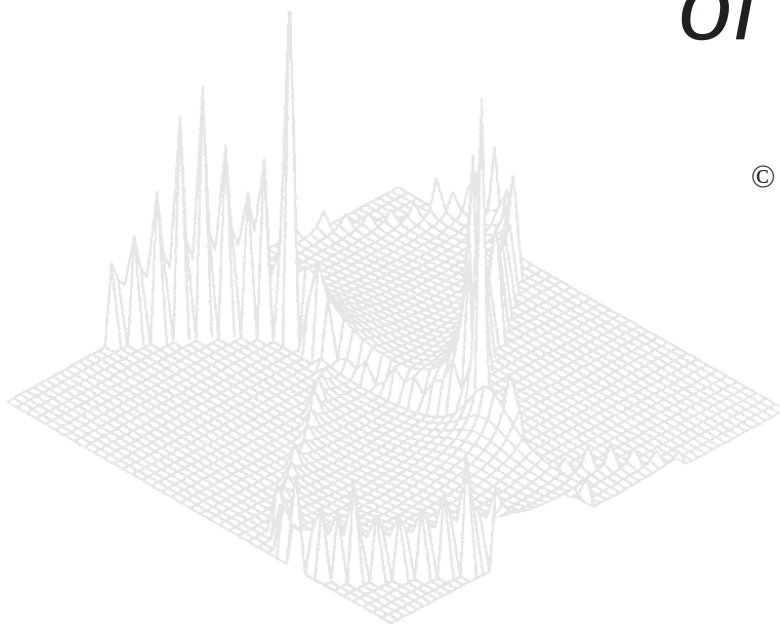

CSIRO PUBLISHING

Australian Journal of Physics

Volume 52, 1999
© CSIRO Australia 1999



A journal for the publication of
original research in all branches of physics

www.publish.csiro.au/journals/ajp

All enquiries and manuscripts should be directed to

Australian Journal of Physics

CSIRO PUBLISHING

PO Box 1139 (150 Oxford St)

Collingwood

Vic. 3066

Australia

Telephone: 61 3 9662 7626

Facsimile: 61 3 9662 7611

Email: peter.robertson@publish.csiro.au



Published by **CSIRO PUBLISHING**
for CSIRO Australia and
the Australian Academy of Science



Nonlinear Field-dependent Susceptibilities of C_{60} and Carbon Nanotubes*

M. F. Ling,^A T. R. Finlayson^A and C. L. Raston^B

^ADepartment of Physics, Monash University,
Clayton, Vic. 3168, Australia.

^BDepartment of Chemistry, Monash University,
Clayton, Vic. 3168, Australia.

Abstract

We have found strongly nonlinear, field-dependent magnetic susceptibilities in a range of carbon-based materials such as C_{60} , carbon nanotubes, diamond and graphite. This nonlinear behaviour is prominent at low fields and it vanishes at relatively high fields. We have interpreted this phenomenon in terms of the field dependence of the spectral energy separations of the van Vleck paramagnetic term of the susceptibility. Our results should have significant bearing on the interpretation of the magnetic properties of this class of materials.

1. Introduction

Members of the family of carbon molecules that includes diamond, graphite, C_{60} and carbon nanotubes have rich magnetic properties (Buntar *et al.* 1997; Ramirez *et al.* 1994; Kotosonov and Kuvshinnikov 1997; Heremans *et al.* 1994; Pople 1962; Elser and Haddon 1987). Most previous measurements and calculations have indicated that the susceptibilities of these molecules are field-independent and diamagnetic. We demonstrate that this interpretation is valid only in the limit of high magnetic fields. Our susceptibility-versus-field measurements of these materials have found strongly nonlinear field dependence, which vanishes only in the high-field regime. This field dependence is interpreted in terms of the effect of the magnetic field on the spectral energy separations in the van Vleck paramagnetic component of the susceptibility (van Vleck 1932; Pople 1962; Elser and Haddon 1987; Davies 1961). This is the first time that such nonlinear behaviour in this class of materials has been reported and explained. This field dependence will profoundly influence future interpretations of the magnetic properties of fullerene materials and their derivatives. Our result also presents an important challenge to theorists for rigorous theoretical explanations at a fundamental level.

Over the past decade, much experimental work has been done on the magnetic properties of carbon molecules with ring structures, such as fullerene materials, and in particular the C_{60} molecules and their derivatives (Buntar *et al.* 1997;

* Refereed paper based on a contribution to the Eighth Gordon Godfrey Workshop on Condensed Matter Physics held at the University of New South Wales, Sydney, in November 1998.

Ramirez *et al.* 1994; Kotosonov and Kuvshinnikov 1997; Heremans *et al.* 1994; Elser and Haddon 1987). The magnetic behaviour of these materials is commonly studied by magnetisation measurements at a relatively high field of about 10,000 Oe (1 Oe = 79.577 A m^{-1}). Under such conditions, the susceptibilities of these materials are usually reported to be negative (diamagnetic) and field-independent. Our interpretation of the magnetic properties of these materials is often based on the implicit assumption of field independence. Here we demonstrate that the magnetic behaviour of carbon molecules is in fact more complex, and that it exhibits strongly nonlinear field dependence. Indeed, our susceptibility measurements have revealed that the susceptibilities of synthetic diamond, carbon nanotubes, C_{60} and graphite vary with applied magnetic field according to a functional form of stretched exponential decay which is largely independent of temperature (~ 50 to 300 K). As far as we are aware, this is the first time that this nonlinear field dependence has been systematically studied and explained, although such an effect could have been inferred from previous theoretical work (Pople 1962; Elser and Haddon 1987; Davies 1961).

2. Experiment

Our susceptibility measurements on synthetic diamond, carbon nanotubes, C_{60} and graphite samples were carried out in a Quantum Design SQUID magnetometer over a temperature range of 5 to 300 K. Both the multi-walled nanotube and C_{60} samples were high-purity commercial products. The C_{60} was kept in dry nitrogen to minimise oxygen contamination and oxidation. On the other hand, the nanotube and diamond samples were considered sufficiently stable to require no special handling. The graphite sample was cut from a high-quality industrial graphite rod. Before the measurement it was cleaned with methylated spirit and dried.

A range of magnetic fields was used for our susceptibility-versus-temperature measurements under zero-field-cool (ZFC) conditions, and the results for C_{60} are shown in Fig. 1. The small rise in the susceptibility of C_{60} at temperatures below 15 K indicates that there is minute trace of impurity in the sample. While the increases in susceptibilities at low temperatures in the graphite and the synthetic diamond samples were somewhat greater than that for C_{60} , the temperature dependence of their susceptibilities became negligible above 50 K. Our nanotube sample exhibited a small degree of temperature dependence consistent with that reported in the literature (Kotosonov and Kuvshinnikov 1994).

At the high-field limit, the ratio of the susceptibility for nanotubes to that of C_{60} is 87, whereas the nanotubes-to-graphite ratio is 17. The nanotubes-to- C_{60} ratio is very similar to that found in the literature (Ramirez *et al.* 1994). On the other hand, the nanotubes-to-graphite ratio is substantially larger than that obtained by Ramirez *et al.* It should be noted that our graphite sample was an ordinary industrial product, albeit a high-quality one, while a highly oriented pyrolytic graphite (HOPG) sample was used in the work of Ramirez *et al.* As the susceptibilities of this class of materials depend strongly on their structures, it is clear that the ratios for the two different types of graphite should not be compared directly.

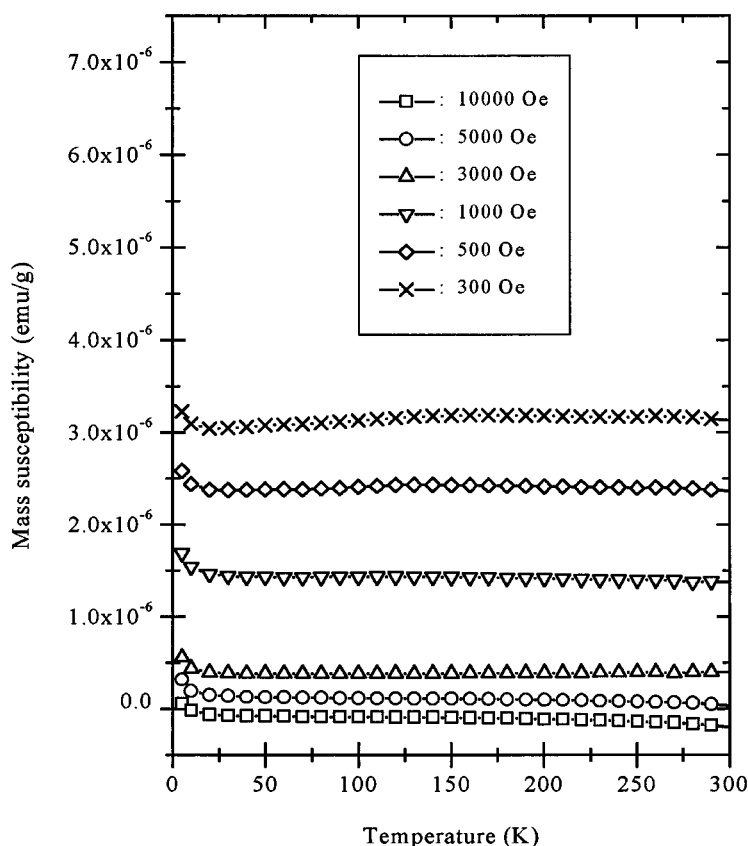


Fig. 1. Mass susceptibilities (emu per gram) versus temperature (K) of C_{60} at different magnetic fields.

3. Results and Analysis

All samples exhibited strongly nonlinear field dependence. Fig. 2 shows plots of mass susceptibility versus field for the four samples at 200 K. It is clear that this field dependence cannot be attributed to paramagnetic impurities because no noticeable temperature dependence is observed above 50 K in the cases of C_{60} , graphite and diamond. Pauli susceptibility can also be ruled out on the ground that minute traces of impurities in our nanotube and C_{60} samples simply cannot account for the large, field-dependent variations. Finally, a Jahn–Teller effect cannot be the origin of this field dependence since our samples have very different bonding properties and geometries, yet they all exhibit the same nonlinear behaviour. Also, the susceptibilities of graphite, diamond and C_{60} are of the same order of magnitude, although the near-metallic band structure of carbon nanotubes has resulted in greater susceptibility (Kotosonov and Kuvshinnikov 1994). Clearly, the universal nature of the nonlinear behaviour demands that an alternative mechanism for this phenomenon be considered.

In carbon molecules, there is no net magnetisation in the absence of an external magnetic field. It is well known that the response of the electrons in

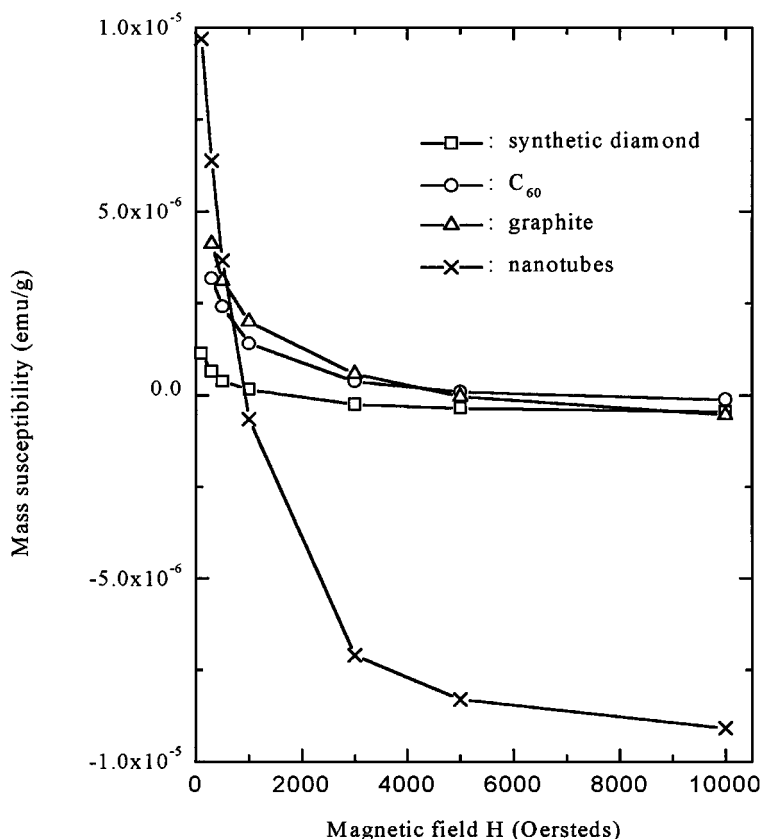


Fig. 2. Mass susceptibilities (emu per gram) versus magnetic field (Oe) of nanotubes, graphite, synthetic diamond and C₆₀ at 200 K.

these molecules to an applied field can be expressed as the sum of a diamagnetic contribution, χ^D , and a van Vleck paramagnetic term (Pople 1962; Elser and Haddon 1987; Davies 1961), χ^P , where the latter can be expressed as

$$\chi^P = \frac{2N_0}{3} \sum_{n \neq 0} \left| \langle n | \sum_i \mathbf{m}_i^0 | 0 \rangle \right|^2 / (E_n - E_0), \quad (1)$$

where N_0 is Avogadro's number, E_0 and E_n are the unperturbed energy levels, $\mathbf{m}_i^0 = (-e/2mc)(\mathbf{L}_i + 2\mathbf{S}_i)$ is the instantaneous magnetic dipole moment of the i th electron at $\mathbf{r}_i$, and $\mathbf{L}_i$ and $\mathbf{S}_i$ are the orbital and spin angular momenta respectively. First note that equation (1) has been derived from second-order perturbation theory based on the assumption of a vanishingly small magnetic field. In a realistic, finite-field calculation, the change in spectral energy separations due to an applied field must be treated rigorously. While it is well known that the spectral energy separations are altered in the presence of a magnetic field (Hegstrom and Lipscomb 1968; Slichter 1978), the exact manner in which the change occurs is difficult to determine as it involves the calculation of the excited

states (Pople 1962). The validity of replacing the summation over the excited energy levels with an averaged energy (Pople 1962) is now clearly questionable in view of our results. An alternative approach to the problem is to use a modified, finite-field London theory due to Elser and Haddon (1987), and it can be shown that the change in energy-level separation with applied field, H , can be expressed as, to the lowest order,

$$\Delta E \approx |k| + \frac{1}{2} \frac{H^2}{|k|}, \quad (2)$$

where k is a scaling parameter ($k \approx 1$ for this discussion). It follows that the van Vleck paramagnetic susceptibility should vary with the field, H , according to the expression

$$\chi^P(H) \approx \frac{1}{1 + \frac{1}{2}H^2}, \quad (3)$$

which illustrates the diminishing contribution from the van Vleck paramagnetic term at higher fields. For the data presented in Fig. 2 the field dependence is somewhat different from that predicted by equation (3). Instead, our analysis shows that the susceptibility variation can be well fitted to a stretched exponential form

$$\chi(H) = \chi_0 + A \exp(-H/H_0). \quad (4)$$

The fitted values of χ_0 , A and H_0 for our four samples are shown in Table 1. Equation (4) shows that the total magnetic susceptibility decreases exponentially with applied field, H , reaching a minimum, constant value of χ_0 at higher fields. As most susceptibility measurements on this class of materials have been carried out in an applied field of about 10,000 Oe, this nonlinear field dependence is likely to have been suppressed in a majority of measurements reported in the literature. It should be emphasised that equation (4) is a phenomenological expression for the total susceptibility $\chi(H)$ in the presence of a magnetic field, and not χ^P from equation (1).

Table 1. Fitted parameters of equation (4)

	C ₆₀	Carbon nanotubes	Graphite	Synthetic diamond
χ_0 (emu/g)	-1.05×10^{-7}	-9.1×10^{-6}	-5.1×10^{-7}	-4.5×10^{-7}
A (emu/g)	4.2×10^{-6}	2.0×10^{-5}	5.2×10^{-6}	1.7×10^{-7}
H_0 (Oe)	1072	1159	1682	893

4. Conclusion

In summary, the origin of the field dependence can be traced to the fact that the spectral energy separations in these materials can be significantly modified by an external magnetic field. The variation in energy-level separations alters the contribution from the van Vleck paramagnetic term. It is via this highly complex,

underlying mechanism that the nonlinear field dependence of the susceptibilities of these materials arises. As our samples differ not only in their crystallographic structures and bonding geometries, but also in their types of bonding, namely sp^3 in diamond and sp^2 in graphite, C_{60} and nanotubes, the mechanism is clearly universal and not sample-specific. We have demonstrated that in interpreting magnetisation measurements of materials in which van Vleck paramagnetism is known to be non-vanishing, such as insulators with partially-filled shells, this nonlinear field dependence must be carefully taken into account. This phenomenon is particularly relevant and important to our understanding of the magnetic properties of fullerene materials and their derivatives. A detailed theoretical explanation for this unusual nonlinear effect at a fundamental level should also present an important challenge to theorists.

Acknowledgment

The support of the Australian Research Council (ARC) is gratefully acknowledged.

References

- Buntar, V., Sauerzopf, F. M., and Weber, H.W. (1997). *Aust. J. Phys.* **50**, 329.
 Davies, D. W. (1961). *Trans. Faraday Soc.* **57**, 2081.
 Elser, V., and Haddon, R. C. (1987). *Phys. Rev. A* **36**, 4579.
 Hegstrom, R. A., and Lipscomb, W. N. (1968). *Rev. Mod. Phys.* **40**, 354.
 Heremans, J., Olk, C. H., and Morelli, D. T. (1994). *Phys. Rev. B* **49**, 15122.
 Kotosonov, A. S., and Kuvshinnikov, S. V. (1997). *Phys. Lett. A* **230**, 377.
 Pople, J. A. (1962). *J. Chem. Phys.* **37**, 53.
 Ramirez, A. P., Haddon, R. C., Zhou, O., Fleming, R. M., Zhang, J., McClure, S. M., and Smalley, R. E. (1994). *Science* **265**, 84.
 Slichter, C. P. (1978). 'Principles of Magnetic Resonance' (Springer: Berlin).
 van Vleck, J. H. (1932). 'The Theory of Electronic and Magnetic Susceptibilities' (Oxford Univ. Press: London).

Manuscript received 24 November 1998, accepted 26 March 1999