Multisite Disordered Structure of Ice VII to 20 GPa

R. J. Nelmes, J. S. Loveday, and W. G. Marshall*
Department of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom

G. Hamel,[1] J. M. Besson,[2] and S. Klotz[2]
[1]*Département des Hautes Pressions, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris, France*
[2]*Physique des Milieux Condensés (CNRS UMR 7602), Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris, France*
(Received 5 May 1997; revised manuscript received 1 June 1998)

Neutron diffraction measurements on ice VII and ice VIII at pressures up to 20 GPa provide direct evidence of multisite disorder of both oxygen and deuterium atoms in D_2O ice VII, and give the magnitudes of the site separations. An O-D distance and D-Ô-D angle closest to those found in ice VIII are obtained with oxygen sites displaced along ⟨111⟩ directions. Such displacements imply an H-bond geometry significantly different from that found in ice VIII, and this may have implications for the centering transition to ice X. [S0031-9007(98)07166-X]

PACS numbers: 62.50.+p, 33.15.Dj, 33.15.Fm, 61.12.Ld

Above 2 GPa, the phase diagram of ice simplifies to a high-temperature disordered phase VII and a low-temperature ordered phase VIII with a predicted "symmetric" ice, phase X, at very high pressures. From 2 to ~10 GPa, the transition temperature T_c between VII and VIII is close to 273 K, but falls at higher pressures and reaches 0 K at ~60 GPa [1]. Much recent work has focused on the transition to ice X, in which the protons of ice VII are expected to become centered in the H bonds, transforming ice from a molecular solid to a simple oxide [2–6]. Optical studies show evidence of a transition to a "proton-disordered" ice X [2] at 60 GPa in H_2O [3,4] and 70 GPa in D_2O [3]; recent calculations support this [6]. The transition to fully "proton-ordered" ice X—with a single central H potential well—has been located at pressures from ~100 [4–6] to ~150 GPa [3]. All work on the very high-pressure behavior of ice rests on a detailed characterization of the ice VII structure.

The structures of ices VII and VIII both contain two interpenetrating, tetrahedrally H-bonded networks [7–9]. Figure 1 is a schematic drawing of an oxygen atom surrounded by the four H positions allowed by symmetry in ice VII—P, Q, R, and S—in a tetrahedral configuration. In (cubic) ice VII, the molecules are orientationally disordered, and all four positions are 50% occupied on average [7,9]. The inset reproduces P, Q, R, and S on a reduced scale—labeled p, q, r, and s—and shows the inverse configuration of H positions around one of the four neighboring oxygen atoms in the same H-bonded network—p', q', r', and s'. (p and p' coalesce in ice X.) The neighboring oxygens in the second network are in the directions $[\bar{1}\,\bar{1}\,\bar{1}]$, $[1\,1\,\bar{1}]$, $[\bar{1}\,1\,1]$, and $[1\,\bar{1}\,1]$. In (tetragonal) ice VIII the molecules become orientationally ordered and the hydrogens occupy (100%) two of the positions around each oxygen atom [7,8]. If they occupy P and Q (p and q in the inset), they are at r' and s' around the neighboring oxygen in the same network. The other network then has hydrogens at the r and s and p' and q' positions—such that the networks are oppositely polarized in an antiferroelectric arrangement. In the standard description of ice VII [7,9], the O atoms are at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ with the H at x, x, x ($x \sim 0.42$)—and symmetry related positions. This will be referred to as the "single-site" model of ice VII. In other, "site-disordered" models, the atoms are disordered over sites displaced from the mean O and H positions.

The two previous diffraction studies yielded very similar results for ice VIII with an O-D distance of 0.97 Å and a D-Ô-D angle of ~105°, close to gas-phase values [7,8]. But in ice VII, Kuhs *et al.* [7] obtained a surprisingly short O-D distance of ~0.89 Å in the single-site model, contrary to the expectation that ice VII is a disordered analog of ice VIII with essentially the same O-D distance. Refinement of an anharmonic model for the oxygen thermal motion showed a bulging along ⟨100⟩ directions [10], so the authors proposed disordering over six sites, displaced $\delta \sim 0.1$ Å along ⟨100⟩ from the mean position at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, as marked by the open circles in Fig. 1. The dashed lines show how this allows the true O-D distance to be longer than its apparent value (measured from the mean O position) and the true D-Ô-D angle to be less than 109.5°.

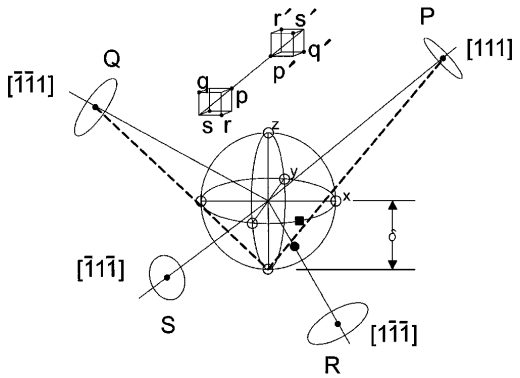

FIG. 1. Tetrahedral configuration of the hydrogen positions around an oxygen atom in ice VII and VIII. Details are discussed in the text. O-site displacements are exaggerated.

However, it proved impossible to refine δ freely [7]. Since its magnitude is only $\sim$0.1 Å, that is unsurprising with data to a resolution of $\sim$0.7 Å, but it is then difficult to understand why the anharmonic model refined; that and the multisite model are equivalent within the resolution of the data. Also, Kuhs *et al.* [7] found that when the O-D distance was allowed to vary freely, it increased to 1.016(2) Å—a significant overcorrection [9].

The time-of-flight data of Jorgensen and Worlton yielded a larger—but still significantly reduced—value of 0.943(2) Å for O-D in the single-site model of ice VII [9]. They, too, could not obtain any improvement in the fit with a $\langle 100 \rangle$ disorder model for the O atom. However, they found evidence for site disordering of the D atom that increases the O-D distance to 0.96 Å, but at the expense of improbable D-Ô-D angles of 98.2°, 100.7°, and 114.0° [9]. Kuhs *et al.* also recognized that the D atom may be site disordered, but could not distinguish this from anharmonicity of thermal motion [7].

Thus, although site disordering of some form appears necessary to account for the reproducibly low value of the apparent O-D distance in ice VII, there is, as yet, no clear direct evidence for it, and the *detailed* nature of this key structure remains unknown. It would be very difficult to obtain data with sufficient resolution to determine site separations $<$0.2 Å reliably, and so we have adopted a different approach of studying the atomic thermal motion. Disordering over displaced sites would be expected to appear as an apparent additional component of thermal motion in the single-site model. The results reported in this Letter reveal evidence of this kind for site disordering of both the O and the D atoms, but with the O atoms displaced along $\langle 111 \rangle$ rather than $\langle 100 \rangle$.

Powder diffraction data were collected on the POLARIS station of the UK pulsed neutron source, ISIS, using the Paris-Edinburgh cell [11]. Samples of deuterated water [12] from EURISO-TOP were loaded as previously described [13], except that the cell was cooled after sealing at low pressure and then compressed at 240 K to $\sim$3 GPa, so as to use the transitions in the range 0–2 GPa to produce a good, random powder. The temperature and pressure were then raised well into the ice VII field, at $\sim$290 K and a pressure measured as 5.1 GPa from the ice VII equation of state [14]. Samples made this way showed less than 5% variation in intensities with the angle around the incident-beam direction. Below 13 GPa, there is a $\sim$10 K hysteresis in T_c [1], and this was exploited to obtain data from the two phases at overlapping temperatures in the sequence: 288 (ice VII), 273 (VII), 270.5 (VIII), 274 (VIII), 280 (VIII), 283 (VII), 278 (VII), and 265 K (VIII). Similar data were also collected from another sample at 3.3 GPa and temperatures of 286 (VII), 272 (VII), 258 (VIII), and 271.5 K (VIII). The data were corrected for attenuation [15] and used for structure refinement with the program GSAS [16].

All atomic coordinates not fixed by symmetry were refined, along with the lattice constants, and peak shape, background, and atomic thermal motion parameters—using the single-site model for ice VII. The (anisotropic) D thermal motion is constrained by the site symmetry to have just two independent components in ice VII: one parallel to O-D, $U_{\parallel}(\mathrm{D})$, and one perpendicular, $U_{\perp}(\mathrm{D})$. To simplify comparisons between the two phases, this constraint was also applied to ice VIII, and did not significantly alter the results or worsen the fit. A single isotropic parameter $U_{\mathrm{iso}}(\mathrm{O})$ was used for the O atom.

The refined values of the thermal-motion parameters are plotted in Fig. 2. There is a clear step of 0.0064(5) Å^2 in the average value of $U_{\mathrm{iso}}(\mathrm{O})$ at T_c for the sample at 5 GPa, and a step of about 0.004(1) Å^2 in $U_{\perp}(\mathrm{D})$, while $U_{\parallel}(\mathrm{D})$ is unchanged within error. (The second sample gave the same results within 1 esd.) The thermal motion of the D atom "rides" on that of the O atom, and so the lack of change in $U_{\parallel}(\mathrm{D})$ suggests that there is no significant change in the true thermal motion of either atom. The steps in $U_{\mathrm{iso}}(\mathrm{O})$ and $U_{\perp}(\mathrm{D})$ can then be interpreted as direct evidence of multisite disorder of both the O and the D atoms in ice VII, and the magnitudes of the site displacements $\delta(\mathrm{O})$ and $\gamma(\mathrm{D})$ can be obtained by refinement of the ice VII data sets with all the atomic thermal parameters fixed at their mean values in ice VIII. Several different displacement directions were explored, and all gave the same mean values of 0.135(10) Å for δ and 0.09(3) Å for γ. (These are similar to the values obtained in Refs. [7] and [9] but cannot be compared directly because of differences in the models used.) To proceed further, it is necessary to test the various possible directions of displacement for both O and D to find which produce the most plausible molecular geometry, on the expectation that the true O-D bond length and D-Ô-D angle in ice VII are close to the values found in ice VIII [7,9].

Several different displacement directions were examined. For the O atoms, these are the 6-fold sites along $\langle 100 \rangle$, shown by open circles in Fig. 1; the 4-fold sites

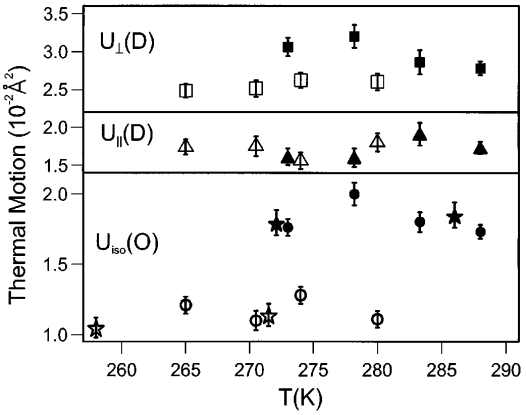

FIG. 2. Temperature dependence of the thermal motion of ice VIII (open symbols) and ice VII (solid symbols) at 5 GPa for the two components of the deuterium thermal motion $U_{\perp}$ (squares) and $U_{\parallel}$ (triangles), and the isotropic oxygen thermal motion $U_{\mathrm{iso}}(\mathrm{O})$. Solid (open) stars show the $U_{\mathrm{iso}}(\mathrm{O})$ values obtained from a second sample at 3.3 GPa.

along ⟨111⟩, one of which is shown as a filled circle in Fig. 1; the other set of 4-fold sites along $\langle\bar{1}\,\bar{1}\,\bar{1}\rangle$; and the 12-fold sites along ⟨110⟩, shown as a filled square in Fig. 1. For the D atoms, they are 3-fold sites, 120° apart around ⟨111⟩, at $(x + u, x, x)$, $(x, x + u, x)$, and $(x, x, x + u)$, with $u = \gamma/(\sqrt{2}\,a)$; another set of 3-fold sites at $(x - u, x, x)$, etc.; and 6-fold sites, 60° apart around ⟨111⟩, at $(x + v, x - v, x)$ with $v = \gamma/(\sqrt{6}\,a)$, etc. The displacements of the D atoms are perpendicular to the O-D bond, and so do not affect its length significantly. This makes it reasonable to simplify the presentation by omitting details of the D-atom displaced sites—e.g., they are not shown in Fig. 1. However, the D displacements do affect the D-Ô-D angle significantly, and this is the basis for the choice of the D sites as described below. Refinements of the ice VII data sets at 5 GPa were carried out with the O and D thermal motion fixed to the mean values found in ice VIII—$\overline{U_{\rm iso}(\mathrm{O})}^{\rm VIII}$, $\overline{U_{\parallel}(\mathrm{D})}^{\rm VIII}$, and $\overline{U_{\perp}(\mathrm{D})}^{\rm VIII}$—and using as structural models each of the twelve combinations of the four O and three D displacement directions. This procedure provides unbiased estimates of the molecular geometry given by all twelve models for each observed data set.

Possible molecular configurations can be identified by choosing the combination of O and D sites that give the O-D distance and D-Ô-D angle closest to the mean values for ice VIII (0.970 Å and 107.3° in our refinements). For example, the O site at the apex of the dashed lines in Fig. 1 is about 1.01 Å from D sites at P and Q (Fig. 1), and two of the 3-fold $(x - u, x, x)$ sites at P and Q give a D-Ô-D angle of about 107°. This is the best fit to the ice VIII molecular dimensions that can be achieved with *any* combination based on O displacements along ⟨100⟩. A similar analysis for O sites along ⟨110⟩ gives a best fit of 0.95 Å for O-D, with an angle of 105° using two of the 6-fold D sites. The closest fit with sites along $\langle\bar{1}\,\bar{1}\,\bar{1}\rangle$ is poor—0.90 Å for O-D, with an angle of 108°. But sites displaced δ along ⟨111⟩—for example, the one shown as a filled circle in Fig. 1, linked to two of the 3-fold $(x + u, x, x)$ D sites at P and Q—give 0.977(7) Å for O-D and 107(1)° for D-Ô-D averaged over the four data sets in ice VII, remarkably close to the ice VIII values above. The ⟨111⟩ model clearly allows the molecular geometry—both O-D and the D-Ô-D angle—to remain constant within error through the transition. The 3.3 GPa data lead to the same conclusions.

Figure 3 shows the individual O-D distances obtained from this analysis for each of the data sets at 5 GPa, along with results for ice VIII and the single-site model of ice VII. (The poorly fitting $\langle\bar{1}\,\bar{1}\,\bar{1}\rangle$ model is excluded.) The single-site model reproduces the apparent shortening of O-D found in the earlier studies [7,9].

The magnitude of δ, and hence of O-D, depends critically on the difference, $\Delta U(\mathrm{O})$, between the observed $U_{\rm iso}(\mathrm{O})$ in ice VII and $\overline{U_{\rm iso}(\mathrm{O})}^{\rm VIII}$, taken as 1.18×10^{-2} Å^2 (see Fig. 2) in obtaining the results in Fig. 3. The sensitivity to $\Delta U(\mathrm{O})$ was explored by repeating the analysis with different values of $\overline{U_{\rm iso}(\mathrm{O})}^{\rm VIII}$.

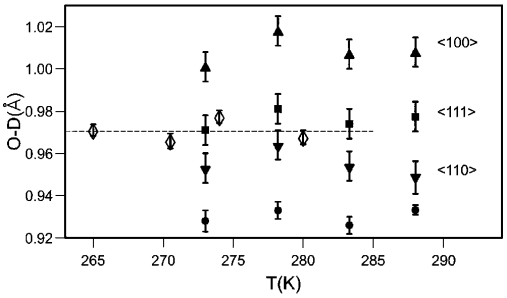

FIG. 3. Temperature dependence at 5 GPa of the O-D bond length in ice VIII (◇), and in ice VII for the single-site model (•) and for site-disordered models with O-atom displacements along ⟨100⟩ (▲), ⟨111⟩ (■), and ⟨110⟩ (▼). The dashed line shows the mean O-D distance in ice VIII.

This confirmed that the discrimination between the ⟨100⟩ and ⟨111⟩ models is robust. It would require a $\Delta U(\mathrm{O})$ less than 0.3×10^{-2} Å^2 to obtain an O-D of ~0.97 Å for the ⟨100⟩ model, compared with observed values of over 0.6×10^{-2} Å^2 in both samples (Fig. 2). This difference is much larger than any likely error in attenuation corrections or in the adoption of $\overline{U_{\rm iso}(\mathrm{O})}^{\rm VIII}$ as an estimate of the true ice VII thermal motion. Also, the mean O-D distances of 1.010(7) Å and 1.016(10) Å obtained for the ⟨100⟩ model with our two samples are consistent with the 1.016(7) Å reported by Kuhs *et al.* [7]. Thus diffraction studies clearly and *consistently* show that the ⟨100⟩ model requires an implausibly large increase in O-D at T_c. The discrimination between the ⟨111⟩ and ⟨110⟩ models is less certain (see Fig. 3), but ⟨111⟩ is clearly preferred at the mean observed $\Delta U(\mathrm{O})$ value of 0.0064(5) Å^2. Moreover, as Fig. 3 shows, the displacement directions are certainly between ⟨111⟩ and ⟨110⟩, rather than between ⟨111⟩ and ⟨100⟩. In fact, tests reveal that the directions must be within ~15° of ⟨111⟩ to retain an O-D distance within 0.01 Å of the ice VIII value. While displacements close to but not exactly along ⟨111⟩ cannot be ruled out, ⟨111⟩ directions give the most plausible geometry and the lowest number of configurations. In the discussion that follows, the ⟨100⟩ and ⟨111⟩ models will be taken as representative of structures in which the O-atom displacements are along these principal directions or closer to them than to ⟨110⟩.

The ⟨100⟩ and ⟨111⟩ models predict significantly different H bonding. In the ⟨100⟩ model, the possible H-bonded O...O distances at 5 GPa are one of 2.833 Å and two of 2.839 Å [17]—all very close to the ice VIII bond length of 2.834 Å. But, the possible contacts for the ⟨111⟩ model are 2.75 Å, 2.92 Å, and 2.93 Å [18], which are all ~0.1 Å shorter or ~0.1 Å longer than in ice VIII. Such changes in H bond length are not small; 0.1 Å is ~20% of the total change in O...O from 2 GPa to centering [2]. (An O-D...O distance ~0.1 Å different from ice VIII might appear to conflict with the small changes in both the vibron and lattice mode frequencies at T_c [19]. However, none of the lattice modes studied to data is a probe solely of the O-D...O bonds [20]. And

the vibron frequency is a probe of the entire close environment and hence responds to other interactions in addition to the bonded D...O distance. Comparison of vibron frequencies at constant O-D...O in different ices [19,21] suggests that the O-D...O bond length is not the only significant factor in determining the vibron frequency.) In addition to the difference in H bond length from ice VIII, the need to construct an H-bond network that satisfies the ice rules implies that ice VII must contain a mixture of both the ~2.75 Å and ~2.93 Å H bond lengths. Thus, oxygen displacements along or close to ⟨111⟩ imply a short-range structure quite unlike that of ice VIII.

It is of much interest to know whether these conclusions hold at higher pressures, and so we have carried out further studies up to 20 GPa. Measurements of $U_{\mathrm{iso}}(\mathrm{O})$ in ice VII and ice VIII at 4.5, 8.8, 12.8, 16.5, and 20.6 GPa show a slight increase in the magnitude of $\Delta U(\mathrm{O})$; more detailed measurements at 20.6 GPa, cycling through the VII/VIII transition as at 5 GPa, gave $\Delta U(\mathrm{O}) = 0.0056(8)$ Å^2 and $\delta(\mathrm{O}) = 0.13(2)$ Å. The balance of evidence is thus that there is no significant change in $\Delta U(\mathrm{O})$ or $\delta(\mathrm{O})$ to 20 GPa. An analysis of the 20 GPa data identical to that illustrated in Fig. 3 gave the results shown in Fig. 4. The similarities to the 5 GPa results are striking and support the same conclusions. In particular, the best fit to the ice VIII molecular geometry is still given by the ⟨111⟩ model, and the H bond lengths remain ~0.1 Å longer and ~0.1 Å shorter than those in ice VIII [22]. These results strongly suggest that some difference may persist up to centering.

Our principal conclusions are thus (i) that the structure of ice VII is significantly different from previous interpretations and more complex, and (ii) that the proposed structure is likely to have important consequences for theoretical and experimental studies of the centering transition. The O-D...O bond length is a critical parameter in such studies, and to date it has been assumed that this dimension could be obtained simply from the ice VII lattice parameter a as $a\sqrt{3/4}$ [2,4,5]. But the ⟨111⟩ model gives a difference in value that could displace the relationship between bond length and pressure by tens of GPa. Furthermore, the centering behavior of a network of H bonds of two different lengths has never been considered and raises new possibilities. The range between ice VII and fully centered ice X—from ~70 to ~100 GPa [4–6] or more [3]—could represent a mixed intermediate state in which proton disorder [5,6] progressively develops in bonds of different lengths. Although the difference in bond length may be reduced from ~0.2 Å as centering is approached, as little as ~0.06 Å could account for a ~30 GPa range at the pressures concerned.

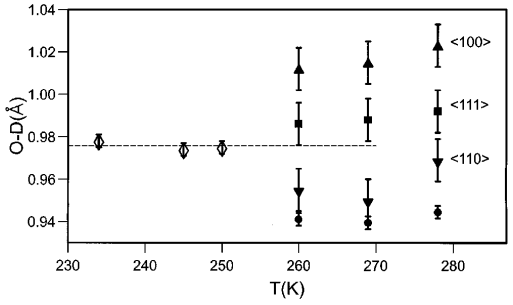

FIG. 4. Temperature dependence at 20.6 GPa of the O-D bond length in ice VIII (◇), and in ice VII for the single-site model (•) and for site-disordered models with O-atom displacements along ⟨100⟩ (▲), ⟨111⟩ (■), and ⟨110⟩ (▼). The dashed line shows the mean O-D distance in ice VIII.

We thank W. F. Kuhs for helpful discussions of his work in Ref. [7] and D. D. Klug and I. M. Morrison for their insights into the vibrational spectroscopy of ice. Our work is supported by funding from the U. K. Engineering and Physical Sciences Research Council, and Council for the Central Laboratory of the Research Councils, from the Institut National des Sciences de l'Univers, and from the French National Programme in Planetary Science, and by resources made available by the ISIS Facility.

*Now at ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxon OX11 0QX, U.K.

[1] P. Pruzan *et al.*, J. Chem. Phys. **99**, 9842 (1993).
[2] P. Pruzan, J. Mol. Struct. **322**, 279 (1994).
[3] A. F. Goncharov *et al.*, Science **273**, 218 (1996).
[4] K. Aoki *et al.*, Phys. Rev. B **54**, 15 673 (1996).
[5] P. Pruzan *et al.*, J. Phys. Chem. **101**, 6230 (1997).
[6] M. Benoit, D. Marx, and M. Parrinello, Nature (London) **392**, 258 (1998).
[7] W. F. Kuhs *et al.*, J. Chem. Phys. **81**, 3612 (1984).
[8] J. D. Jorgensen *et al.*, J. Chem. Phys. **81**, 3211 (1984).
[9] J. D. Jorgensen and T. G. Worlton, J. Chem. Phys. **83**, 329 (1985).
[10] ⟨*hkl*⟩ denotes the direction [*hkl*] and all other directions related to it by the symmetry of the structure.
[11] J. M. Besson *et al.*, Physica (Amsterdam) **180–181B**, 907 (1992).
[12] Deuteration eliminates the high background given by incoherent neutron scattering from hydrogen atoms.
[13] R. J. Nelmes *et al.*, Phys. Rev. Lett. **71**, 1192 (1993).
[14] R. J. Hemley *et al.*, Nature (London) **330**, 737 (1987).
[15] R. M. Wilson *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. A **3354**, 145 (1995).
[16] R. B. von Dreele and A. C. Larson, Los Alamos National Laboratory Report No. LAUR-86748, 1986 (unpublished).
[17] Between O sites at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4} - \frac{\delta}{a}$ and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4} - \frac{\delta}{a}$ (2.833 Å); and at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4} - \frac{\delta}{a}$ and $\frac{3}{4}, \frac{3}{4} - \frac{\delta}{a}, \frac{3}{4}$ or $\frac{3}{4} - \frac{\delta}{a}, \frac{3}{4}, \frac{3}{4}$ (2.839 Å).
[18] Between O sites at $\frac{1}{4}+, \frac{1}{4}+, \frac{1}{4}+$ and $\frac{3}{4}+, \frac{3}{4}+, \frac{3}{4}-$, etc. (2.75 Å); at $\frac{1}{4}-, \frac{1}{4}-, \frac{1}{4}+$ and $\frac{3}{4}-, \frac{3}{4}+, \frac{3}{4}+$, etc. (2.92 Å); and at $\frac{1}{4}-, \frac{1}{4}-, \frac{1}{4}+$ and $\frac{3}{4}+, \frac{3}{4}-, \frac{3}{4}-$, etc. (2.93 Å), where + and − designate $\pm\delta/\sqrt{3}a$. The sites at $\frac{1}{4}+, \frac{1}{4}+, \frac{1}{4}+$ and $\frac{3}{4}-, \frac{3}{4}-, \frac{3}{4}-$ are too close for bonding (2.55 Å).
[19] J. M. Besson *et al.*, Phys. Rev. B **55**, 11 191 (1997).
[20] P. T. T. Wong and E. Whalley, J. Chem. Phys. **64**, 2359 (1976); S. P. Tay *et al.*, J. Chem. Phys. **83**, 2708 (1985).
[21] B. Minceva-Sukarova *et al.*, J. Phys. C **17**, 5833 (1984).
[22] R. J. Nelmes *et al.*, Rev. High Pressure Sci. Technol. **7**, 1138 (1998).