

The neutron diamagnetic form factor of graphite

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 3833

(<http://iopscience.iop.org/0953-8984/1/24/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.93

The article was downloaded on 10/05/2010 at 18:19

Please note that [terms and conditions apply](#).

The neutron diamagnetic form factor of graphite

C Wilkinson[†], D A Keen^{†‡}, P J Brown[§] and J B Forsyth^{||}

[†] Physics Department, King's College London, Strand, London WC2R 2LS, UK

[§] Institut Laue–Langevin, 38042 Grenoble Cédex, France

^{||} Neutron Science Division, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, UK

Received 17 October 1988

Abstract. The form factor of the diamagnetic moment induced by a field of 4.62 T in a single crystal of graphite has been measured by polarised neutron diffraction. The data are consistent with a π -electron orbital current having a radius of 1.38(8) Å, slightly smaller than that of the carbon rings in the planar sheets of the graphite structure (1.42 Å). The corresponding effective mass ratio for the π -electrons is $m^*/m = 0.019(3)$.

1. Introduction

Graphite exhibits strong anisotropy in many of its physical properties which may be understood in terms of its layered hexagonal crystal structure, illustrated in figure 1.

The high value of the diamagnetic susceptibility (figure 2) measured parallel to the c axis (-21×10^{-6} emu g^{-1} at room temperature) (Krishnan and Ganguli 1939, Maaroufi *et al* 1982) has been ascribed to the motion of π -electrons in orbits in the (001) sheets of carbon atoms (Peacock and McWeeny 1959). The susceptibility measured perpendicular to the c axis is independent of temperature, is much lower (-0.6×10^{-6} emu g^{-1}) and is representative of the electron orbital motion within the carbon atoms.

This anisotropy has previously been studied by measurement of optical constants (Greenaway *et al* 1969), cyclotron resonance (Nozières 1958), the de Haas–van Alphen effect (Sharma *et al* 1974), secondary-electron spectroscopy (Willis *et al* 1974) and Compton scattering (Cooper 1971). Several band-structure calculations have been made to explain the observed experimental observations (McClure 1957, Nagayoshi *et al* 1976, Maaroufi *et al* 1982).

In the present paper, we describe a polarised neutron diffraction experiment undertaken to investigate the spatial distribution of the diamagnetic density in a single crystal of graphite. This is only the second study of diamagnetism which has been attempted by neutron scattering. The first was on bismuth by Collins and Shull (Collins 1979), who found evidence of diamagnetic scattering from the five Bi valence electrons in only one of the Bragg reflections which they measured.

[†] Currently at: Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK.

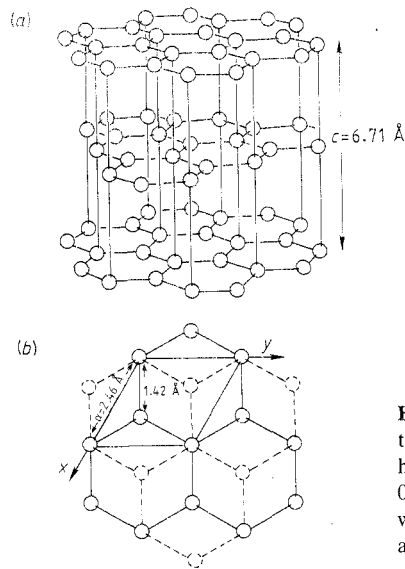


Figure 1. The crystal structure of graphite. (b) In the view down the c axis the full lines connect hexagons of carbon atoms in the basal plane ($z = 0$) of the hexagonal unit cell, which is outlined, while the broken lines show equivalent hexagons at $z = \frac{1}{2}$.

2. Theory

The diamagnetic volume susceptibility of an element is described by the Langevin equation

$$\chi = (-Ze^2 N / 6mc^2) \langle r^2 \rangle$$

where $\langle r^2 \rangle$ is the mean square radius for the atomic electron wavefunctions, Z is the atomic number, N is the number of atoms per unit volume and the other symbols have their usual meanings. This formula may be used to predict χ_1 , the volume susceptibility perpendicular to the c axis, in graphite.

The same formalism may be used to predict χ_π , the volume susceptibility due to the π -electron orbits:

$$\chi_\pi = -[pe^2(N/2)/6m^*c^2] \langle R^2 \rangle$$

where p is the number of orbiting π -electrons per hexagonal carbon ring, m^* is their effective mass and $\langle R^2 \rangle$ is the mean square radius of the orbit. This is almost the entire contribution to χ_3 , the susceptibility parallel to the c axis, and the ratio χ_3/χ_1 may be used to predict the mean square radius $\langle R^2 \rangle$ for the π -electron orbits since

$$\chi_3/\chi_1 = (P/2Z)(\langle R^2 \rangle / \langle r^2 \rangle)(m/m^*).$$

One may calculate $\langle r^2 \rangle$ for the carbon atom using wavefunctions computed by the Roothaan–Hartree–Fock method (Clementi and Roetti 1974). Its value for the $1s^{(2)}2s^{(2)}2p^{(1)}$ carbon atom is 0.489 \AA^2 and, using $m^*/m = 0.058$ for the majority electron carriers estimated from de Haas–van Alphen measurements (Sharma *et al* 1974), we obtain $\langle R^2 \rangle = 5.95 \text{ \AA}^2$ for $p = 2\pi$ -electrons per orbit. The effective radius of these orbits is therefore 2.44 \AA , larger than the 1.42 \AA radius of the hexagons which make up the sheets (figure 1).

By Ampère's theorem, a current loop is equivalent to a sheet of uniform magnetisation, which will scatter thermal neutrons. If the π -electron orbits are the exact

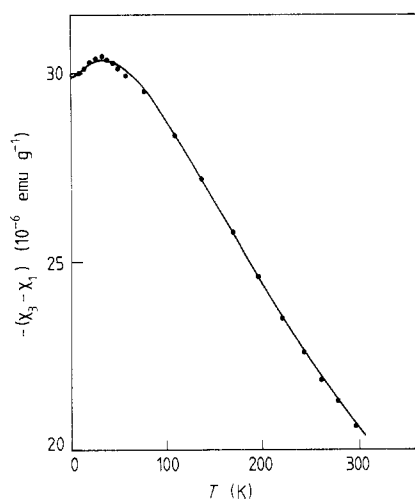


Figure 2. The difference between χ_3 , the diamagnetic susceptibility of graphite parallel to c below 300 K, and χ_1 , the susceptibility in the basal plane (after Maaroufi *et al* 1982).

shape of the carbon atom rings, the tiling of these interlocking hexagons will fill the basal plane and the Bragg scattering from the extended array will be non-zero only in the forward-scattering direction, inaccessible to diffraction. Any deviations from this perfect tiling, however, such as an increase in radius of the current loop as described above would lead to finite values of the magnetic structure factors of Bragg reflections.

The size of the magnetic moment of the π -electron orbit depends upon the applied field; with an applied field of 5 T parallel to the c direction it is $0.0027\mu_B$ per carbon atom. This corresponds to a scattering length of 0.0084×10^{-12} cm, small in comparison with the nuclear scattering length of carbon (0.665×10^{-12} cm), and detectable only in a polarised beam experiment.

3. Diffraction measurements

The single crystal of graphite used (kindly loaned by A Magerl) was a large natural flake of mass 125 mg, with a thickness of 0.6 mm (parallel to c) and a face area of some 250 mm². In a preliminary unpolarised beam experiment it was found that the peak intensities of some ($hk0$) reflections could be considerably enhanced if the flake was mounted with its plane making an angle of about 18° with the incident beam direction, since this reduced the neutron path lengths in the crystal compared with an orientation with [001] vertical. The specimen was therefore supported with [001] at this angle to the vertical axis of a superconducting magnet on the D3 polarised neutron diffractometer at the Institut Laue–Langevin, Grenoble. The crystal was maintained at 100 K, a temperature near the largest value of the c axis susceptibility (see figure 2) and the maximum available field of 4.62 T was applied.

The flipping ratios of (100), (101), (110), (200), (201), (112) and (103) reflections were measured at a wavelength of 0.924 Å over a period of 2 weeks and were each derived from about 10^8 counts. The values obtained for several equivalent (100) and (101) reflections were equal within the uncertainties introduced by the counting statistics. Values of γ , the ratio of the magnetic to the nuclear structure factor were calculated from the observed flipping ratio \mathcal{R} using the approximation $\mathcal{R} = 1 + 4\gamma$, applying a small correction for lack of perfect beam polarisation (Brown and Forsyth 1964). No correction

Table 1. γ -values, their standard deviations and magnetic structure factors measured for selected Bragg reflections from a graphite single crystal at 100 K with a field of 4.6 T applied parallel to the *c* axis. Also shown are the geometrical structure factors per cell taking carbon rings (each containing two atoms) as scattering units, and the form factor deduced for a ring.

<i>hkl</i>	$\gamma(\Delta\gamma) \times 10^6$	$(\mu_B/\text{cell}) \times 10^5$	Ring geometrical structure factor	Ring form factor $\times 10^3$
100	-16(48)	-4(12)	-1	-7(21)
200	-57(69)	-14(17)	-1	-25(30)
110	+52(16)	+51(16)	+2	-46(14)
101	+35(58)	-15(25)	$+\sqrt{3}$	+16(27)
201	+159(49)	+68(21)	$-\sqrt{3}$	+70(22)
112	-9(33)	+9(33)	-2	+8(29)
103	-199(193)	-85(82)	$-\sqrt{3}$	-88(82)

for Schwinger scattering is necessary, since the structure is centrosymmetric and the imaginary component of the scattering length of carbon is only 3.7×10^{-4} times the real component at the wavelength of our measurements. We estimate the effect of extinction on our data from the increase in the intensity of the (110) nuclear reflection (by a factor of 3.8) produced by tilting the sample to reduce the effective path length in the sample (by a factor of 10). Using a simple model (Zachariassen 1963), we calculate the effect on the γ -value for this reflection to be about 8%. Of the reflections measured, this is the most extinguished case, since (110) has the maximum structure factor and occurs at the smallest angle. We therefore believe that extinction effects are much smaller than the statistical uncertainties in our measurements and have made no correction for them. The γ -values and the magnetic structure factors (in μ_B per unit cell) obtained using the calculated nuclear structure factors are listed in table 1.

4. Interpretation of diffraction measurements

Although in general in a polarised beam diffraction experiment on a magnetic sample the magnetisation may be reconstructed by Fourier summation of the observed magnetic structure factors, it was not possible in this case since the very small magnetic cross sections meant that only a few reflections could be measured in the time available. It was therefore necessary to use a model for the π -electron orbits and to compare calculated and observed form factors. The geometrical structure factors for the carbon rings within one unit cell are given in table 1. The observed form factor values may be obtained by dividing the observed magnetic structure factors by the induced diamagnetic moment ($0.00558\mu_B$ per ring at 100 K) and by the appropriate ring geometrical structure factor. The resulting form factor values are also listed in table 1. As stated above, for perfectly tiled hexagonal current loops, the Bragg reflections occur at nodes in the hexagon form factor. The full curve in figure 3(a) shows the calculated (*h*00) section and the broken curve the (*hh*0) section of the transform of a hexagonal sheet of magnetisation with edge 1.42 Å. Data points are shown as full circles and calculated values (which are

Figure 3. The form factors of (a) a hexagon of magnetisation with edge 1.42 Å and (b) a circular disk of magnetisation with radius 1.42 Å: ●, experimental measurements; ○, calculated values (all zero); —, (h00) transforms; - - -, (hht0) transforms.

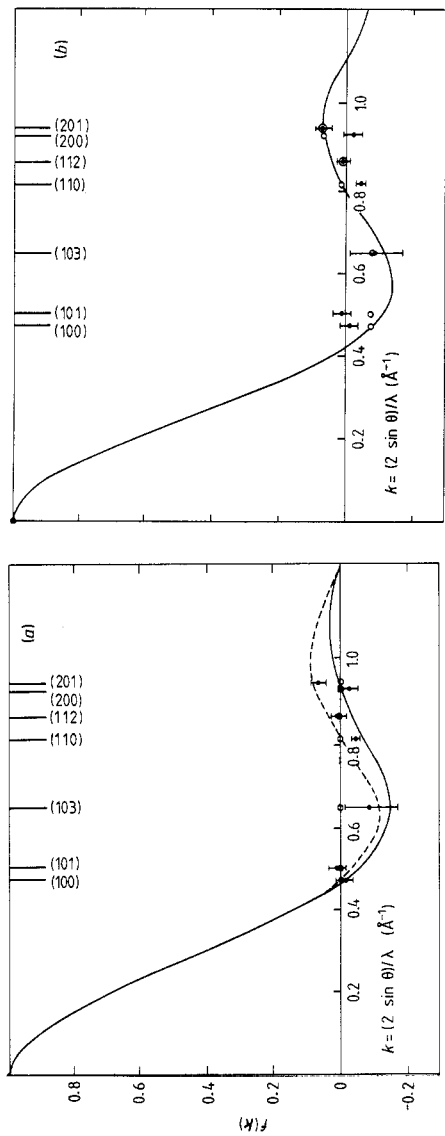
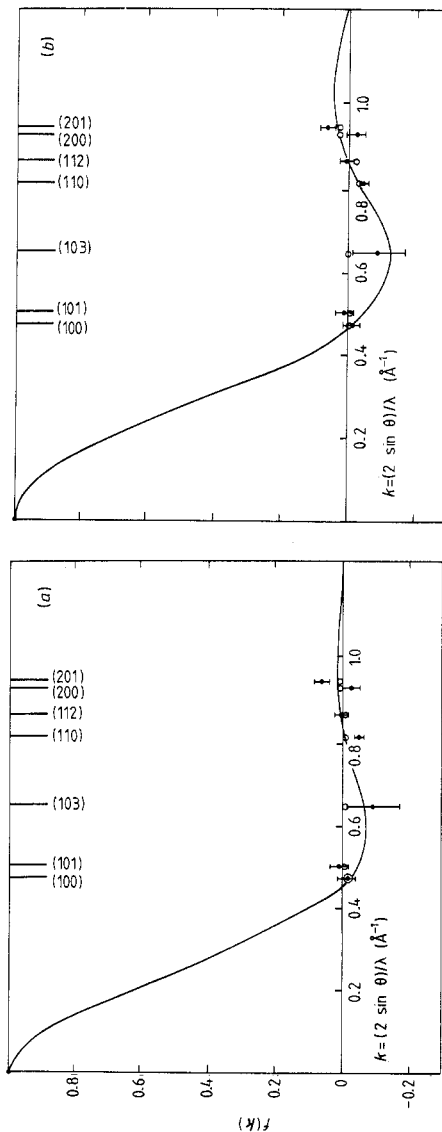


Figure 4. The form factor of the magnetisation due to the π -electron density distribution suggested by a simple LCAO model for carbon rings (a) of edge 1.42 Å and (b) of radius 1.3 Å: ●, experimental measurements; ○, calculated values. The distribution of electron density perpendicular to the plane in (b) is the same as for 4(a), but the distribution in the plane of the rings is much sharper.



zero) at the positions of Bragg reflections are shown as open circles. Defining G , a goodness-of-fit criterion, as

$$G = \frac{1}{n-1} \sum^n \frac{(f_{\text{obs}}^2 - f_{\text{calc}}^2)}{\sigma_{\text{obs}}^2}$$

gives $G = 5.2$ over the $n (= 7)$ observations.

An alternative model for the orbits is a circular current loop of radius R , containing a uniform disc of magnetisation which has a Bessel function form factor $J_1(2\pi k_r R)/\pi k_r R$, where k_r is the component of \mathbf{k} in the plane of the rings. This is shown in figure 3(b) for $R = 1.42 \text{ \AA}$. The G -value is 7.9, a rather worse fit than for the hexagonal orbits. However, the above models for the conduction electron density are probably too simple. A more realistic approximation for the expected distribution of the π -electrons would be Gaussian density functions placed symmetrically above and below the carbon atoms in the layers. This distribution may be expressed in cylindrical polar coordinates as

$$\rho(r, z) = (1/4\pi\sigma_z\sigma_R) \exp[-(r-R)^2/2\sigma_R^2] \\ \times \{\exp[-(z-z_0)^2/2\sigma_z^2] + \exp[-(z+z_0)^2/2\sigma_z^2]\}$$

where z_0 is distance of the centres of the Gaussian distributions from the centres of the carbon atoms, and σ_R and σ_z are the standard deviations in the radial and azimuthal directions.

On the assumption that under the influence of a field applied parallel to the c axis the electrons move in circular orbits whose centres are the centres of the carbon rings and whose radii correspond to the electron positions in the static density, the form factor corresponding to $\rho(r, z)$ is

$$f(k_r, k_z) = \cos(2\pi k_z z_0) \exp(-2\pi^2 k_z^2 \sigma_z^2) \exp(-2\pi^2 k_r^2 \sigma_R^2) J_1(2\pi k_r R)/\pi k_r R$$

where k_z is the azimuthal component of the scattering vector. Measurements made on an electron density map generated from a simple linear combination of atomic orbitals (LCAO) suggest $z_0 = 0.476 \text{ \AA}$, $\sigma_z = 0.194 \text{ \AA}$ and $\sigma_R = 0.283 \text{ \AA}$. The $f(\mathbf{k})$ values calculated using this distribution and $R = 1.42 \text{ \AA}$ are plotted in figure 4(a). The curve shows the form factor for $(hk0)$ reflections. The G -value obtained using these parameters is 2.87 and can be improved by allowing R and σ_R to vary. (The fit is relatively insensitive to z_0 and σ_z since the k_z -values of the observed reflections are mainly small.) The effect of reducing R is to expand the form factor, but this can be partially compensated by an increase in σ_R . For $R = 1.42 \text{ \AA}$ the optimum value of σ_R indeed occurs at approximately the LCAO value of 0.283 \AA , although the minimum in G is shallow. Fixing σ_R at the LCAO value and varying R produces a sharper minimum at $R = 1.38 \text{ \AA}$ with $G = 2.7$. The overall minimum value of $G (= 1.56)$ occurs at $R = 1.3 \text{ \AA}$ and $\sigma_R = 0.05 \text{ \AA}$, when the form factor curve (figure 4(b)) is rather similar to the mean (circular average) of the hexagonal transforms shown in figure 3(a). This arises because the circularly averaged radius $\langle R \rangle$ of a sharp hexagonal orbit ($\sigma_R = 0.0 \text{ \AA}$) of edge 1.42 \AA is $1.42 \times 3/\pi \text{ \AA}$ ($\langle R \rangle = 1.36 \text{ \AA}$), giving a similar transform to a truly circular orbit with $R = 1.3 \text{ \AA}$ and $\sigma_R = 0.05 \text{ \AA}$.

5. Discussion

From the analysis above, it seems that the best models for the diamagnetic currents in graphite are fairly tight loops somewhat smaller than the 1.42 \AA radius of the carbon

rings which make up the structure. We believe, however, that the numerically optimum fit which has $\sigma_R = 0.05 \text{ \AA}$ is physically not very reasonable and prefer to fix σ_R at its LCAO value of 0.283 \AA . In view of the shallowness of the minimum in the least-squares fit, the difference of 0.04 \AA between the best value of R (1.38 \AA) when σ_R is fixed and the ring radius of 1.42 \AA from the crystallographic structure does not seem to be particularly meaningful. Radii significantly less than 1.30 \AA are ruled out, however, as the form factor becomes too broad to fit the observed nodes at the (100) and (101) reflection positions and G becomes very large. We therefore estimate the uncertainty in the fitted value of R to be 0.08 \AA . These values can be translated directly into an effective mass of $m^* = 0.019(3)m$, rather less than the value of $0.058m$ obtained for the majority electron carriers from de Haas–van Alphen experiments, but consistent with an average over majority and minority electron and hole carriers (Sharma *et al* 1974).

Ideally we should have liked to sample the form factor of the hexagonal rings at smaller values of k in order to have a larger effect to measure. This is clearly not possible in graphite but in principle can be done with structures containing other aromatic molecules, which make similar large contributions to the diamagnetic susceptibility. Materials such as benzene, naphthalene, anthracene and chrysene all have large diamagnetic susceptibilities and crystallographic structures which allow the ring transform to be sampled by Bragg reflections closer to the forward direction but, because the carbon rings are not as efficiently connected as they are in graphite, the maximum value of the ratio of diamagnetic to nuclear structure factor is roughly an order of magnitude less. We have attempted the experiment using a large crystal of deuterated naphthalene but found that, despite a huge increase in the volume relative to the graphite specimen, we could not obtain the precision required in the flipping ratios to make a significant statement about the diamagnetic form factor. It therefore seems that, with fluxes at present available no further details of the ring form factor can be obtained from neutron scattering experiments.

It is interesting to note that the conclusion of the neutron diffraction study of bismuth, which was that the diamagnetism of the valence electrons gives almost zero scattering at Bragg positions, also applies in the case of π -electrons in graphite.

References

- Brown P J and Forsyth J B 1964 *Br. J. Appl. Phys.* **15** 1529
Clementi E and Roetti C 1974 *At. Data Nucl. Data Tables* **14** 178
Collins S R 1979 *PhD Thesis* Massachusetts Institute of Technology
Cooper M J 1971 *Adv. Phys.* **20** 453
Greenaway D L, Harbeke G, Bassani F and Tosatti E 1969 *Phys. Rev.* **178** 1340
Krishnan K S and Ganguli N 1939 *Z. Kristallogr. A* **100** 530
Maaroufi A, Flandrois S, Coulon C and Rouillon J C 1982 *J. Phys. Chem. Solids* **43** 1103
McClure J W 1957 *Phys. Rev.* **108** 612
Nagayoshi H, Nakao K and Uemura Y 1976 *Solid State Commun.* **18** 225
Nozières P 1958 *Phys. Rev.* **109** 1510
Peacock T E and McWeeny R 1959 *Proc. Phys. Soc.* **74** 385
Sharma M P, Johnson L G and McClure J W 1974 *Phys. Rev. B* **9** 2467
Willis R F, Fitton B and Painter G S 1974 *Phys. Rev. B* **9** 1926
Zachariasen W H 1963 *Acta Crystallogr.* **16** 1139