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Hydrogen Storage in Metal-Modified Single-Walled Carbon Nanotubes

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Abstract/Motivation:

We are studying the suitability intercalants used in graphites in order to expand or swell the rope structure of single-walled nanotubes (SWNTs). The intercalation of SWNTs opens up the possibility of accessing interstitial regions of this material which normally remain inaccessible to adsorbed gases, due to the van der Waals forces which promote rope formation. These rope structures normally limit the surface area of SWNT materials from 300 to 400 m^2/gm, even though the theoretical surface area of SWNTs should be closer to 2600 m^2/gm. Our previous work using nitrogen Brunauer-Emmett-Teller (BET) surface area analysis of SWNTs[1] suggested that such analysis was capable of probing only the outer surface area of the rope structure. Our previous work on SWNTs has also shown that the cohesive energy responsible for rope formation can be overcome by hydrogen adsorption at low temperatures and high pressures, yielding close to the theoretical limit of incommensurately packed hydrogen molecules, if both endohedral and interstitial sites are taken into account. If intercalants behave in SWNTs the way they behave in graphites, we would expect the individual tubes to separate in a way that would allow for gas adsorption without having to overcome this cohesive energy.

To gain experience in the synthesis and handling of these materials, we began this project by using the Neutron Powder Diffractometer (NPD) at the Lujan Center at Los Alamos National Laboratory (LANL) to analyse the structure of deuterided KC_{24}. Beamtime for this instrumetn is awarded on a competition based on scientific merit and NPD was significantly oversubscribed. This experiment was also motivated by previous studies which noted the affinity for hydrogen in K-intercalated graphites[2] at LN_2 temperature, a phenomenon which is still not well understood. We hope to move beyond a phenomenological appreciation of this interaction in order to gain real physical insight into this system. Hopefully, these insights will lead to the design of a SWNT-based sorbent that will ultimately prove to be of use for hydrogen storage systems.

The initial goal of our work is to find the occupancy sites of deuterium atoms. Unlike hydrogen, deuterium is an effective coherent scatterer for neutrons. Thus we would expect the presence of deuterium to alter the diffraction pattern in a way that would reveal its location in the lattice. Deuterium is similar enough in size and physical behavior, that such information would guide strategies for determining optimal positions for potassium on a graphite lattice, and provide a suitable foundation from which to calculate and understand hydrogen uptake in these intercalated graphites.

The Stage 2 intercalated graphite, KC_{24}, consists of a graphite lattice in which K atoms form a dodecal structured layer between graphene layers as shown below. The stacking sequence is a-K-a-b, in which the a and b designation represent the normal stacking designation typically used to describe graphite. To define an entire unit cell, the actual sequence would be a-Kα-a-b-Kβ-b…, for a perfect unit cell, where Kα and Kβ are alternating stacking sequences for potassium layers. Each potassium layer of the Stage 2 compound is separated by an a-b graphene stacking sequence.

From Fig. 1, we might appreciate that on the basis of a space filling model, that only a limited number of sites for deuterium (D_2) occupancy exist. A precise determination of these sites however, would yield information on the nature of the interaction between K and D_2. For instance, our initial calculations shown in Fig. 2, indicate that by using the model of Fig. 1, that the presence of D_2 would alter the relative intensities of basal plane diffraction peaks and would also result in changes to the relative intensity of minor diffraction peaks. We are still working on the analysis of the data to determine whether this information can be extracted from our data.

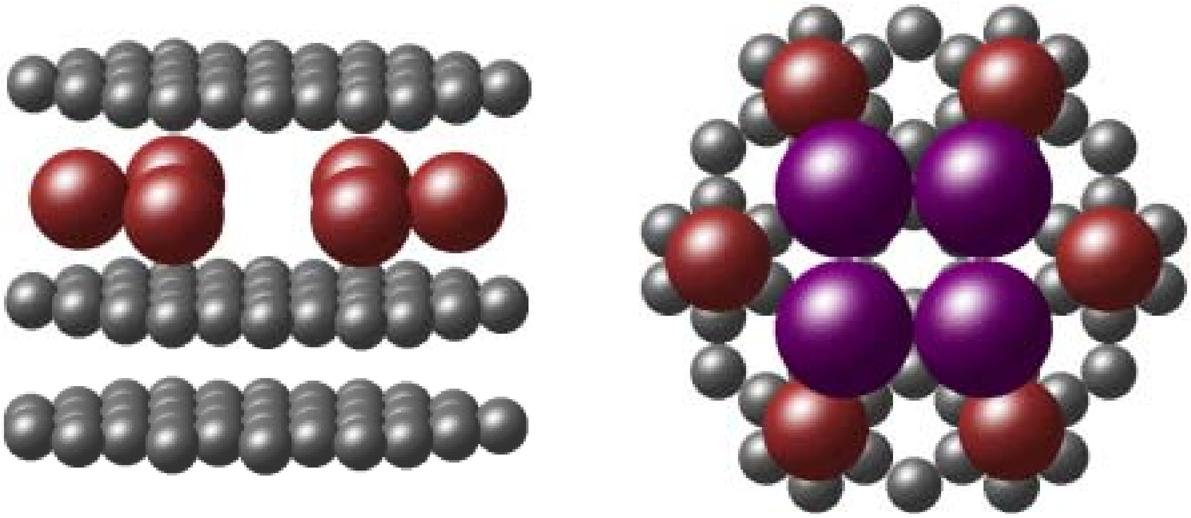

Fig. 1. The left figure shows the stacking sequence for KC_{24}. The gray atoms represent carbon and the larger red atoms show the dodecal structure of potassium atoms. The right figure shows a view down the basal direction of the dodecal K (red atoms) structure atop a single graphene layer. In addition, a possible arrangement for four larger deuterium molecules is depicted in purple. The optimal packing of hydrogen or deuterium into this structure would result in $KC_{24}2H_2$, or 1.2 wt%.

Experimental:

The Stage 2 K-intercalated graphite for this work was prepared by one of us (Dr. John Vajo of HRL Laboratories), using the 2-zone furnace technique. The starting material was a battery anode grade graphite designated G-1 from the company Diemasters. In addition to this sample, we attempted to synthesize this compound using a battery grade anode designated SL-20 from Superior Graphite. SL-20 has been shown to display excellent cycling and capacity behavior for Li battery applications.

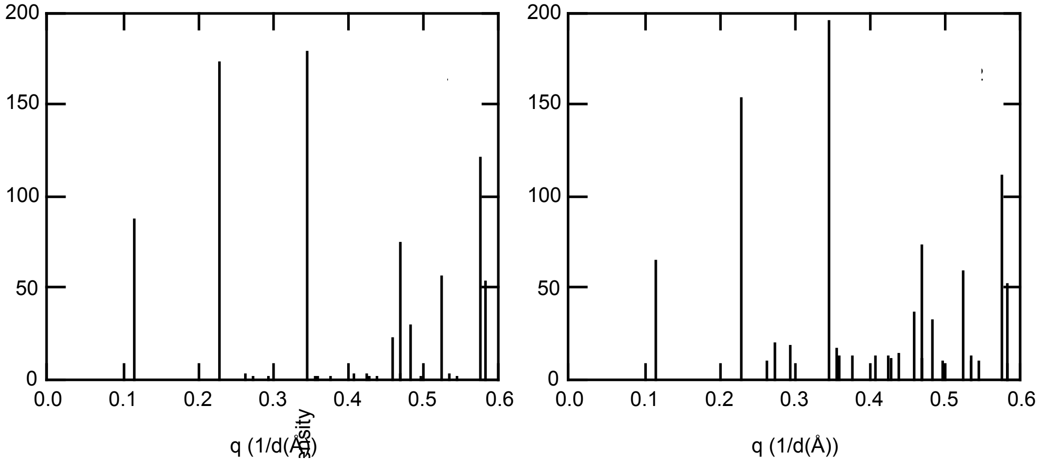

Fig. 2. Simulation of neutron diffraction data for perfect unit cells of KC_{24} and $KC_{24}2D_2$. We forced the basal plane spacing in this model to remain constant.

Three vanadium can assemblies, for the sample environment on the NPD neutron powder diffractometer at the Los Alamos National Laboratory, were designed and constructed at Caltech. These assemblies incorporated conflat and VCR fittings in such a way as to accommodate the large temperature range available to us using the displex cooler on NPD. The vanadium cans were purchased from B&J Enterprises, a company that specializes in the manufacture of V cans for neutron diffraction work. The stainless components were purchased from Norcal. All components were silver-soldered except for the vanadium-to-stainless joint, which was assembled using a high performance strain-gauge epoxy, M-bond 610 from Micro-measurements. These assemblies were tested to 77 K and 10 bar pressure of hydrogen. In addition, a gas manifold was assembled at Caltech in order to provide a range of D_2 overpressures, necessary to accommodate absorption during sample cooling.

Fig. 3 shows the V can assembly suspended from the displex assembly. Stainless tubing used to evacuate and admit D_2 can be seen running from the top of the V can assembly downwards and looping upwards toward the manifold. One of us (Dr. Donald Brown, the instrument scientist for NPD), performed the initial set-up and run prior to our arrival in order to insure that the sealed V can assemblies arrived with the Stage 2 compound intact. Fig. 4 below shows one of the first runs of the stage 2 compound IC-5 taken over a period of ~4 hrs. The lower trace shows a simulation of diffraction data for a perfect crystal of the KC_{24} compound. Lack of the basal plane graphite reflection at 3.35 Å indicates that no decomposition, or air exposure of this sample occurred.

Due to their air sensitivity, samples were analyzed by x-ray diffraction at Caltech by loading them into glass capillaries, sealing the capillaries, and then using an Inel 120° diffractometer with Co Kα radiation. The HRL sample designated IC-5 showed that no graphite remained and that the sample consisted essentially of pure KC_{24}, which was consistent with the blue color of the sample. The Caltech sample was shown to be a two phase material consisting mostly of Stage 4 compound with smaller amounts of Stage 3 material and trace amounts of graphite.

Fig. 3. Left figure shows the V can assembly sitting within the cryo-shield above the sample well of the NPD diffractometer at LANL. The right figure shows the experimental configuration with the sample assembly loaded into the neutron beam path. The displex unit can be seen atop of the sample well. The manifold is in the background and a turbo-molecular pump to the right center.

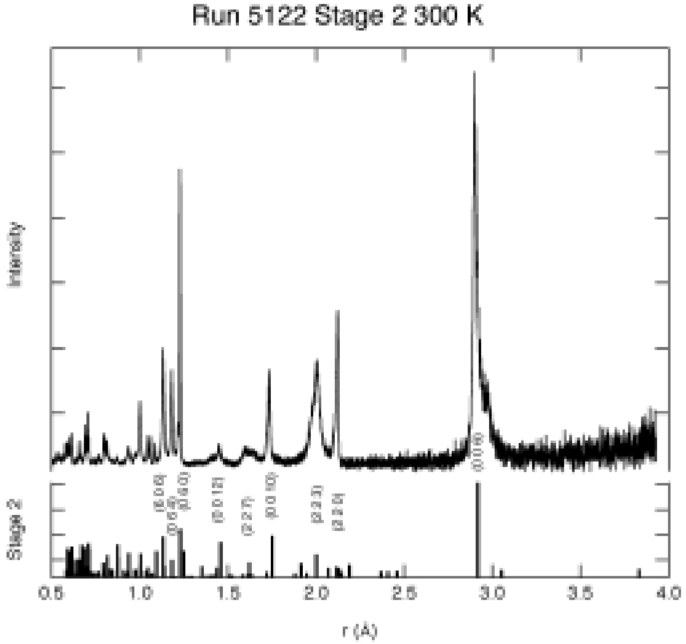

Fig. 4. NPD initial run of sample IC-5, a KC_{24} intercalated graphite compound. Simulated data is shown in the lower trace with major planar indices as noted.

Approximately 1 gm of each of these samples were loaded into the vanadium assemblies under Ar atmosphere in our glove box at Caltech and sealed and shipped to LANL. The third assembly was filled with a KC_8 sample, also prepared at HRL Laboratories.

We performed a series of runs at various temperature on both sample IC-5, the stage 2 compound, as well as the Caltech stage 4 compound. These runs were performed under both vacuum conditions, and deuterided conditions. A temperature series of experiments of this type has not been performed before.

The temperature series of runs for both samples is summarized below in Fig. 5. For the Stage 2 compound, we measured lattice parameter changes in basal plane reflections using the (0 0 6) diffraction located at 2.9 Å. This value is consistent with 1/6 of the value of the stacking sequence a-Kα-a-b-Kβ-b where the a-Kα-a separation is 5.4 Å and the a-b graphite spacing is 3.35 Å (for a total of 17.5 Å lattice parameter). The lower set of traces represent the temperature series collected under vacuum. For this set, we can see a reduction in the basal plane lattice spacings for the Stage 2 compound as the sample temperature is reduced. Lattice parameter shifts for both (0 0 6) and (0 0 10) reflections were measured as a check for consistency and we observe that both sets of reflections track.

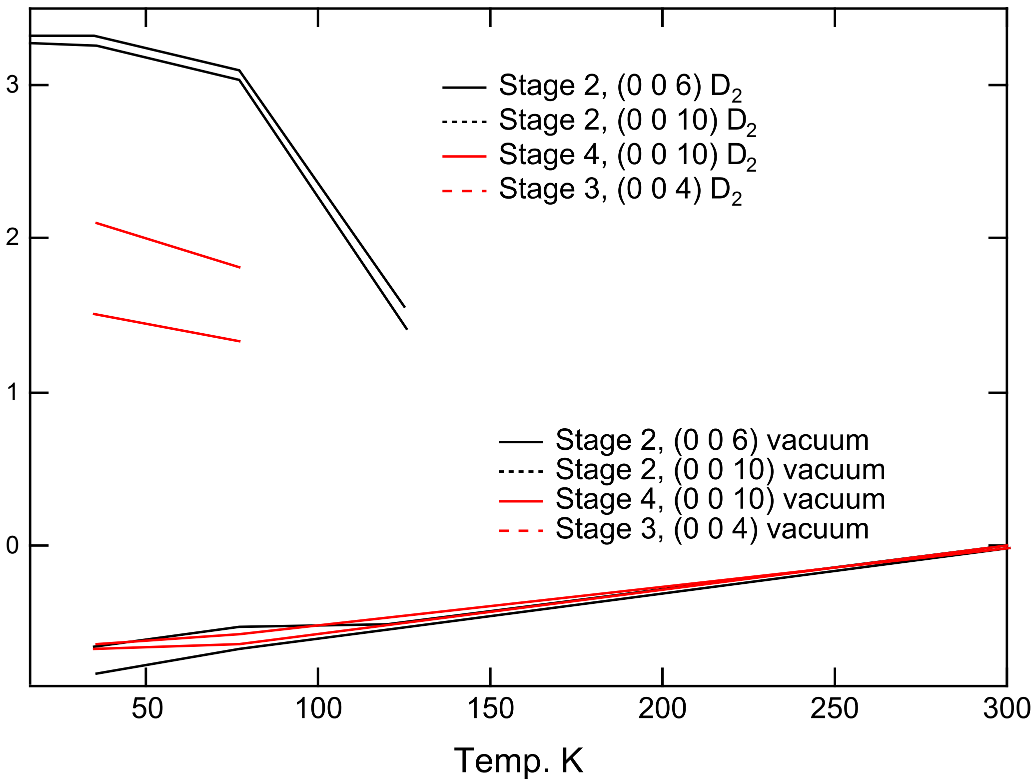

Fig. 5. Basal plane lattice parameter changes as a function of temperature for Stage 2 and Stage 4 compounds under vacuum (lower traces) and deuterided (upper left traces).

After the vacuum temperature series of data was obtained, we initially attempted to introduce D_2 to the sample at 77 K. No lattice expansion or other effect of the deuterium could be seen under these conditions. There is a possibility that at this temperature, the lattice is configurationally frozen and unable to accommodate D_2. There is also a possibility that the ends of the graphitic planes, which serve as conduits for D_2, became contaminated.

The sample was heated back up to 310 K under vacuum and D_2 reintroduced to a pressure of ~4 bar. When the temperature was reduced, an increase in the lattice parameter was then observed as seen in the upper left traces of Fig. 5. Again, both sets of basal plane reflections for the Stage 2 compound tracked and increased, indicating that deuterium was being accomodated by the lattice. We took measurements down to ~16 K but the lattice expansion appeared to saturate at ~35 K.

The NPD data for the 300 K run of the Stage 4 compound synthesized at Caltech is seen in Fig 6.

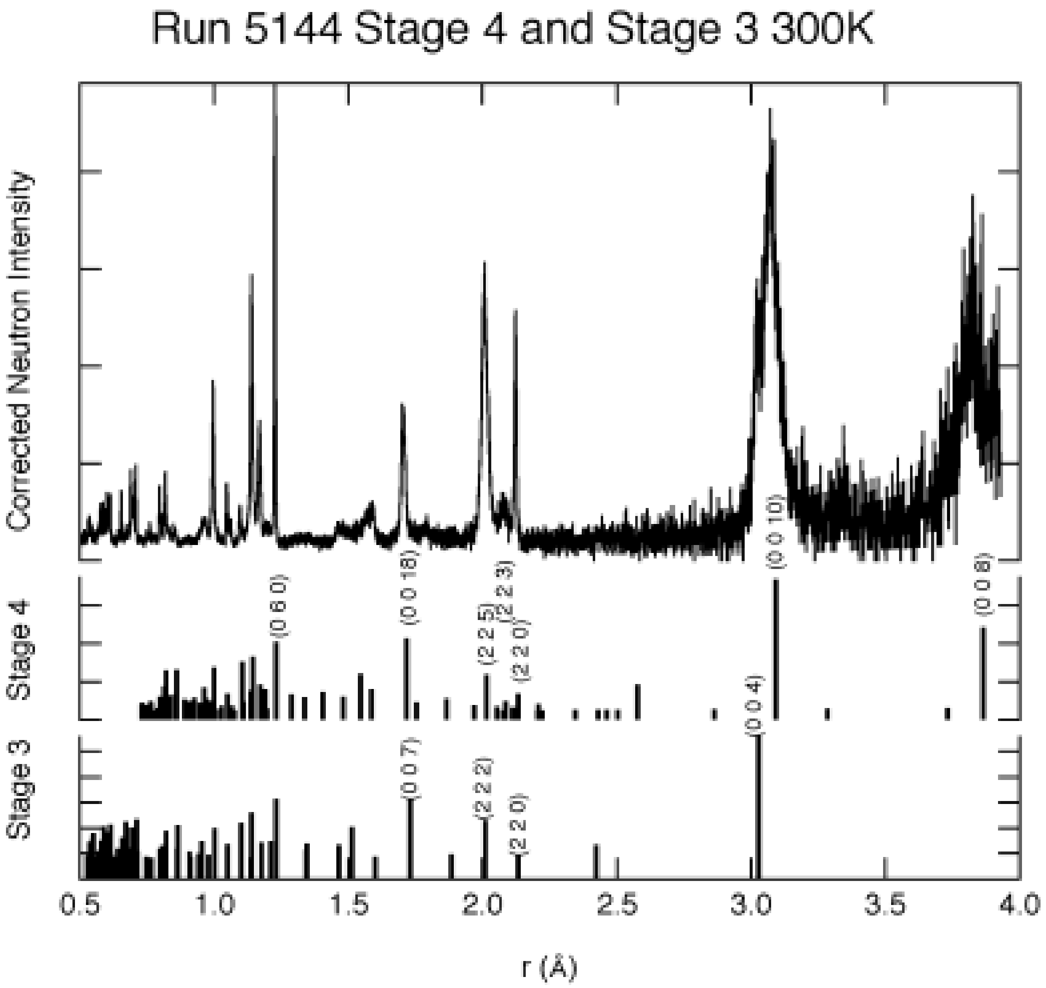

Fig. 6. Neutron diffraction pattern from Caltech Stage 4 intercalated graphite. Indexed simulated peaks appear in the lower traces. Reflections from a Stage 3 phase (0 0 4) at 3.02 Å overlap with the Stage 4 (0 0 10) reflection at 3.09 Å. Lattice spacing measurements were determined by gaussian deconvolution.

While the synthesis conditions used to make this sample were similar to the conditions used to make the sample IC-5 from HRL Laboratories, we believe that subtle differences in the nature of the starting graphite resulted in slower intercalation kinetics. Both the (0 0 10) reflection from the Stage 4 phase as well as the (0 0 4) reflection corresponding to the Stage 3 phase can be observed in Fig. 6. Simulated and indexed diffractions for both phases can be seen in the lower traces. For the Stage 4 compound, we used a 200 atom stacking sequence of a-Kα-a-b-a-b-Kβ-b-a-b (30.9 Å thickness) to define the lattice for our simulation. Each potassium layer of this compound is separated by four graphene layers. The stacking sequence for the Stage 3 simulation was a-Kα-a-b (12.1 Å thickness) and each potassium layer is separated by the graphene stacking sequence a-b-a.

Discussion:

The error in the Caltech synthesis which resulted in a Stage 4 and Stage 3 mixed phase compound, rather than a Stage 2 compound, turned into a fortuitous circumstance from an analysis standpoint. First, the lattice contraction of each phase of the mixed phase material (shown in red in Fig. 5), shows that under vacuum, the contraction of each phase is consistent with the lattice contraction of the Stage 2 material.

Of note however, is that an analysis of peak shifts of the basal plane reflections for each deuterided phase is consistent with lattice expansion occuring on the K-containing planes. On the basis of the relative distance difference between K layers, in a Stage 4 compound we would expect the expansion to be roughly half of that as in the Stage 2 material. In a stage 3 compound, we would expect the lattice expansion to be roughly 70% of that of the stage two compound. The deuterided traces of Fig. 5 seen in the middle of the left-hand side of the figure show this behavior. We believe that this is the first time that absorption of D_2 into higher stage intercalated graphites has been observed. We might also infer from this data that the nature of the interaction between D_2 is confined to the K-containing layer, and that this interaction is independent of the number of intervening graphene layers. This will be an important consideration for an intercalation type of graphitic system designed to maximize hydrogen storage sites.

We are still in the process of analyzing data from NPD but we are extremely pleased with the temperature trends that have emerged to this point.

There are two data analyses packages from LANL that we have yet to fully explore but which we will be using with our data over the next few months. The first of these is a Rietveld refinement package that comes as part of the Generalized Structure Analysis Software (GSAS) from LANL. The broadening of the peaks in our data indicates that the materials we prepared are not perfect crystallographically. We can use GSAS to gauge the level of strain-broadening which occurred as a result of synthesis and during deuteriding. We also hope that this package will provide some insights into extra diffraction peaks which have appeared in our data at lower temperatures in the presence of deuterium as seen in Fig. 7. This figure shows Stage 2 data under three different conditions. The vacuum data shows that the basal planes contract as discussed earlier, and also shows the large shift to higher lattice spacing upon deuteriding. In addition, new peaks at 2.63 and 2.78 Å appear in the data that were not present in the vacuum data. We are uncertain at this point as to the origin of these peaks but hope that GSAS will provide us with crystallographic insights. Even though our simulations on a particular model did not indicate new diffraction peaks, it may be that these peaks actually indicate a discernible degree of ordering of deuterium. For instance, The 2.78 Å reflection would correspond to a half-spacing distance of the C-K-C spacing, the layer within which the deuterium molecules occupy and it may be that the combination of lattice expansion of the C-K-C layer upon deuteriding yields three-dimensional ordering within this layer.

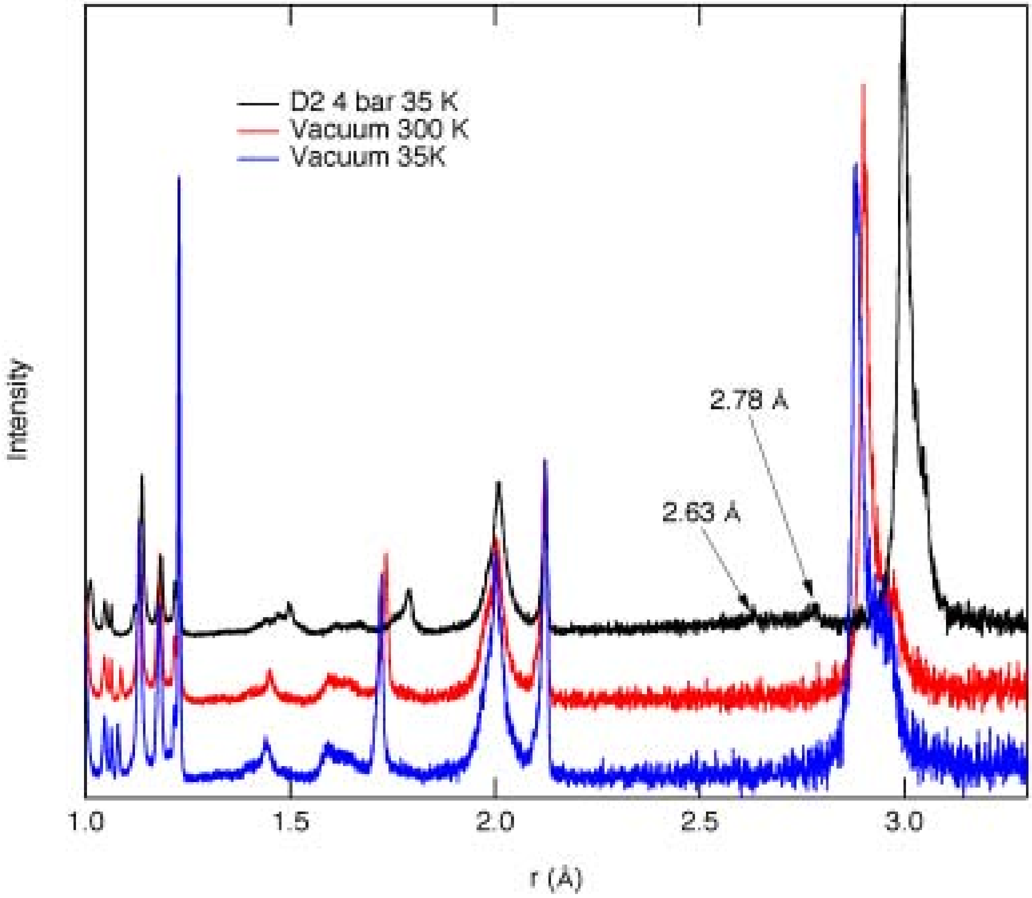

Fig. 7. NPD data from Stage 2 compound IC-5 obtained under both vacuum conditions and deuterided. Extra diffraction peaks appear in the deuterided phase at 35 K.

Another analysis approach that we can use with our data is Pair Distribution Function analysis (PDF). This analysis relies on back-transforming data from NPD in order to obtain near-neighbor distances.

Future Work:

We have already gained considerable experience in the synthesis and analysis of intercalated graphites and with help of Superior Graphite in providing pure flaked graphites, will continue experiments in optimization of intercalation of graphites. We have obtained SWNT material from Carbolex in order to test out the graphite intercalation "recipes" we have used so far, in order to study their suitability for intercalation. Unfortunately, this material is only available in as-prepared form and contains a NiY catalyst as a contaminant of the SWNT as shown in Fig 8. Regions of the nanotube rope structure can nonetheless be seen in this micrograph. Over the course of the next half year, we will begin to purify this material and obtain baseline measurements of isotherms of the as-purified materials.

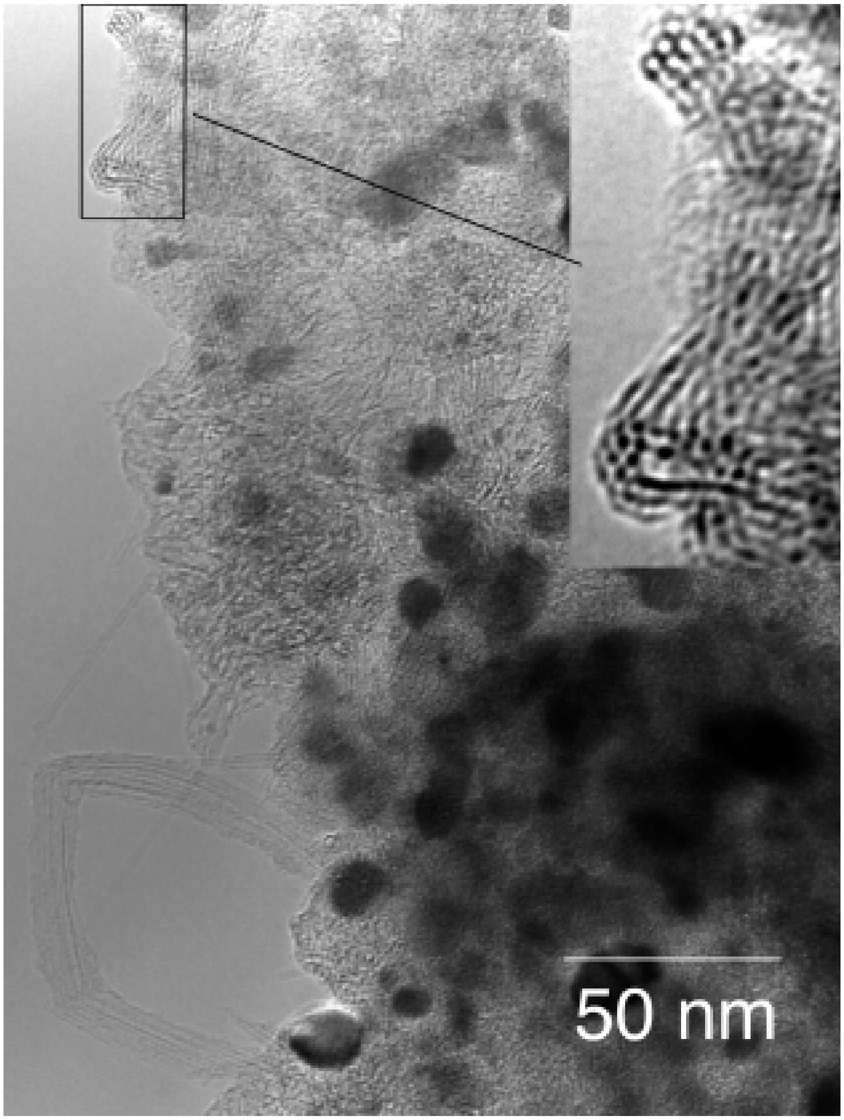

Fig. 8. Transmission electron micrograph showing AP-grade Carbolex SWNT material with 10 to 20nm sized catalyst particles sitting within the carbon matrix. In the upper right inset is a blow-up of the boxed region, showing some of the nanotubes, oriented in a way that the tube/rope cross-section is apparent.

To conduct isotherm measurements, we will be using the Sieverts apparatus of R. C. Bowman, Jr. at the Jet Propulsion Laboratory. This system is fully computer controlled is available for our use now.

References:

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