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LETTER TO THE EDITOR

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Abstract
New magnetic forms of C_{60} have been identified which occur in the rhombohedral polymer phase. The existence of previously reported ferromagnetic rhombohedral C_{60} is confirmed. This property has been shown to occur over a range of preparation temperatures at 9 GPa. The structure is shown to be crystalline in nature containing whole undamaged buckyballs. Formation of radicals is most likely due to thermally activated shearing of the bridging bond resulting in dangling bond formation. With increasing temperatures this process occurs in great enough numbers to trigger cage collapse and graphitization. The magnetically strongest sample was formed at 800 K, and has a saturated magnetization at 10 K, in fields above 3 kOe, of 0.045 emu g^{-1}.

1. Introduction

The recent discovery of ferromagnetism in rhombohedral C_{60} polymers [1] has opened up the possibility of a whole new family of magnetic fullerenes. However it has not yet been realized what are the optimum pressure temperature conditions for their formation. Also coupled to this, the cause of the magnetism and the mechanisms of formation of these regions are unknown.

The formation of magnetic carbon species is not an entirely new phenomenon and can be traced back to times before its discovery in fullerenes. Identifications have been made of ferromagnetic and superconducting hysteresis loops in highly oriented pyrolytic graphite [2]. Some super-high-surface-area carbons with micro-graphitic structures [3, 4] tended to have ferromagnetic properties in regions of high surface area. In a recent study, ferromagnetic carbon powder has been used in the production of ferromagnetic carbon electrodes [5]. The removal of hydrogen from an aromatic hydrocarbon adsorbed to charcoal resulted in an electrode capable of attracting free and ion radicals. In organic species, electron spin resonance and magnetization measurements showed that alkylene-aromatic polymers [6] exhibited ferromagnetic coupling between triphenylmethyl radicals. This resulted in the formation of spin clusters of triplet or higher spin multiplet states. Also, soft

organic molecular ferromagnets have been produced by using tetrakis(dimethylamino)ethylene (TDAE) derivatives of fullerene [7]. These functionalized C_{60} species illustrate a T_c of 16.1 K and unconventional ferromagnetic behaviour below this temperature. Also theoretical [8] studies indicate that the introduction of an azupyrene defects (two pentagons/two heptagons replacing four hexagons) into graphite and graphitic-like structures will result in magnetic properties.

Pristine C_{60} was discovered in 1985 by Kroto *et al* [9] and exists in a van der Waals fcc crystalline structure. However under the influence of UV [10] or temperature and pressure [11–13] it was found that the cages could be linked together in a variety of dimers, one-dimensional orthorhombic, two-dimensional tetragonal, two-dimensional rhombohedral and three-dimensional cubic polymers [14–17]. The adjacent cages are locked in place by a square four-membered bridge formed by [2 + 2] cycloaddition of two adjacent '66' bonds. In this case we focus on the two-dimensional polymers especially the rhombohedral phase near its stability limit, which has a structure analogous to pyrolytic graphite, but with semiconductor behaviour.

2. Experimental details

Rhombohedral polymers of C_{60} were prepared at the Osaka National Research Institute with the high-pressure, high-temperature treatments being performed on a multi-anvil octupole press. The precursor powdered C_{60} was acquired from the Materials and Electrochemical Research (MER) Corporation with a purity of 99.9%. A pressure of 9 GPa was applied to all the samples in advance of heating. The samples were then heated to preparation temperatures in the range 700–1200 K where they were held for 1 min. Previous *in situ* x-ray diffraction work [18] indicates that this isobar will go through an almost pure rhombohedral phase straight into the graphitic hard carbon phase. The temperature gradients on heating and quenching were 30 and 200 K min^{-1} respectively. The XRD experiments were undertaken using a Rigaku RAD-2A diffractometer utilizing Cu Kα radiation as its source. Experimental details for both the hardness and TEM measurements have already been discussed in a previous paper [14] and the high-resolution imaging was performed on a Phillips/FEI Technai F20 field emission unit. Magnetization versus magnetic field (M versus H) loops were collected using an Oxford Instruments vibrating sample magnetometer (VSM).

3. Results and discussion

The samples studied here were prepared on an isobar that runs through soft rhombohedral C_{60}, at temperatures up to 800 K, then through a phase change into graphitic 'hard' carbon. The hardness data [14] in figure 1 illustrate this change at ~850 K, with an increase in hardness to 25 from 2.5 GPa. The material hardness reaches its peak due to cross linking in the graphitic layers. At higher preparation temperatures the graphitic layers unzip themselves and the interlayer spacing relaxes, softening, but stabilizing the graphitic carbon. Previous reports [1] suggest that the magnetic behaviour could be caused by defects formed during cage collapse resulting in self-doping or by promotion of an electron in a strained 90° sp^2–sp^3 bridge, hence the possibility of magnetic ordering. Hence there is a need to measure the magnetic character of all the samples in the series.

The evolution of the M versus H loops collected at 10 K for the various C_{60} samples can be seen in figure 2. It is notable that the first two samples in the temperature series show a co-existence of paramagnetic and ferromagnetic character, with the 800 K sample showing by far
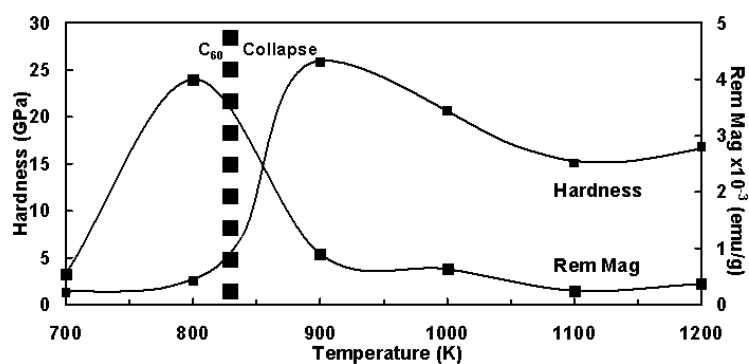
Figure 1. Hardness and remanent magnetization graph for samples treated at 9 GPa, indicating the region of radical centre generation.
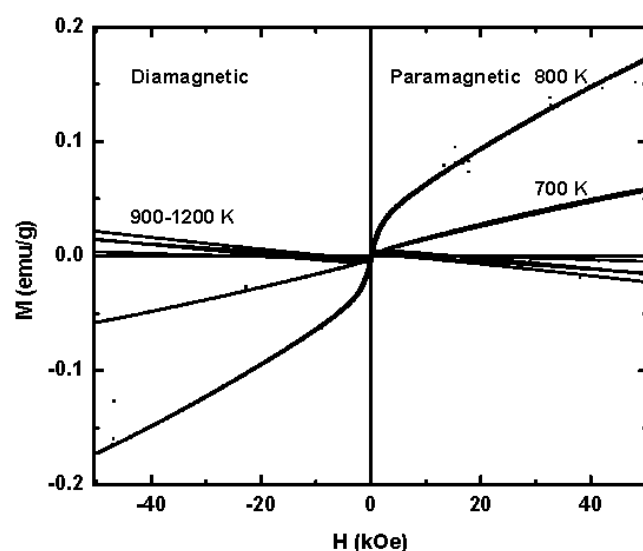
Figure 2. M versus H loops of high T/P treated C_{60} at 9 GPa over the range 700–1200 K.

the strongest magnetic behaviour. This indicates that the formation of carbon centres with non-zero spins, analogous to radical molecules, is happening at an increasing rate up to $\sim$800 K. For the sample prepared at 800 K the ferromagnetic component of the M versus H loop saturates in magnetic fields above 3 kOe and gives a lower limit for the magnetic moment per C_{60} molecule atom of 0.34 μ_B, a value that is around six times larger than previously reported [1]. Magnetization versus temperature data for this sample confirm that the material appears to be made up of a mixture of paramagnetic and ferromagnetic material. The system remains ferromagnetic up to at least 400 K, the highest temperature measured. One concern is that the C_{60} molecule has a great affinity for oxygen, hence the paramagnetism could be generated by adsorbed oxygen on the surface of the sample. Using the 700 K sample as a control for the 800 K sample and comparing their properties this possibility may be eliminated. Both samples contain oxygen attractive C_{60} cages so both should have similar paramagnetic contributions from this. As there is a factor of three difference in paramagnetic response between the two samples, it can be assumed that the oxygen may make a contribution, a significant faction of the paramagnetic signal is intrinsic to the samples. Thus the increase in magnetism observed
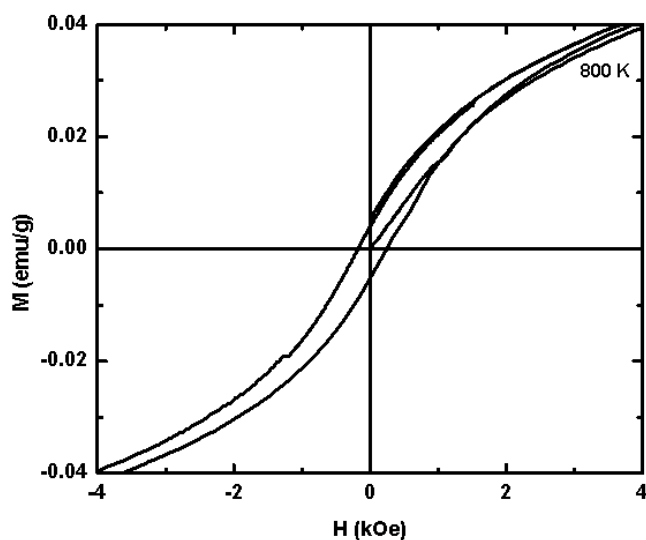
Figure 3. An enlarged M versus H loop indicating ferromagnetism in the 800 K 9 GPa sample.
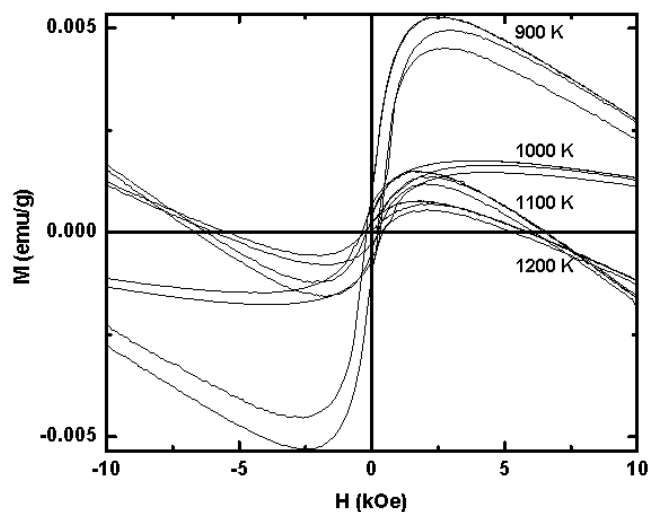

Figure 4. An enlargement of the M versus H loops showing the presence of ferromagnetism in all samples.

is controlled by carbon radical formation.

As the preparation temperature increases above 800 K the ferromagnetic character is reduced and eventually becomes dominated by diamagnetic behaviour, indicating a considerable loss of magnetic centres during graphitization, although it can be seen that all the samples do exhibit a positive χ (gradient) near to the origin, showing that some small proportion of the magnetic volumes formed have been trapped after cage collapse. This property weakens with temperature, as would be expected with the increasing thermal energy forcing cage failure.

A more detailed study of the M versus H loops, figures 3 and 4, shows that all samples exhibit some hysteresis. The variation in remanence magnetization (remanence) with
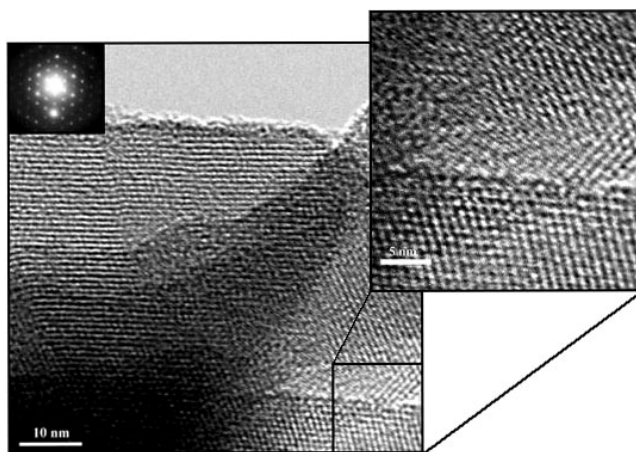
Figure 5. TEM images of the ferromagnetic phase illustrating its crystalline polymeric structure.
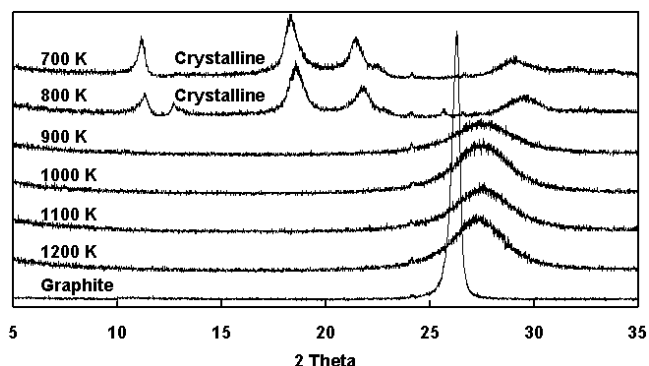

Figure 6. The evolution of XRD traces with temperature for C_{60} at a pressure of 9 GPa [14].

preparation temperature is compared with hardness data in figure 1. The remanence shows a dramatic increase from 700 to 800 K as the radical species are formed then tails off equally sharply at 900 K, where the destruction of cages has already begun. Some ferromagnetic character is present however, even for the sample prepared at 1200 K where small volumes are able to remain intact.

We can postulate on the processes and mechanisms for magnetism in these polymers. The radical sites are initially being generated at temperatures of about 700 K and are formed more readily up to and probably a little over 800 K. Thus, the formation of the magnetic species seems to be temperature dependent. This temperature dependence would indicate that the process occurring is of a bond breaking nature, but whether this is taking place inter- or intra-molecularly is not yet clear. If we compare the temperatures of ferromagnetic formation and C_{60} cage collapse however, it is evident that the generation of magnetic species is occurring at temperatures ≈ 100 K less than the onset of cage collapse. Therefore it can be inferred that the radical centres are being formed in the polymeric state before collapse, without damage to the buckyballs. For this to be the case we would expect the structure of the 700 and 800 K samples to be polymeric and crystalline in nature. The confirmation of this is given by TEM and XRD in figures 5 and 6. The XRD shows graphitic hard carbon phases at 900 K and above, whereas below it is clear that the phases are indeed crystalline fullerene polymers. To

add weight to this argument, ordered periodic lattice fringes and atomic columns are evident in the TEM micrograph accompanied by a rhombohedral crystalline diffraction pattern indicating a $[0003]_{Rh}$ zone axis. This verifies beyond doubt that the magnetism is being generated in the rhombohedral polymeric phase with no damage to the C_{60} molecule.

The fact that the buckyballs are intact in the most magnetic 800 K sample indicates that the source of the radical species is the intermolecular bridging bond. This correlates with the fact that the bridging bond cannot strictly adhere to the $109.5°$ tetrahedral bond angle and hence is in a strained state. Therefore, it is much more likely to cleave than the stable bonds in the buckyball, consequently forming two carbon radical centres. As a result it can be concluded that the magnetic character is generated when the thermal energy is great enough for carbon bond cleavage to occur in the intermolecular bridge and hence form a radical species in the form of a 'dangling' bond.

If we refer back to the original report on ferromagnetic fullerene by Makarova $et~al$ [1] it is evident that the ferromagnetism exists at preparation pressures other than 9 GPa. In this earlier report the material was prepared at 6 GPa. This indicates that the ferromagnetism occupies a considerable area of the $C_{60} P/T$ field. This area is a strip that runs parallel to the graphitic–polymer phase boundary with a breadth of 50–100 K. The only discrepancy between our results and those in [1] is the temperature at which the magnetic species are formed. The 6 GPa set are produced at over 1000 K and the 9 GPa set much lower at 800 K. This may be an indication of the pressure dependence of ferromagnetic formation or just an example of the effect of variable shear stresses on the P/T diagram of C_{60}. Further work examining variations in the pressure field isotropy and its effect on the temperature of ferromagnetic fullerene formation is required.

4. Conclusion

It had been demonstrated that at preparation pressures of 9 GPa it is possible to form a whole family of magnetic carbons with varying degrees of ferromagnetic content. We can confirm the previous report on the existence of ferromagnetic fullerenes [1]. This unusual material is generated by the coupling of near neighbour carbon radical centres, which are formed by thermally activated cleaving of the strained tetrahedral sp^3 bridging bond. This process has been found to occur in the polycrystalline rhombohedral polymeric phase, with the process initiating at a temperature of ≈ 700 K and increases until graphitization occurs. These magnetic centres are retained during and after C_{60} cage collapse giving these observed variations in magnetic behaviour with temperature. It could be postulated to be the trigger for buckyball destruction, i.e. when the rate of radical formation reaches a critical point the number of destabilized cages becomes too great, thus collapse occurs. This results in our most strongly magnetic carbon being produced at 800 K. Further studies could be performed, using smaller increments in production temperature enabling production as near to the graphitic phase boundary as possible. This could result in the formation of a polymer with more advantageous properties.

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