PHYSICAL REVIEW B VOLUME 51, NUMBER 21 1 JUNE 1995-I

Brief Reports

Negative pressure effects in high-pressure oxygen-intercalated C_{60}

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(Received 12 April 1994)

We have observed unexpected and as yet unexplained negative pressure effects in high-oxygen-pressure-treated C_{60} in which the orientational ordering temperature is greatly depressed. Such effects are not observed in identical studies with nitrogen.

INTRODUCTION

Solid C_{60} crystallizes in a face-centered-cubic structure, space group $Fm3m$, in which the C_{60} molecules are in continuous uncorrelated motion resulting in an orientationally disordered phase. Near 250 K, a first-order transition occurs to a phase with $Pa3$ symmetry in which there is motion of the molecules between symmetry-equivalent orientations.[1] We have employed high-pressure techniques to the study of this transition since pressure allows a continuous and reversible tuning of the strength of the intermolecular potential governing these structural changes. In the course of these experiments we discovered[2] a large increase of the transition temperature T_o with pressure (10–15 K/kbar depending upon the nature of the hydrostatic pressure medium). With N_2 or pentane, the value of dT_o/dP was 16 K/kbar while with He the value was near 11 K/kbar. We attributed this behavior to the relative ease with which He can penetrate into the interstitials of the C_{60} lattice resulting in a situation in which the pressure is acting upon each C_{60} molecule to a certain extent resulting in less compression of the lattice than with a pressure medium with larger species which cannot penetrate and acts predominantly upon the exterior of the crystal.

In this work we study the case of the situation when the pressure is applied for sufficient time to attain a measure of filling of interstitial lattice sites and the time constant for emptying these sites is long enough to observe negative pressure effects. The ordering temperature T_o is substantially *decreased* until such time elapses as to empty the sites occupied by the pressure medium.

EXPERIMENT

Samples were $>99.4\%$ pure C_{60} from Texas Fullerene. The material was sized by sieving so as to be between 75 and 85 μm and annealed at 500 K for 24 h under dynamic vacuum and subsequently stored in the dark. Characterization with uv and ir gave literature values for the C_{60} bands and powder x-ray diffraction gave sharp lines. Approximately 0.5 g samples were subjected to high-pressure loading of N_2 and O_2 at room temperature for various periods of time from 48 to 500 h. The ordering temperature T_o was monitored after release of the pressure by differential scanning calorimetry (DSC). Weight changes were monitored as a function of time using a Cahn microbalance for both the N_2- and O_2-loaded samples.

RESULTS

Figures 1 and 2 show reproductions of DSC scans of C_{60} exposed to 1 kbar of O_2 and N_2, respectively, for 48 h at room temperature. The scans were taken about $\frac{1}{2}$ h after release of the pressure. In the case of the O_2-pressure-treated sample, there are two well-resolved peaks or signatures, one at $\sim$240 and one at $\sim$260 K. The nitrogen-charged sample shows a broadened peak with a feature near 260 K, the usual position of the ordering temperature of an uncharged C_{60} sample. Similar sweeps were taken, several times in the first 24 h after

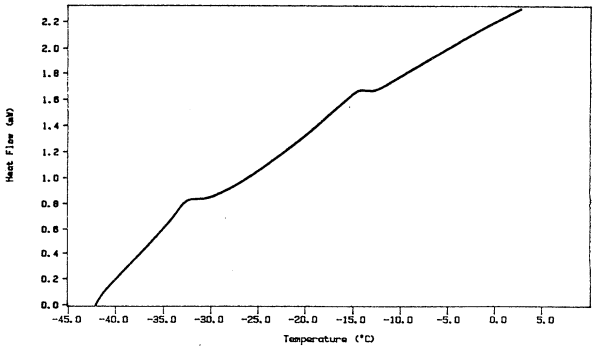

FIG. 1. Differential scanning calorimetry (DSC) scan vs temperature for sized C_{60} exposed to 1 kbar O_2 at room temperature for 48 h. Scan is about 30 min after pressure release.

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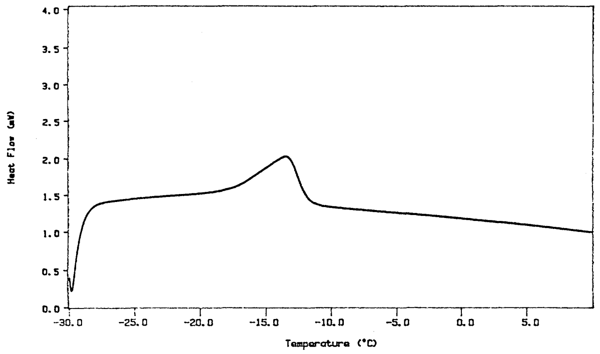

FIG. 2. All conditions identical to Fig. 1 except with N_2. The only difference between this plot and an uncharged (or long time after release) plot is a slight broadening of the peak.

release of the pressure, and then less frequently as the changes became smaller. Figure 3 shows the *difference* in temperature between signatures for an uncharged sample and the O_2-charged sample as a function of time in hours. We observe a very rapid change initially, followed by a much slower approach to the value of an uncharged sample where the two signatures converge.

In the case of the N_2-charged sample, the initial shift is at least an order of magnitude smaller and results in discernible broadening in some of the runs. This is difficult to quantify, but the broadening appears to disappear in roughly the same time frame as the O_2-charged material.

We have made weight loss measurements of 500–1000 mg quantities of both the O_2- and N_2-charged materials. These results are shown in Figs. 4 and 5 for samples exposed at room temperature for 48 h to 1 kbar of O_2 and N_2, respectively. In each case, good reproducibility was obtained on at least two runs on material which was sized and heat treated as described above.

DISCUSSION

Our weight loss experiments (Figs. 4 and 5) show that considerably more O_2 is intercalated into the C_{60} lattice than is the case of N_2 under identical loading conditions on the same material. It is difficult to accurately determine the initial doping of the C_{60} from the weight loss because of the rapid initial drop in weight and the very long (several weeks) tail on the loss curves. Our best estimate is that the O_2 occupancy of the octahedral sites is five times that of N_2 for the identical loading conditions. This is somewhat surprising because the sizes of the two molecules are really quite similar.

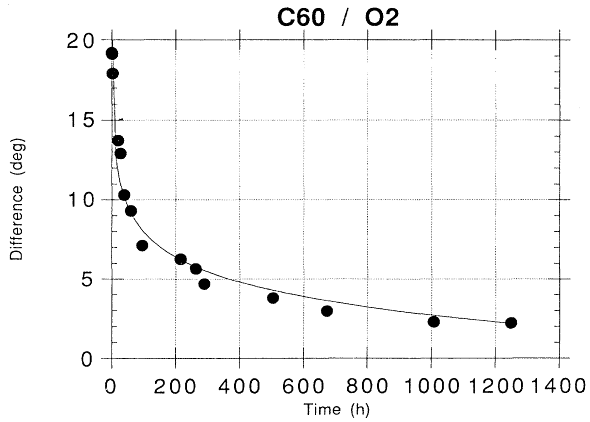

FIG. 3. Difference between peaks in O_2-charged C_{60} as shown in Fig. 1 as a function of time after release of pressure. The solid line is a smooth curve to guide the eye.

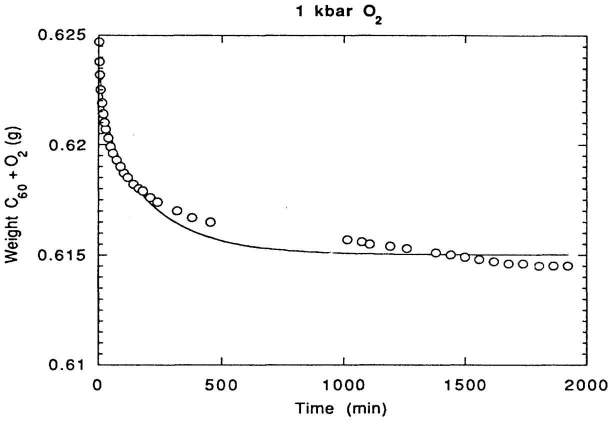

FIG. 4. Weight of sized C_{60} charged with 1 kbar O_2 at room temperature for 48 h vs time after release of pressure. The solid line is the best fit for gas diffusion out of a collection of spherical particles of uniform size.

From magic-angle spinning ^{13}C NMR we can *quantitatively* measure the O_2 occupation of the octahedral sites[3] and find that with 48 h 1 kbar pressurization about 40% of the sites are occupied. A 30 day pressurization results in about 75% of the sites being filled with O_2 using the same-sized C_{60} material. With N_2, at 1 kbar, 48 h pressurization at room temperature results in about a factor of 5 less incorporation of gas in the lattice. We expect that the N_2 is also in the octahedral sites but we have no direct confirmation of this as we do for O_2. We have been unable to detect any substantive structural changes in charged and uncharged C_{60} with x-ray diffraction. Direct measurement of the occupation site for O_2 and N_2 by

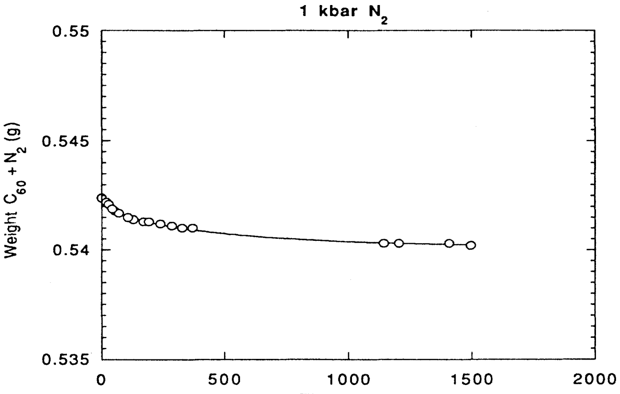

FIG. 5. All conditions identical to Fig. 4 except with N_2.

neutron diffraction will be carried out in the near future.

The large depression of the ordering temperature caused by intercalated O_2 is not easy to understand. While the larger shift with respect to N_2 can be partially accounted for by the greater amount of intercalate, the actual shift is considerably larger than what one would expect from a "negative pressure" alone. Since only 1 kbar was applied, a shift of $\sim 15\,^{\circ}\mathrm{C}$ at most would be predicted.[2] Instead $\sim 20\,^{\circ}\mathrm{C}$ is observed and the actual shift is probably larger at true zero time because of the ubiquitous very rapid initial change observed in all of our pressure-loading experiments.

Whether a chemical effect with O_2 is operative perhaps involving only a few percent of the C_{60} molecules is difficult to assess. We found that, under conditions of higher temperature and/or exposure to light and oxygen, there is formation of an amorphous polymerlike material which was difficult to characterize by any of the characterization techniques we have employed.

At this juncture, we can only conclude that there are very large "negative pressure" effects with O_2 which depress the ordering temperature of C_{60} substantially more than would be expected and which are not observed under identical conditions with N_2. This real difference in the behavior of O_2 from that of N_2 deserves further study as it could lead to techniques for separating these two gases—a goal of considerable technological importance.[4]

ACKNOWLEDGMENTS

This work was supported by the United States Department of Energy under Contract No. DE-AC04-94AL85000.

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