.06	0.02	110	23	17.21
propylene oxide	17.124	0.005	135	12	17.25
	17.10	0.06	110	12	17.25
1,3-dioxolane	17.118	0.004	135	12	17.25
	17.099	0.005	100	12	17.25
	17.10	0.05	110	12	17.25
	17.09	0.02	110	23	17.24
	17.11	0.02	120	this work	17.25
furan	17.30	0.10	263	1	17.31
2,5-dihydrofuran	17.165	0.004	135	12	17.29
	17.22	0.01	233	12	17.26
	17.2	0.1	110	12	17.35
tetrahydrofuran	17.166	0.004	135	12	17.29
	17.13	0.03	110	12	17.28
	17.15	0.02	110	23	17.30
	17.18	0.10	263	1	17.19
acetone	17.16		235	26	17.20
cyclobutanone	17.159	0.004	135	12	17.28
	17.23	0.01	233	12	17.27
	17.14	0.02	110	23	17.29
	17.09	0.07	110	12	17.24

TABLE I (*continued*)

Values of the cubic lattice parameter of structure II hydrates

Guest molecule	$a(T)/\text{Å}$	$\pm E/\text{Å}$	T/K	Reference	$a(0°\text{C})/\text{Å}$
isoxazole	17.17	0.09	120	27	17.31
1,3-dioxane	17.23	0.03	125	28	17.36
1,4-dioxane	17.28	0.04	125	29	17.41
ethanethiol	17.12	0.02	170	this work	17.22
dimethyl sulfide (D_2O)	17.27	0.09	170	this work	17.37
thietane (trimethylene sulfide)	17.275	0.02	170	this work	17.38
propylene sulfide	17.22	0.02	170	this work	17.32
tetrahydrothiophene	17.265	0.01	170	this work	17.37

[a] From neutron diffraction.

type II hydrates at a variety of temperatures. Except for two values from low-temperature neutron diffraction, all results are from X-ray powder diffraction. Unless D_2O is specified, results refer to hydrates prepared from H_2O. The values in the estimated error ($\pm E$) column are taken from the original authors and vary in significance from estimates of "absolute error" (von Stackelberg) to standard error (present work).

Equation (1) is assumed to apply to all type II hydrates; it has been used to convert all the lattice parameters to 0°C. The results are shown in the last column of Table I. For hydrates for which a number of values are given, the result given first is taken to be the most accurate.

DISCUSSION

Molecules which form structure II hydrates

The observation that oxygen and nitrogen, like argon and krypton,[8] preferentially form hydrates of structure II makes it possible that the recently prepared[15] but not yet characterized hydrate of carbon monoxide is also of this structure. Almost certainly, this is the case, as well, of "air hydrate," a mixed hydrate of nitrogen and oxygen which occurs naturally at considerable depth in the Antarctic[16] and Greenland[17] ice covers.

The above examples, all with guest molecules less than 4.2 Å in maximum van der Waals diameter, may exhaust the list of *small* guest molecules which prefer to form hydrates of structure II because of

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:51 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:51 19 February 2013

their affinities for the small 12-hedral cages which make up two thirds of structure II cages but only one quarter of the cages of structure I.

The next larger group of clathrate-hydrate-forming molecules consists of methane, hydrogen sulphide, and xenon—all some 4.5 to 4.6 Å in size—which give structure I diffraction patterns.[8] It is clear that structure I is the stabler hydrate for molecules which, for reasons of size, are more readily accommodated in the 14-hedral cages of this structure than in the 12-hedra.[18] Examples of the many type I hydrate-formers which are too large to appreciably occupy the 12-hedra are SO_2F_2 and ClO_3F, which are between 5.6 and 5.7 Å in van der Waals diameter. Ethylene sulphide, about 5.9 Å in size, not only forms type I hydrate but from the NMR evidence[6] very likely forms a stable type II hydrate as well. Other molecules which form hydrates of both structures are cyclopropane[19] (5.8 Å) and trimethylene oxide[20] (oxetane) (6.1 Å).

Structure II again becomes stable for guest molecules too large to easily occupy the 14-hedral structure I cages but still able to enter the 16-hedral cages of structure II. The great majority of structure II hydrates are formed by molecules of this size. The hydration numbers are about 17, in contrast with the limiting hydration number of 5 2/3 which corresponds to full occupancy of both the 12- and 16-hedral cages by very small molecules. SF_6 appears to be the smallest (5.9 Å) of the major group of relatively large molecules which form type II hydrates.

Structure II hydrate lattice parameters

Perhaps the most remarkable feature of the 0°C lattice parameters given in Table I is the absence of appreciable variation with the nature of the guest molecule. The average of 40 values of *a* is 17.30 Å. The values[1] which depart most from the average are suspect: 17.57 Å was obtained by von Stackelberg and Müller for a sample of isobutane hydrate which appears to have been mainly ice, while von Stackelberg and Jahns encountered problems with the CH_3I hydrate for which they reported $a = 17.14$ Å. All the remaining 0°C lattice parameters lie between 17.20 and 17.41 Å.

Uncertainties in the measured lattice parameters clearly limit any attempt to correlate small variations with the nature of the guest molecule. In most cases, there is an uncertainty of 10 to 20 K in the (low) temperature at which the diffraction pattern was recorded, which makes the uncertainty at 0°C about 0.01 Å larger than the low-

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:51 19 February 2013

temperature estimate of error. Some hydrates were prepared in the presence of air; this is known to produce a small stabilizing effect but is unlikely to have an appreciable effect on the unit cell size. For hydrates which have been studied several times, the range of values around that chosen as most accurate (the first of those listed) is almost always well within the estimated error limits, which suggests that these were conservative estimates.

The most probable lattice parameters at 0°C for the hydrates of the small argon and krypton molecules are close to 17.21 Å. This is probably the best value to take for the hypothetical empty or undistorted type II lattice.

At the other extreme of size, the large molecules of CCl_4, $CHCl_3$, CF_2Cl_2, $(CH_3)_2CHCl$, $(CH_3)_2CF_2$, and the dioxanes form hydrates with probable values of $a = 17.36 \pm 0.05$ Å and thus appear to cause some dilation of the lattice.

Thermal expansivities

The lattice of THF hydrate expands by 0.19 Å with increase of temperature from 0 K to 0°C. This is equivalent to a *volume* expansion of 3.4%. If the density of ice is taken as 0.9333 g/ml at 0 K[21] and 0.92671 at 0°C[22] its volume increases by 1.80% over the same temperature range.

Since the thermal expansivity of clathrate hydrates is mainly determined by the anharmonicity of the oscillations of the water molecules, it is unlikely to vary much with the nature of the guest molecules for hydrates with the same structure and nearly the same lattice parameters. Some limited experimental confirmation of this is provided by the constancy of the 0°C lattice parameters obtained, particularly for the hydrates of 1,3-dioxolane and cyclobutanone (Table I), by applying Eq. (1) to the relatively accurate data of Sargent and Calvert[12] at a number of temperatures. Very recently McMullan and Kvick[30] have measured by neutron diffraction, lattice parameters of CCl_4 structure II hydrate containing xenon in some of the small cages; the unit cell was found to expand by 0.048 ± 0.002 Å between 13 and 100 K. The change calculated from Eq. (1) is 0.040 Å.

It is worth mentioning that powder diffraction methods of determining thermal expansivity should be superior to macroscopic methods of dilatometry for clathrate hydrates of water-insoluble species which, unlike THF, are difficult to prepare except in polycrystalline form.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:51 19 February 2013

References

1. M. von Stackelberg and H. R. Müller, *Z. Elektrochem.*, **58**, 25 (1954); M. von Stackelberg and W. Jahns, *ibid.*, **58**, 162 (1954); M. von Stackelberg and B. Meuthen, *ibid.*, **62**, 130 (1958).
2. R. K. McMullan and G. A. Jeffrey, *J. Chem. Phys.*, **42**, 2725 (1965); T. C. W. Mak and R. K. McMullan, *ibid.*, **42**, 2732 (1965).
3. S. R. Gough, S. K. Garg, J. A. Ripmeester and D. W. Davidson, *J. Phys. Chem.*, **81**, 2158 (1977).
4. K. W. Allen and G. A. Jeffrey, *J. Chem. Phys.*, **38**, 2304 (1963).
5. R. K. McMullan, G. A. Jeffrey and T. H. Jordan, *J. Chem. Phys.*, **47**, 1229 (1967).
6. J. A. Ripmeester and D. W. Davidson, *Mol. Cryst. Liq. Cryst.*, **43**, 189 (1977).
7. D. W. Davidson and J. A. Ripmeester, in "*Inclusion Compounds*," (J. L. Atwood, J. E. D. Davies and D. D. MacNicol, eds.), Academic Press, London, 1984, Vol. 3, p. 69.
8. D. W. Davidson, Y. P. Handa, C. I. Ratcliffe, J. S. Tse and B. M. Powell, *Nature*, **311**, 142 (1984).
9. J. S. Tse, Y. P. Handa, C. I. Ratcliffe and B. M. Powell, *J. Inclus. Phenom.*, (submitted).
10. J. E. Bertie, L. D. Calvert and E. Whalley, *J. Chem. Phys.*, **38**, 840 (1963).
11. D. N. Batchelder and R. O. Simmons, *J. Chem. Phys.*, **41**, 2334 (1964).
12. D. F. Sargent and L. D. Calvert, *J. Phys. Chem.*, **70**, 2689 (1966).
13. J. S. Tse and J. R. Dahn, (to be published).
14. R. B. Roberts, C. Andrikidis, R. J. Tainsh and G. K. White, *Proc. Tenth Internat. Crogenic Eng. Confer.*, Helsinki, 1984, Butterworth, p. 499.
15. CO hydrate has been prepared in this laboratory by S. R. Gough and Y. P. Handa.
16. S. L. Miller, *Science*, **165**, 489 (1969).
17. H. Shoji and C. C. Langway, Jr., *Nature*, **298**, 548 (1982).
18. D. W. Davidson, S. K. Garg, S. R. Gough, Y. P. Handa, C. I. Ratcliffe, J. S. Tse and J. A. Ripmeester, *J. Inclus. Phenom.*, **2**, 231 (1984).
19. D. R. Hafemann and S. L. Miller, *J. Phys. Chem.*, **73**, 1392 (1969).
20. S. R. Gough, S. K. Garg and D. W. Davidson, *Chem. Phys.*, **3**, 239 (1974).
21. D. C. Ginnings and R. J. Corruccini, *J. Res. Nat. Bur. Stand.*, **38**, 583 (1947).
22. P. V. Hobbs, "*Ice Physics*," (Clarendon Press, Oxford, 1974), p. 348.
23. J. E. Bertie and S. M. Jacobs, *J. Chem. Phys.*, **69**, 4105 (1978).
24. T. A. Wittsruck, W. S. Brey, Jr., A. M. Buswell and W. H. Rodebush, *J. Chem. Eng. Data*, **6**, 343 (1961).
25. S. L. Miller, S. R. Gough and D. W. Davidson, *J. Phys. Chem.*, **81**, 2154 (1977).
26. A. S. Quist and H. S. Frank, *J. Phys. Chem.*, **65**, 560 (1961).
27. S. R. Gough, S. K. Garg, J. A. Ripmeester and D. W. Davidson, *Can. J. Chem.*, **52**, 3193 (1974).
28. D. W. Davidson, S. R. Gough, F. Lee and J. A. Ripmeester, *Rev. Chim. Miner.*, **14**, 447 (1977).
29. S. R. Gough, J. A. Ripmeester and D. W. Davidson, *Can. J. Chem.*, **53**, 2215 (1975).
30. R. K. McMullan and A. Kvick, personal commun.