Detailed Mapping of Reaction Diagrams for Metastable Phases

Journal:	2012 MRS Fall Meeting
Manuscript ID:	Draft
Manuscript Type:	Symposium MM
Date Submitted by the Author:	n/a
Complete List of Authors:	Sundqvist, Bertil; Umeå University,
Keywords:	Raman spectroscopy, polymerization, C

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Detailed Mapping of Reaction Diagrams for Metastable Phases

Bertil Sundqvist

Department of Physics, Umeå University, SE-90187 Umeå, Sweden

ABSTRACT

A method is presented to map reaction diagrams for metastable phases by treating a rod-shaped sample under high pressure in a known temperature gradient, such that each point on the sample is treated at a unique, known temperature. After quenching to ambient conditions the structural properties of the sample can be studied by spectroscopic or other techniques. The accuracy and resolution in temperature is mainly limited by the uncertainties in the measured temperature distribution during treatment and the uncertainty in position during analysis. The method is tested by re-mapping the polymerization reaction of C_{60} under high pressure in the range 0.8 – 2 GPa. Preliminary data show surprisingly sharp "reaction boundaries" at certain temperatures, signalling the onset of dimerization and polymerization of the material.

INTRODUCTION

One of the largest sub-fields in High Pressure Materials Science is the use of high pressure as a tool to create new materials with novel, interesting and advanced properties. The ultimate goal is usually to be able to bring such materials back to atmospheric pressure in the form of metastable structures or phases. When such metastable phases have been identified, it is useful to make a reaction map to optimize the reaction conditions for practical production of the new material. Making such a map can be extremely time-consuming, since a large number of high pressure experiments need to be carried out, and because of the unavoidable measurement errors in temperature and pressure in each experiment the details of such maps are not always very accurate. As a case in point, the high pressure polymerization reaction of C_{60} has been studied by many authors (see reviews [1-3]), but there are still many gaps in our knowledge and in many cases there is a strong disagreement as to what polymeric structures, and in what ratio, are produced after treatment at a given pressure and temperature.

In this contribution, a simple method to speed up the mapping of such diagrams is presented. In this method a single sample is treated over a wide range of temperatures at constant pressure by submitting a long thick film (or rod) specimen to a known temperature distribution. After quenching, the sample is recovered at atmospheric pressure and any metastable phases can be studied by spectroscopic or other methods. Because the treatment temperature at any point on the sample is known, the sample provides in effect a constant-pressure profile through the pressure-temperature plane along its length. The pressure error should be practically the same at all points, and at least the relative temperatures will always be very well defined compared with those measured in a set of individual single-point experiments.

This contribution gives a detailed description of a practical realization of the method, discussing many experimental problems. To illustrate the usefulness of the method it has recently been applied to a re-mapping of the polymerization reaction diagram of C_{60} and preliminary results from this experiment are presented below.

EXPERIMENTAL METHOD

The high pressure experiments were carried out in a large piston-cylinder device with an internal diameter of 45 mm. The pressure was calculated from the load by an empirical function obtained in a separate experiment using a Manganin gauge calibrated against the freezing point of mercury [4]. The sample assembly was placed in a TeflonTM cup with an internal diameter of 39 mm and height 20 mm, fitting into this cylinder. All connecting wires (3-4 Cu wires and six Constantan wires) were fed through the bottom of the cup and along the edges of a 7 mm thick TeflonTM plate, pressed down into the bottom of the cell to act as both pressure transmitting medium, thermal insulator and sample support. After some preliminary experiments it was found that a temperature difference of up to 200 K could be generated between the ends of a 0.3 mm thick copper strip, 4 mm wide and about 35 mm long. This strip was provided with a heater at one end and was placed horizontally on the TeflonTM support as a substrate for the sample, as shown in Figure 1. The sample, in the form of a fine powder, was distributed evenly on this substrate. The amount of powder used was calculated/weighted to form a 0.2 mm thick layer after compression into a solid film. In most experiments, a 50 μ m thick copper foil was then used to cover the sample before a thin layer of talc was applied to improve the hydrostatic conditions. The remaining volume in the cell was filled with a second 7 mm thick TeflonTM plate and, if necessary, a small amount of talc powder, before the cell was inserted into the pressure vessel.

A rather large heater power is required in this experiment and a very good heat transfer between heater and substrate is desirable. At the same time the sample substrate is used as part of the temperature sensor system and the heater must be very well insulated electrically from the substrate. In the first set of experiments, the heater was placed on the mantle of a copper cylinder with the substrate end in the centre. The cylinder was split along the axis and the two halves were placed one on each side of the copper strip, after which the composite cylinder was inserted into a cylindrical (insulating) pyrophyllite sheath with a KanthalTM heater wire. Because the average distance between heater and copper strip was several mm this heater was rather inefficient, and a heater power of 45-70 W (depending on pressure) was needed to obtain a sample temperature of about 600 K at the hot end of the strip. In a later modification, thin (1.5 mm) pyrophyllite insulating plates were glued directly on each side of the strip and the heater wire was wound onto this, resulting in more efficient heat transfer. In both cases, a layer of ceramic cement on the outside of the heater wire provided both mechanical protection and further electrical and thermal insulation. Openings were cut in the Teflon support plates to make space for the heater, as shown in Figure 1. To reduce heat loss (see below), this space was filled with a thermally insulating mixture of glass beads and talc powder [5].

The temperature T was measured at six approximately equidistant points along the copper substrate by putting six thin (0.25 mm) Constantan wires perpendicularly across it, as shown in Figure 1. These thin wires were connected to 0.4 mm Constantan connection wires by soldering near the outer wall of the cell, such that most of the temperature drop occurred over the thin wires

Figure 1. A typical pressure cell containing a copper substrate with heater and Constantan thermocouple wires before filling with sample material.

close to the sample. The thermocouples were completed by soldering a copper connection wire to the cold end of the copper substrate. The Cu-Constantan (type T) combination used was calibrated in a separate experiment against a calibrated Si diode, a previously calibrated type K thermocouple and a standard Pt-100 sensor, the outputs of which all agreed to well within their combined uncertainties. The thermocouple error is believed to be smaller than ± 0.2 K below 450 K, increasing smoothly with temperature to ± 1.5 K at 750 K. However, the error in the measured temperature distribution is larger because of geometrical uncertainties. To avoid impurities the Constantan wires were not fixed to the sample substrate before the application of pressure, and in some cases these wires moved during the initial stage of the experiment. The relative final positions of the Constantan wires could in principle be measured very accurately from the imprints of the wires in the copper strip and the thin foil cover, but even a small deviation from the perpendicular position gives an appreciable uncertainty in the actual position of the contact point. The estimated uncertainty in the absolute temperature at any particular point in the sample may thus be of the order of 1-5 K, although the inaccuracy of the relative temperatures is very much smaller.

An additional difficulty in estimating the true treatment temperature is the fact that the high power level used leads to a continuous increase in the temperature of the pressure cell. This means that while it was possible to keep the indicated temperature T_1 at one single point stable to within better than ± 0.2 K over one hour by slowly decreasing the heater power by a few percent, the temperatures at all other points drifted slowly with time. Since the bulk cell temperature always increased, T slowly increased at all measurement points with temperatures lower than T_1 and decreased at all points with a higher temperature. Using the original large heaters the maximum change over one hour was about 2-3 K, usually at the lowest temperature point. To minimize the temperature drift, care was taken to make the heat transfer from heater to sample as large as possible and to insulate the heater thermally from the bulk of the cell using glass beads (see above), such that the waste heat was minimized.

In the present experiments the sample was always quenched to room temperature at the end of the treatment period, before the pressure was reduced to zero. After the experiment the original sample powder had always been compressed into a solid film or plate. Because the

material did not adhere strongly to the Cu surface and the thickness of the sample film after compression was similar to the diameter of the thermocouple wires, it was usually possible to remove the sample in the form of thin plates corresponding to the sections between the thermocouples. The sample plates were flipped over and glued to glass microscopy slides with the heated side upward, carefully keeping track of their original positions and orientations in the cell.

After the experiment all samples were studied by Raman spectroscopy using a Renishaw 1000 notch filter spectrometer. Spectra were obtained from the side of the sample in contact with the copper strip. The temperature at each measurement point was deduced from its position along the strip, measured by moving each sample plate in the spectrometer on a sample stage equipped with a micrometer screw with 10 μm resolution, corresponding to a resolution in relative temperature of the order of 0.1 K.

EXPERIMENTAL TEST: MAPPING THE POLYMERIZATION REACTION OF C_{60}

Experimental details for the study on C_{60}

The method described above was tested by re-mapping the polymerization reaction diagram for C_{60} in the range up to 2 GPa and about 500 K. To obtain accurate results we used nominally 99.8 % pure C_{60} , obtained from Term USA, Fort Bragg, CA. The sample was pre-sublimed to get rid of all solvent impurities and before the experiments it was further treated at 200°C for at least 24 h under dynamic vacuum to remove water and atmospheric gases. Raman measurements on this pre-treated material showed sharp Raman lines from monomeric C_{60} only. To avoid photopolymerization the purified samples were always stored in the dark under pure argon gas and the pressure cells were loaded in the same argon-filled glove box as used for sample storage. In most experiments the pressure was first increased to the desired value before the sample was heated to the final temperature. However, at the lowest pressures (at and below 1 GPa) the sample was brought to its final temperature at 0.5 GPa before the pressure was increased to the final value in the polymerization zone. At 1 GPa, one sample was treated by each method but no significant difference could be found between the final results.

All samples were heat treated for one hour at the selected pressures. Earlier studies have shown that the high pressure polymerization reaction is usually fully completed within a few minutes to half an hour [1-3, 6], and the results obtained here should thus represent the end-point of the polymerization reaction at each pressure-temperature condition visited. As discussed above, the temperature is not perfectly stable with time. Considering that the polymerization reaction should be completed within about 15 minutes and that no de-polymerization reaction involving a decrease in the number of intermolecular bonds has been observed when re-treating a polymerized sample at lower temperatures in this range of pressures [7], the "true treatment temperature" at each thermocouple position was estimated as the highest average temperature measured during any 15 minute period of the experiment.

To avoid photopolymerization all Raman studies reported here were carried out using a low energy (IR) excitation laser with a wavelength of 830 nm. Lasers with an energy exceeding the band gap of C_{60} (such as 514 or 488 nm Ar^+ ion lasers) rapidly polymerize the material, while the standard 633 nm HeNe laser gives a very strong fluorescence signal. Also, all pressure cells were opened under red darkroom light only and the pressure treated samples were stored in closed (dark) containers.

Experimental results

In the work reported here, high pressure experiments were carried out at each 0.2 GPa in the range 0.8 to 2.0 GPa, with maximum temperatures in the range 540–650 K. In this part of the pressure-temperature plane, C_{60} may form dimers $(C_{60})_2$, longer chains, or even two-dimensional structures in the form of a layered tetragonal structure [1–3]. Polymerization changes the lattice and molecular symmetries in characteristic ways, shifting some Raman peaks and allowing other, previously forbidden, lines to appear. Both the original C_{60} monomer and the various polymeric phases have well defined Raman fingerprints. The simplest way to identify the various structures is to study the so-called "pentagonal pinch" mode which in pristine C_{60} is found at 1470 cm^{-1} . The formation of intermolecular bonds changes the molecular surface electron density, leading to a predictable shift of this line with the number of intermolecular bonds. For dimers, which have one pair of intermolecular C-C bonds, the shift is -5 cm^{-1} , while molecules in chains have bonds to two neighbors and a shift of -10 cm^{-1} . In the preliminary analysis of the high pressure treated samples, a peak fit software [8] has been used to fit Voigt peaks at the known Raman frequencies of the pentagonal pinch line to the experimental data. Plotting the relative intensities (areas) of these peaks as a function of temperature at each pressure we get diagrams such as that shown in Figure 2. It should be noted that the relative intensities cannot be translated directly into relative concentrations of different structures because of their very different Raman cross sections.

The intensity diagrams show some interesting and unexpected features. The most obvious one is the presence of sharp boundaries at which the relative intensities of different lines show sudden changes, for example near 377 and 401 K in Figure 2. Below 377 K the intensity of the dimer line is low ($< 10\%$ of the total intensity) and increases very slowly with increasing T, but above 377 K it is significantly higher and increases rapidly with T. This increase is mirrored by

Figure 2. Relative Raman intensities obtained from fits to the various components of the pentagonal pinch mode near 1470 cm^{-1} for a sample treated at 1.4 GPa. Blue circles monomer, red squares dimer, black inverted triangles linear chains, red triangles branched chains, and filled triangles tetragonal 2D phase. Lines are guides for the eye only.

a corresponding decrease in the intensity from monomers. Above the same boundary a small, almost temperature independent contribution from linear chains appears. Similar observations can be made near 401 K: there is a sudden drop in the intensity from monomers, a corresponding increase in that from dimers, and the intensity from linear chains starts to increase rapidly with T. At temperatures above 450 K, finally, the total intensity is dominated by the signal from linear chains, but small contributions from monomers, dimers, and even 2D structures, can be identified. The sharp onsets of the dimerization/polymerization reactions at certain temperatures have never been observed in earlier experiments due to the limited resolution in temperature. At most pressures studied the onsets, with the corresponding jumps in the intensity from monomers and/or dimers, are clearly defined to well within 1 K. Considering that the temperature drift during the experiment may be larger than this, it is a very surprising and unexpected feature.

Results similar to those shown in Figure 2 were obtained at all pressures and may be used to create a detailed map of the polymerization reaction of C₆₀ under pressure. Further work along these lines is now in progress, including an extension to higher temperatures to identify the onset of 2D polymerization, and the full results of this study will be reported elsewhere.

CONCLUSIONS

Reaction diagrams of metastable phases can be mapped very rapidly and with high accuracy by treating samples over a large range in temperature at each pressure studied. The method described here provides a semi-permanent record and allows later re-analysis if necessary. Although only preliminary data are yet available for C₆₀, it is found that the method provides very accurate data on the pressure and temperature dependence of the polymerization reaction and allows a much more detailed analysis of the actual reaction as well as of the relative amounts of the different structural phases produced than any method used earlier.

ACKNOWLEDGMENTS

This work was financially supported by the Swedish Research Council, grant no. 621-2010-3732.

REFERENCES

1. V.D. Blank, S.G. Buga, G.A. Dubitsky, N.R. Serebryanaya, M. Yu. Popov and B. Sundqvist, *Carbon* **36**, 319 (1998).
2. B. Sundqvist, *Adv. Phys.* **48**, 1 (1999).
3. B. Sundqvist, *Structure and Bonding* **109**, 85 (2004).
4. G.F. Molinar, V.E. Bean, J. Houck and B. Welch, *Metrologia* **28**, 353 (1991).
5. B. Sundqvist, *Rev. Sci. Instrum.* **69**, 3433 (1998).
6. P.A. Persson, U. Edlund, P. Jacobsson, D. Johnels, A. Soldatov and B. Sundqvist, *Chem. Phys. Lett.* **258**, 540 (1996).
7. T. Wågberg, A. Soldatov and B. Sundqvist, *Eur. Phys. J. B* **49**, 59 (2006).
8. PeakFit[®], SeaSolve Software Inc., Framingham, MA