Generalized Density of States for Confined Molecular Oxygen from Inelastic Neutron Scattering

Low Energy Neutron Source

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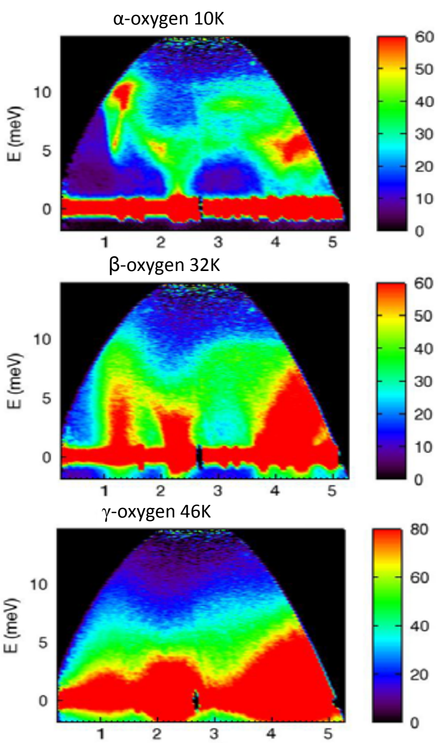
Inelastic neutron scattering measurements were carried out on condensed bulk and confined molecular oxygen using the disc chopper spectrometer (DCS) at the Center for High Resolution Neutron Scattering at NIST. Depending on cooling rate we find that we are able to suppress crystallization in pores with 130Å diameter. Slower cooling allows crystallization, but the density of states reveal a mixing of crystal excitations from different phases

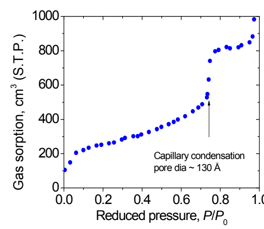
The DCS instrument was used with an incident neutron wavelength of 2.3 Å (15.46 meV).

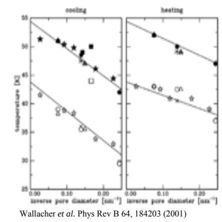


Full contour plots of $S(Q,E)$ for bulk molecular oxygen in its three solid phases. The plots are integrated along the two axes to give structural and vibrational information about the crystals

Confinement in SBA-15

Oxygen is loaded into the porous silica glass SBA-15. This is a templated glass giving rise to uniform cylindrical pores. It is therefore an ideal system for testing models of confinement. The adsorption isotherm for nitrogen in SBA-15 is shown (right). A monolayer is deposited in the pressure range $P/P_0 <$ 0.075. Subsequent layers are adsorbed up to $P/P_0 = 0.75$ where capillary condensation occurs. A modified Kelvin equation approach yields a mean pore diameter of ~ 130 Å.





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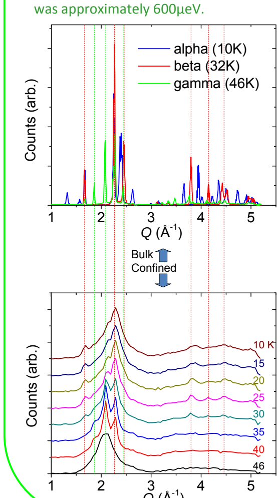
Upper symbols are freezing/melting, Lower symbols are γ-β transition.

Previous measurements on oxygen in confinement have focused on the changes to equilibrium crystal structure and phase transition temperatures. As is commonly found, the temperatures are suppressed in pores with smaller radii, with the suppression being proportional to 1/R where R is the pore radius.

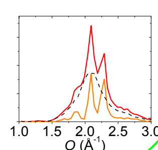
It is found that the beta-alpha transition is not detectable under confinement.

Elastic Peaks

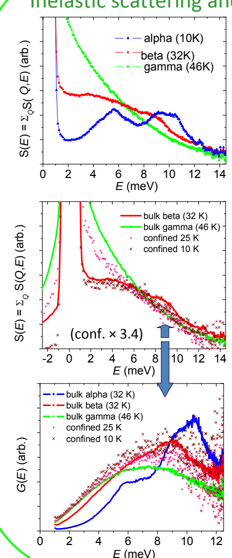
These plots are achieved by integrating around the elastic region. We integrate from -1 meV to 1 meV. The FWHM of the resolution function was approximately 600μeV.



From the plots of $S_{el}(Q)$ below it can be seen that an amorphous structure persists below the bulk freezing temperature of 54 K, and that an amorphous component (~ 71% see figure below, and isotherm) is evident at lower temperatures. The transition temperatures are suppressed, but gamma and then beta peaks are seen with decreasing temperature. We see no evidence of the alpha phase even at 10 K, in particular the peak at 1.32 Å^{-1} due to long range anti-ferromagnetism is not present.



Inelastic scattering and density of states



The generalized density of vibrational states, $G(Q,E)$, is calculated from the one phonon scattering function, $S(Q,E)$, using:

$$S_{c,+1}(Q,E) = \exp^{-2W} \frac{\hbar^2 Q^2}{2\overline{M}E} \langle n+1 \rangle G(Q,E)$$

The effective vibrational density of states is then defined by

$$G(E) = \frac{1}{(Q_2 - Q_1)} \int_{Q_1}^{Q_2} G(Q,E)\,dQ$$

For confined oxygen, the plot of $S(E)$ at 25K clearly has a large non beta-like component. It is only when the temperature is 10 K that $S(E)$ is unambiguously beta-like in shape. The intensity of the density of states for confined oxygen is approximately 1/3 that of bulk oxygen. This therefore corresponds to the proportion of oxygen observed as crystalline from the elastic line. The question then presents itself: where is the missing scattering intensity? Because of the large amount of scatter in $g(E)$ as E increases it is difficult to differentiate between the values at 25 K and 10 K. What is clear is that the density of states is higher at lower energies than for the bulk crystal (in the alpha form for the same temperature). This therefore suggests confined oxygen for further consideration as a moderating material for a very low energy neutron source. More generally it recommends the study confining materials as a way of modifying vibrational density of states to make them more useful as moderators.

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