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Structural changes in amorphous solid water films on heating to 120–140 K and 150–160 K seen by positronium annihilation spectroscopy

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Abstract

Changes in the structure of amorphous solid water films, grown by vapour deposition on a copper substrate at 75 K and then held at 120 K for 10 min to effect pore collapse, have been observed in the ranges 122–139 K and 150–162 K using positronium annihilation spectroscopy. It is proposed that the former is associated with the glass transition, with an effective activation energy of 0.266(3) eV. The data for the latter, which exhibit minima suggesting the temporary introduction of molecular disorder, can be processed to yield an effective activation energy of 0.47(2) eV, and are consistent with either a structural reorganization of the crystalline lattice or a relaxation of the amorphous structure mediated by defect migration.

Keywords: positronium, water ice, structure

(Some figures may appear in colour only in the online journal)

1. Introduction

The nature of, and transitions between, structures of water ice films at temperatures between 120 and 190 K continues to be the focus of extensive research using many different techniques. Most experimental studies are of films of a few nm in thickness and deposited on atomically flat substrates [1–5]. Aspects attracting particular attention include such basic features as the glass transition [6–9], crystallization [10–15] and the nature of the crystalline state below 180 K [16–19]. In this paper we use positronium (Ps) annihilation spectroscopy [20–22] of amorphous solid water (ASW) at temperatures between that for pore collapse (~ 120 K) and 160 K, to attempt to gain new information on some of these issues.

2. Experimental method

Ps annihilation spectroscopy is based on the measurement of the fraction F of mono-energetic positrons of energy E implanted normally into the film which forms the spin triplet

state of Ps, ortho-Ps, and subsequently decays into three gamma photons [22]. Unless there exist large closed or interconnected pores this happens only via ortho-Ps diffusing through the ice and decaying in the vacuum above, because interaction with bulk electrons leads to quenching and decay into two photons. Any lattice imperfections which trap ortho-Ps, or the positrons which may form ortho-Ps, therefore lead to lower values of F —which is thus a sensitive measure of disorder [23]. Finally, by changing E in the range from 1.5 to 30 keV one can control the mean positron implantation depth from ~ 75 nm to $10 \mu\text{m}$.

The $\sim 20 \mu\text{m}$ thick ice films were grown by vapour deposition of distilled, de-ionized water vapour on to a machine-polished copper substrate held at 75 K (see [22] for details). Film thicknesses, although of secondary importance here as no significant thinning via sublimation occurs at the temperatures used, were estimated by using growth pressures and times suggested by the extensive measurements of positron annihilation lineshape parameters $S(E)$ and knowledge of the positron implantation depth profiles at each E , as described in [22]. The growth pressure, 20 mPa, was $>10^3$ times

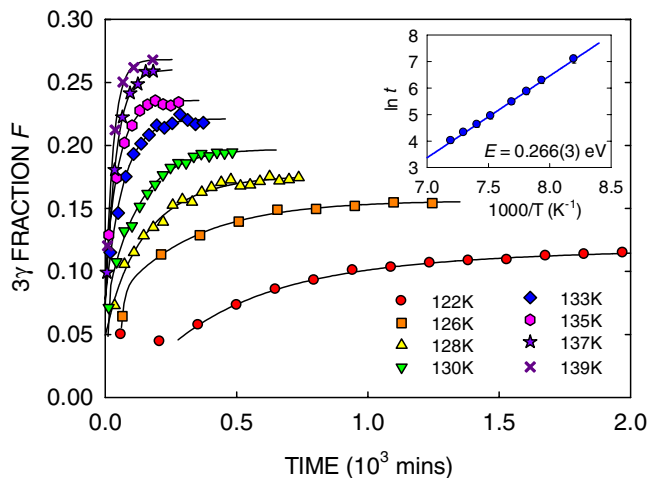


Figure 1. Ortho-Ps three-gamma fractions F measured as a function of time at eight different temperatures for ice films grown at 75 K and sintered at 120 K. Incident positron energy $E = 1.5$ keV. The Arrhenius plot (inset) uses times for F to increase from 0.05 to 90% of their asymptotic values.

higher than the system base pressure (which is in any case not wholly due to water vapour) and changes in film thickness during the measurements is expected to be ~ 10 nm at most. This is negligible when compared with the mean implantation depth of the positrons. In earlier experiments with the same system it was found that measurable thicknesses of films grown at the base pressure over $\sim 10^3$ min time scales were only seen at temperatures of 50 K or lower, and these were not water ice films but presumably frozen residual molecular gases.

The as-grown ice films are highly porous, with both closed pores of up to several nm in size—in which some ortho-Ps can decay before being quenched—and interconnected pores which provide channels by which ortho-Ps can reach the surface [5]. In these films, therefore, the three-gamma fraction F is relatively high. After growth the films were then raised to 120 K and held there for 10 min in order to effect pore collapse [24]. This collapse, to what is generally termed low-density amorphous (LDA) ice, is often described in terms of the formation of sintered ASW, a collapsed state similar to hyperquenched glassy water (HW). After this transformation F decreases precipitously [25] (e.g. from ~ 20 to 3% at $E = 2$ keV) because in the absence of large or interconnected pores ortho-Ps has to diffuse through the highly disordered sintered ASW and a much lower fraction survives to decay naturally.

3. Experimental results and discussion

3.1. Heating to 122–139 K

On heating to temperatures between 122 and 139 K a return to high F values is seen, to final values which are temperature-dependent (figure 1)—10 to 27% as T is increased from 122 to 139 K. The time taken to reach these final asymptotic values is also temperature-dependent. The measured time-dependence of the parameters was similar for a range of

implantation energies E from 1.5 to 30 keV (and hence probed depths beneath the surface of between 0.1 and 10 μ m), supporting the assertion that the measured parameter changes are not associated with near-surface film growth but with changes throughout the films as the trapping sites are annealed. If this were not the case, then only the parameters measured at the lowest E values would exhibit the changes observed.

The authors believe that this annealing of defects is facilitated by a glass transition, above which the greatly increased molecular diffusivity promotes the migration of defects to sinks. The inset in figure 1 shows an Arrhenius-type plot of $\ln t$ for F to increase from 0.05 to 90% of its asymptotic value versus reciprocal temperature. Although a glass transition should not be directly amenable to such treatment, it is interesting to note that the gradient of the straight-line plot yields an effective activation energy of 0.266(3) eV, which agrees with the measurement by Jenniskens and Blake of 0.25(5) eV which they attribute to the onset of the formation of the ‘restrained amorphous form’ of ice in regions included in a crystalline matrix [26]. Although the F data reflect defect annealing rather than the formation of amorphous enclaves, both may be happening as the ice passes through the glass transition. Conversion into a form of crystalline water ice may be occurring in figure 1, but it should be noted that Ps diffusion through defect-free glassy ice appears to be very similar to, if not indistinguishable from, that in crystalline ice. This is evidenced by the measurement here of a maximum value of F approaching 0.3 (figure 1), which is similar to the highest value measured for 1.5 keV positrons entering ice which is known to have crystallized (see, e.g. figure 1 in [22], and the results presented in section 3.2 of this paper). Scott Smith *et al* [27] remark that the molecular structure of both defect-free glassy and crystalline forms is very similar. We would therefore expect similar F values for both forms.

3.2. Heating to 150–162 K

On measuring F as a function of time at temperatures between 150 and 162 K a second novel response in F is recorded, whether the films are grown following the recipe outlined above (i.e., growth at 75 K, sintering at 120 K, and raising to the measurement temperature in a few minutes) or directly at temperatures of 150–162 K. As shown in figure 2, for 20 μ m films grown at 75 K, F drops monotonically—albeit not at a constant rate—and then recovers, although progressively less completely at lower temperatures. This observation has to reflect a temporary increase in the concentration of positron/Ps trapping sites associated with a molecular re-organization.

The nature of this re-organization is intriguing. A prime candidate is the glassy-to-crystalline transition. However, (a) the times associated with the dip in F —e.g. ~ 16 h at 162 K—are longer than might be expected for crystallization and (b) a transition from the glassy state with low defect concentration to the not dissimilar crystalline state would not be expected to proceed via the temporary introduction of extra open-volume

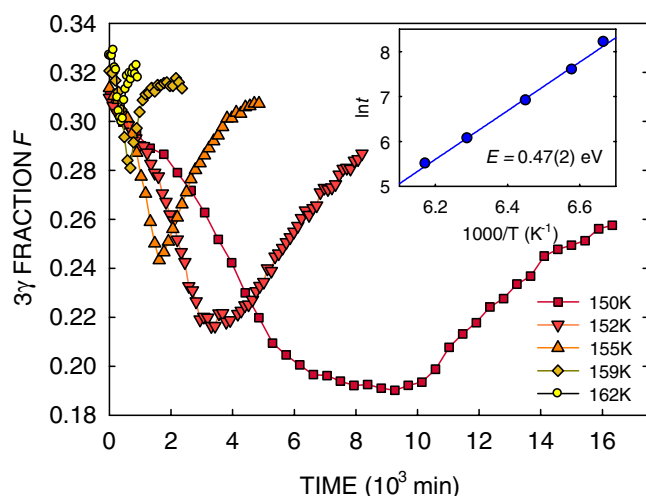


Figure 2. Ortho-Ps three-gamma fractions F measured at $E = 2.5$ keV as a function of time at five different temperatures for $20\ \mu\text{m}$ ice films grown at 75 K and sintered at 120 K. Incident positron energy $E = 1.5$ keV. (Similar results were recorded for films grown at the measurement temperatures.) The Arrhenius plot uses times for F to fall to 90% of its minimum values.

defects. Measurements at incident positron energies E from 1.5 to 30 keV exhibit minima at the same time—whereas if this observation was a response to a structural feature near the surface of the ice films positrons of higher E would respond to the disorder at an earlier time than those of lower E . Therefore it can be concluded that this is a time-dependent, and not depth-dependent, phenomenon which is driven thermodynamically. Consequently, an Arrhenius plot using characteristic times for F to fall to 90% of its minimum value is shown in the inset of figure 2, yielding an effective activation energy of $0.47(2)$ eV. This is consistent with the energy associated with crystallization reported by many, but not all, researchers [26, 28] but (as pointed out in [26]) it is also the energy required to break two H bonds, and thus may be associated with other structural reorganization mechanisms.

One possibility is associated with the reduction in the concentration of included amorphous pockets in the crystalline matrix, but it is difficult to link this process with a reduction in F ; one would expect an approximately constant, or steadily increasing, value.

A second, more plausible, candidate is re-organization associated with the ordering of the crystalline lattice. Kuhs *et al* [18] have described the erstwhile-entitled ‘cubic ice’ as being hexagonal ice with stacking disorder. It is possible that the response seen in figure 2 is a consequence of the temporary molecular disorder introduced while the cubic stacking sequences transform into hexagonal, although the times taken for this process are shorter than those quoted by Kuhs *et al* [18] if one extrapolates the Arrhenius plot to higher temperatures, and the activation energy of 0.464 eV they quote is for temperatures above 180 K. Re-organization associated with the movement and/or evolution of crystallites could also be considered to introduce temporarily more trapping sites, for example at grain boundaries.

Intriguingly, another plausible candidate is the gradual structural relaxation of ASW on thermal annealing reported

by Shephard *et al* [29]. This relaxation, according to those authors, is distinct from crystallization and may be connected to reorientation dynamics mediated by defect migration, in line with our observations.

4. Conclusions

The application of Ps annihilation spectroscopy to the study of ice films has provided evidence of high sensitivity to structural defects and reorganization, and the authors hope that further investigations, both freestanding and in conjunction with other complementary spectroscopies and microscopies, will shed more light on the many intriguing phenomena associated with this system.

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References

- [1] Mitlin S and Leung K T 2002 *J. Phys. Chem. B* **106** 6234–47
- [2] Kohl I, Mayer E and Hallbrucker A 2000 *Phys. Chem. Chem. Phys.* **2** 1579–86
- [3] Scott Smith R, Matthiesen, Knox J and Kay B D 2011 *J. Chem. Phys. A* **115** 5908–17
- [4] Zimbitas G, Haq S and Hodgson A 2005 *J. Chem. Phys.* **123** 174701
- [5] Bartels-Rausch T *et al* 2012 *Rev. Mod. Phys.* **84** 885–944
- [6] Sepúlveda A, Leon-Gutierrez E, Gonzalez-Silveira M, Rodríguez-Tinoco C, Clavaguera-Mora M T and Rodríguez-Viejo J 2012 *J. Chem. Phys.* **137** 244506
- [7] Chonde M, Brindza M and Sadtchenko V 2006 *J. Chem. Phys.* **125** 094501
- [8] Souda R 2008 *J. Chem. Phys.* **129** 124707
- [9] Yue Y Z and Angell A 2004 *Nature* **427** 717–20
- [10] Hallbrucker A, Mayer E and Johari J P 1989 *J. Phys. Chem.* **93** 4986–90
- [11] Haq S, Harnett J and Hodgson A 2002 *Surf. Sci.* **505** 171
- [12] Scott Smith R, Huang C, Wong E K L and Kay B 1997 *Phys. Rev. Lett.* **79** 909–12
- [13] Kondo T, Kato H S, Bonn M and Kawai M 2007 *J. Chem. Phys.* **126** 181103
- [14] Safarik D J, Meyer R J and Mullins C B 2003 *J. Chem. Phys.* **118** 4660–71
- [15] Moore E B and Molinero V 2010 *J. Chem. Phys.* **132** 244504
- [16] Malkin T L, Murray B J, Brukhnob A V, Anwar J and Salzmann C G 2012 *Proc. Natl Acad. Sci. USA* **109** 1041–45
- [17] Thürmer K and Nie S 2013 *Proc. Natl Acad. Sci. USA* **110** 11757–62
- [18] Kuhs W F, Sippel C, Falenty A and Hansen T C 2012 *Proc. Natl Acad. Sci. USA* **109** 21259–64
- [19] Johari G P 1998 *Phil. Mag.* **78** 375–83
- [20] Eldrup M, Vehanen A, Schultz P J and Lynn K G 1985 *Phys. Rev. B* **32** 7048–64
- [21] Wu Y C, Jiang J, Wang S J, Kallis A and Coleman P G 2011 *Phys. Rev. B* **84** 064123
- [22] Townrow S and Coleman P G 2014 *J. Phys.: Condens. Matter* **26** 125402
- [23] Townrow S and Coleman P G 2013 *Rev. Sci. Instrum.* **84** 103908

- [24] Mitterdorfer C, Bauer M, Youngs T G A, Bowron D T, Hill C R, Fraser H J, Finney J L and Loerting T 2014 *Phys. Chem. Chem. Phys.* **16** 16013
- [25] Wu Y C, Kallis A, Jiang J and Coleman P G 2010 *Phys. Rev. Lett.* **105** 066103
- [26] Jenniskens P and Blake D F 1994 *Science* **265** 753–6
- [27] Scott Smith R, Petrik N G, Kimmel G A and Kay B D 2012 *Acc. Chem. Res.* **45** 33–42
- [28] Sack N J and Baragiola R A 1993 *Phys. Rev. B* **48** 9973–78
- [29] Shephard J J, Evans J S O and Salzmänn C G 2013 *J. Phys. Chem. Lett.* **4** 3672–76