RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 17 1 MAY 1995-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Room-temperature compressibility of C_{60}: Intercalation effects with He, Ne, and Ar

J. E. Schirber
Sandia National Laboratories, Albuquerque, New Mexico 87185

G. H. Kwei
Lawrence Livermore National Laboratory, Livermore, California 94550

J. D. Jorgensen and R. L. Hitterman
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

B. Morosin
Sandia National Laboratories, Albuquerque, New Mexico 87185
(Received 27 December 1994)

We report measurements to 6 kbar of the room-temperature compressibilities of C_{60} for both the fcc and sc phases using He, Ne, and Ar as pressure media. The effects of rare-gas intercalation on the fcc-to-sc transition and on the compressibilities are discussed and we compare our results with the widely disparate literature values reported for the fcc compressibility.

INTRODUCTION

Pressure has been shown to be an important variable in the study of C_{60} and intercalated C_{60} compounds. Early studies of the effect of hydrostatic pressure on the orientational ordering temperature of C_{60} uncovered unexpected differences in the pressure dependence of this transition with different pressure media.[1] The observed pressure for this transition was about 30% smaller with pentane or nitrogen than with He. This was interpreted as due to interpenetration of He into the lattice of C_{60} resulting in less compression of the C_{60} lattice than with a pressure medium which did not penetrate the lattice over the time span of the experiment. Magic-angle spinning ^{13}C NMR measurements of high pressure oxygen loaded C_{60} allowed an unambiguous identification of the octahedral sites as the location of the O_2 as well as a quantitative measurement of the release with respect to time from the lattice.[2] Subsequent differential scanning calorimetry (DSC) studies[3] of similar high pressure loaded C_{60} showed an as yet not understood "negative pressure" effect in which the orientational ordering temperature was depressed 10's of degrees with O_2 loaded C_{60} while negligible effects were observed with N_2.

The discovery[4] that C_{60} could be intercalated with alkali metals to form superconductors with transition temperatures, T_c, as high as 40 K has also led to a large field of investigation including extensive studies of the pressure dependence of T_c. These measurements coupled with mixed alloy studies resulted in T_c versus lattice parameter relations which have been important in the theoretical modeling of the superconductivity. However it has been recently shown[5] that, as in the case of pure C_{60}, incorporation of gaseous species in the interstitial location can result in substantial change in the pressure derivatives, particularly for the Na based materials.

In both these situations it is clear that accurate measurements of the compressibility of C_{60} and its compounds with due consideration of the effects, if any, of pressure media intercalation are required in order to convert effects of pressure into effects of lattice parameter. This is important because modeling and theoretical considerations invariably involve volume or lattice parameter variation. Unfortunately there is considerable disagreement in the values of the compressibility currently available in the literature.[6–9]

In order to provide this compressibility information and to attempt to understand these intercalated gas phenomena, we have initiated neutron diffraction experiments under high pressure (to 6 kbar) using various gases as the pressure media. This study describes room-temperature measurements of the lattice parameter of C_{60} using He, Ne, and Ar.

EXPERIMENTAL

C_{60} (99.6% nominal purity) from commercial sources was subjected to slow progressive heating up to 400 °C for several days in order to remove all solvents and occluded N_2 and O_2. The powdered sample (~3 g) was loaded into a thin walled vanadium tube which was inserted into the aluminum

0163-1829/95/51(17)/12014(4)/$06.00

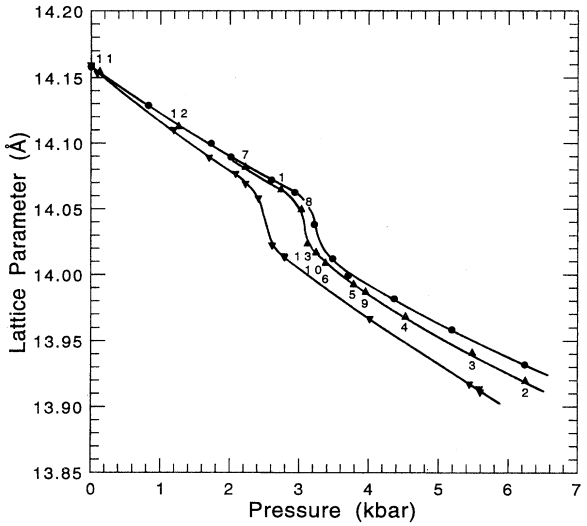

FIG. 1. Lattice parameter vs pressure for C_{60} at room temperature ●, ▲, ▼ denote He, Ne, and Ar data, respectively. The Ne points are numbered in the order they were taken.

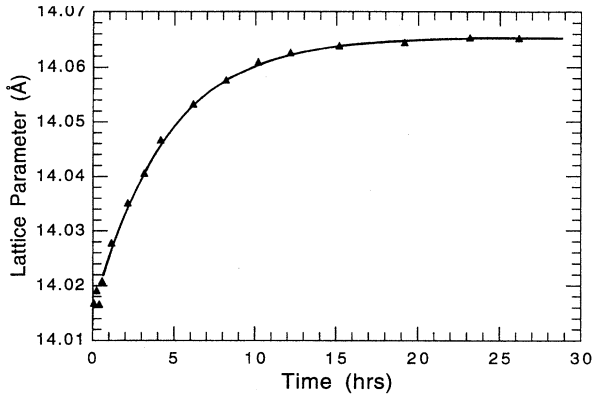

FIG. 2. Lattice parameter vs time for a pristine C_{60} sample exposed to Ne at 2.75 kbar. Note that the material is in the sc structure initially, passes through a mixed phase (evident from the spectra) and ends up in the fcc phase. The error in the lattice parameter is always less than the size of the plotted point.

pressure cell described in detail elsewhere.[10] Data were collected at room temperature (296 K) on the 90° detector banks of the special environment powder diffractometer at Argonne National Laboratory's intense pulsed neutron source (IPNS).[11] Due to shielding that is an integral part of the pressure cell, this scattering angle provides data that are completely free of background scattering from the walls of the cell. In separate experiments with fresh samples, helium, neon, and argon were used as pressure media, with the maximum pressure being 6 kbar in all cases. Typical data collection times were about one hour.

With He as the pressure medium, we know from previous attempts to measure accumulations in the lattice, that the time constant for diffusion into the lattice is very short, probably minutes. Measurements[2] of proton NMR on C_{60} loaded to one kbar H_2 showed that H_2 is released (to half its initial value) in <30 minutes. Therefore, we expected no He retention. With Ne and Ar the degree of penetration was not known, so loading as a function of time was an issue which will be described below.

RESULTS

The lattice constants of C_{60} at 295 K as a function of pressure using He (nominal radius 0.93 Å) gas as the pressure medium are shown in Fig. 1. The lattice parameters were obtained from least-squares refinement of time-of-flight (TOF) neutron spectra using a Rietveld structure refinement code (generalized structure analysis system or GSAS)[12] over a d-spacing range $2.6 \leq d \leq 5.5$ Å. This data range includes seven prominent Bragg peaks which provide a typical statistical standard deviation of 0.0005 Å for data from a one hour run. Date were taken both increasing and decreasing the pressure and the points (for Ne) are numbered to show the sequence in which they were taken. The first-order orientation ordering transition from $Fm3m$ (fcc) to $Pa3$ (sc) is quite evident and the transition pressure agrees well with that reported by Samara *et al.*[1] We could detect no hysteresis; however, our nominal one hour data collection time might obviate observation of effects at shorter time scales. There was no detectable broadening of the lines of the spectra at pressure or with pressure cycling except the expected effects in the transition region which is clearly two phase.

Our results with Ne (nominal radius 1.12 Å) were somewhat unexpected. We found that Ne indeed penetrates the lattice approaching a saturation value in about 24 hours. This is shown clearly in Fig. 2 where we plot the lattice parameter versus time at a pressure of 2.75 kbar. This corresponds to a position on a pressure versus temperature plot where the structure would have fcc symmetry with He as the pressure medium and (according to the data of Samara *et al.*[1]) have primitive symmetry with a nonpenetrating medium. We observed initially the primitive structure with its reduced lattice parameter but with time the lattice parameter increased as shown in Fig. 2 passing through a mixed phase region before transforming completely into the fcc structure. After saturation with Ne we mapped out the lattice parameter versus pressure curve as shown in Fig. 1. We notice that the orientational ordering transition pressure is discernibly lower than with He. Upon release of the Ne pressure, the lattice parameter returned to the same value as that observed at zero pressure with He. In other words, there was no sign of a negative pressure effect[3] such as we observed earlier with O_2. This would suggest that the Ne is released from the lattice much more rapidly than it goes in under pressure.

With Ar (nominal radius 1.54 Å) we expected little or no penetration into the lattice. To check this we held a pristine C_{60} sample annealed as described above at 5.5–6 kbar Ar pressure for six days. We then collected the lattice parameter data versus pressure data shown in Fig. 1. We observe a further decrease in the pressure at which the orientational ordering temperature takes place as suggested by Samara *et al.* for a nonpenetrating pressure medium and substantially smaller lattice parameter at a given pressure than observed in He (and Ne). Release to zero pressure gave the same lattice parameter as we observed with the He experiment.

In order to test for Ar intercalation, we pressurized quickly (~ 30 minutes) a pristine C_{60} sample to 5.5 kbar. We observed exactly the same lattice parameter as we did on the

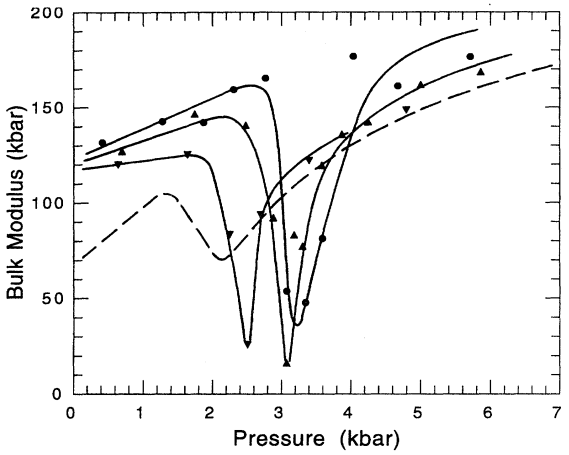

FIG. 3. Bulk modulus B (defined as $-V\,dP/dV$) vs pressure for C_{60}. ●, ▲, ▼ denote He, Ne, and Ar data, respectively. The dashed curve is the data of Lundin and Sundqvist.

sample that had been held for six days near 6 kbar. This provides additional evidence that Ar does not enter the lattice under the time scales of our experiments.

DISCUSSION

The results shown in Fig. 1 indicate that we have spanned the spectrum from facile penetration of the pressure medium with He to complete (for the time scale of weeks) exclusion with Ar, with Ne representing the intermediate situation in which substantial intercalation occurs in 24 hours. There have been a number of determinations of the compressibility or bulk modulus of C_{60} using various techniques.[6–9] The agreement is far from satisfactory. The first determinations[6,7] involved lattice parameter measurements at high pressures (>10–20 kbar) in diamond anvil cells. Experiments at these pressures result in transformation to the sc phase and therefore involve changes in the lattice parameter resulting from the orientational phase change ($\sim 1\%$ in $\Delta V/V$) in addition to the compressibility.

The most comprehensive measurements reported to date are those of Lundin and Sundqvist[9] who used a piston and cylinder technique to 10 kbar on C_{60} at various temperatures. In principle, this technique should give the bulk moduli without any complications of pressure medium intercalation because the C_{60} sample is compressed directly; that is, the C_{60} itself is the pressure medium. Unfortunately, the comparison with extrapolations of other measurements[6,7] differ by a factor of 2 or more. Another surprising feature of the data of Lundin and Sundqvist[9] is a very large pressure dependence of the bulk modulus ($-V\,dP/dV$) in both the fcc and sc phases. In Fig. 3 we show a smoother curve of the B versus pressure data of Lundin and Sundqvist compared with our data for He, Ne, and Ar. Here we have taken the differences between adjacent lattice parameter points, calculated B and plotted at the average pressure for the two points.

Several features are noteworthy in Fig. 3. The B versus pressure plot gives an easily identifiable transition pressure, the region of maximum change in lattice parameter which appears as a sharp minimum. The piston and cylinder work evidently broadens the transition substantially as compared with the gaseous media. The value of the transition as a function of pressure is very sensitive to temperature since dT_0/dP is ~ 16 K/kbar in N_2 and ~ 11 K/kbar in He. Some of the difference in the actual value of pressure for the transitions between our data and that of Lundin and Sundqvist may stem from this effect.

We differ strongly from Lundin and Sundqvist[9] in the value of B_0, the initial $P=0$ bulk modulus, and in the pressure dependence of B in the fcc phase. Our values for B in the simple cubic phase are in much better agreement with these authors for our Ar and Ne data. The He value for B appears to be converging near 6 kbar with all of the determinations as shown in Fig. 3.

The large difference between B_0 for the fcc and simple cubic phases reported by Ref. 9 is not found in our study. For argon, the values of B appear to smoothly merge across the phase transition which unfortunately severely limits the accuracy of determining B_0 for the simple cubic phase. Our estimated uncertainty in B is less than a few percent depending upon the size of the pressure increment over which the lattice constant (± 0.0005 Å) change is calculated. Our pressure uncertainty is ± 0.01 kbar.

In the sc phase, our values for B at about 6 kbar appear to be close to 170 kbar for all three gases. This agrees with the value given by Lundin and Sundqvist. Unfortunately we cannot tell from our data whether B continues to rise at the rapid rate given by Lundin and Sundqvist or at a more modest rate because of the upper limit of 6 kbar for our pressure cell. Also, it is difficult to decide whether the differences between our He and Ar, Ne results in the sc phase stem from intercalation effects or from remnants of the phase transition.

A further point to be drawn from the comparison in Fig. 3 is that the extrapolation to B_0 in the fcc phase for our data for all three gases He, Ne, and Ar gives the same value of $B_0=120$ kbar. This is in spite of the quite different behavior of these three pressure media. The He appears to go in and out of the lattice instantaneously on the time scale (about an hour) of our experiments. Ne penetrates the lattice on a time scale of ~ 24 hours (Fig. 2), and Ar shows no sign of penetration over a time scale of about a week. The fact that our data shows smooth variation with pressure even though the points were taken in somewhat random order indicates that hysteresis effects are not large. If this common value of B_0 is not just fortuitous it would seem to indicate that B varies in a linear fashion with pressure albeit at different rates for these three different situations but from the same initial bulk modulus. Our value of B_0 agrees well with the calculations of Burgos, Haloc, and Bonadeo.[13]

CONCLUSIONS

We have measured the room-temperature lattice parameters as a function of pressure for C_{60} in the range of 0–6 kbar using He, Ne, and Ar as pressure media. Compressibilities were determined as a function of pressure in both the fcc and sc lattice. He intercalated easily resulting in a substantially higher transition pressure for the fcc-sc orientational ordering pressure. Ar does not penetrate the lattice and results in a transition pressure in agreement with the literature value using nonpenetrating media such as pentane or N_2. Ne is shown to slowly penetrate the lattice and the transition

pressure is found to be intermediate to that found with He and Ar. The initial bulk modulus in the fcc structure is found to be 120 kbar with all three media, compared to the value of 68 kbar reported from piston and cylinder measurements. The bulk modulus near 6 kbar determined in He, Ne, and Ar is near 170 kbar in reasonable agreement with accepted literature values. Our work shows the importance of intercalation of gaseous media in pressure studies of C_{60}. Other media may also intercalate. In Ref. 1 it was shown that pentane resulted in irreversible effects at high temperatures, so this effect must be considered in light of the specific conditions of time, temperature, and pressure with any choice of pressure medium.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy and funded in part by its Office of Basic Energy Sciences (OBES), Division of Materials Sciences under Contract No. DE-AC04-94AL85000 at Sandia National Laboratories, under Contract No. W-7405-ENG-48 at Lawrence Livermore National Laboratory, and Contract No. W-31-109-ENG-38 at Argonne National Laboratory. IPNS at Argonne is funded as a national user facility by the OBES, Division of Material Sciences.

[1] G. A. Samara, L. V. Hansen, R. A. Assink, B. Morosin, J. E. Schirber, and D. Loy, Phys. Rev. B **47**, 4756 (1993).

[2] R. A. Assink, J. E. Schirber, D. Loy, B. Morosin, and G. A. Carlson, J. Mater. Res. **7**, 2136 (1992).

[3] J. E. Schirber, R. A. Assink, G. A. Samara, B. Morosin, and D. Loy, Phys. Rev. B (to be published).

[4] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature (London) **350**, 600 (1991).

[5] J. E. Schirber, W. R. Bayless, M. J. Rosseinsky, O. Zhou, R. M. Fleming, D. W. Murphy, and J. E. Fischer (unpublished).

[6] J. E. Fischer, R. A. Heiney, A. R. McGhie, W. J. Romanow, A. N. Denenstein, J. P. McCauley, Jr., and A. B. Smith III, Science **252**, 1288 (1991).

[7] S. J. Duclos, K. Brister, R. C. Haddon, A. R. Kortan, and F. A. Thiel, Nature (London) **351**, 380 (1991).

[8] A. Lundin, B. Sundqvist, P. Skoglund, A. Fransson, and S. Pettersson, Solid State Commun. **84**, 879 (1992).

[9] A. Lundin and B. Sundqvist, Europhys. Lett. **20**, 463 (1994).

[10] J. D. Jorgensen, S. Pei, P. Lightfoot, D. G. Hinks, B. W. Veal, B. Dabrowski, A. P. Paulikas, and R. Kleb, Physica C **171**, 93 (1990).

[11] J. D. Jorgensen, J. Faber, Jr., J. M. Carpenter, R. K. Crawford, J. R. Haumann, R. L. Hitterman, R. Kleb, G. E. Ostrowski, F. J. Rotella, and T. G. Worlton, J. Appl. Crystallogr. **22**, 321 (1989).

[12] A. C. Larson and R. B. Von Dreele (unpublished).

[13] E. Burgos, E. Haloc, and H. Bonadeo, Phys. Rev. B **47**, 13 903 (1993).