Figures

Edge-state effects on the magnetooptical activity of nanographite layers

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Figure 1: Example of a nanographite plan with rectangular shape. The boundaries have two different kinds of edges: the armchair and the zig-zag edges. The wave functions of the edge states are preferentially localized on the zig-zag edges.
Figure 2: Relative variation of the polarizability, \((P(T, \phi) - P(T, 0))/P(T, 0)\), of a nanographite plane with 78 benzene rings as function of the magnetic flux \(\phi\), in units of \(\phi_0\), for \(T \simeq 0.1K\). \(\phi/\phi_0 = 10^{-5}\) corresponds to a magnetic field of 1 tesla approximately. The full line is obtained for 78 electrons (half-filled band); the dotted curve is for 77 electrons. The edge states are populated only at half-filling and therefore responsible for the quadratic dependence seen in this figure.
Edge-state effects on the magneto-polarizability of nanographite layers

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Only very recently a new type of magnetism similar to a spin glass state was found for activated carbon fibers prepared at heating temperatures over 1200 °C [1]. These materials are supposed to be well described by a disordered network of nanographite layers with a characteristic length of some tens angstroem [2]. In connection with recent theoretical works on graphite ribbons, it was suggested by Shibayama et al. that the spins observed in [1] are due to the edge states of the π electrons whose wave functions are mainly localized on the boundaries of the layers. Indeed, several theoretical studies of graphite ribbons [3,4], had predicted the existence of such states. These edge states are expected to effect novel electrical and magnetic properties such as a paramagnetic behaviour at low temperatures [4]. These theoretical predictions could also be of importance for disordered or amorphous carbon materials where effective nanographite areas appear.

The purpose of this letter is to propose a novel way to identify the existence of edge states in activated carbon fibers or any other disordered or amorphous carbon compounds. Indeed, we believe that the study of their polarizability under an uniform and static magnetic field should give a very direct way to identify such states. Similar studies have already been proposed in [5] and [6] for
cylindrical-like systems such as carbon nanotubes, on the base of semi-classical arguments and full quantum calculations, respectively. In these articles, it was pointed out that the static magneto-polarizability of cylindrical systems shows a very intricate behaviour due to the Aharonov-Bohm effect. It was then suggested that the careful analysis of these complicated features should provide a tool to get informations about the excited states of these systems. The same kind of idea is followed in this work.

As a first example, we consider here perfect nanographite layers with rectangular shapes (figure 1); more complicated cases will be subject of subsequent publications. At the boundaries two kinds of edge appear: the so-called armchair and zig-zag edges. The $\pi$ electrons are described by an usual tight binding model. Since we want to discuss only orbital magnetism, they are considered as spinless particles.

$$\hat{H} = \sum_{i,j} t_{ij} a_i^{\dagger} a_j$$

where the operator $a_i^{\dagger}$ ($a_i$) creates (annihilates) a $\pi$ electron on site $i$ of the nanographite, $t_{ij}$ is the transfer integral between sites $i$ and $j$ - a real quantity without magnetic field. The summation in (1) is over nearest-neighbours sites.

As found in references [3,4] for graphite ribbons, our analysis of the eigenstates of (1) for nanographite layers shows the existence of edge states. Moreover, in agreement with the results of these previous studies, these states have non-bonding character, are preferentially localized on the zig-zag edges and their energies are in the middle of the gap, showing a small dispersion. The number of edge states depends on the size of the nanographite rectangles.

Next we apply an uniform magnetic field $\vec{B}$, perpendicular to the nanographite
layer. In the tight-binding model \((\Pi)\) we then proceed to the so-called London substitution, 
\[ t_{ij} \rightarrow t_{ij} e^{i2\pi \frac{e}{\hbar c} \int_{i}^{j} \vec{d}\vec{A}}, \]
where \( \vec{A} \) is the vector potential. For calculations we choose, as in \([4]\), the Landau gauge.

By comparison with the work done in \([5,6]\), one can say that the edge states define an effective rings. We are then again in the situation described in \([5,6]\) of a cylindrical system submitted to a magnetic field applied along the cylindrical axis. The main idea of our proposal is the following: only the edge states will react to a magnetic field sufficiently small that the characteristic length of the corresponding cyclotron radius remains comparable to the system size. We want to stress in this communication that this sensibility of the edge states should be apparent in the behaviour of the polarizability. The analysis of this physical quantity as function of the magnetic-field should then give a complementary experimental tool for the study of carbon materials such as carbon fibers and amorphous carbons.

We apply an electric field \( \vec{E} \), parallel to the nanographite plane. It could be oriented in any direction without changing qualitatively the results shown here. Next, we calculate the polarizability,

\[ P(T, \phi) = \frac{1}{|\vec{E}|} \frac{Tr(\hat{d}e^{-\beta(\hat{H}-\mu)})}{Tr(e^{-\beta(\hat{H}-\mu)})} \]

where, as usual, \( \beta = \frac{1}{k_B T} \) \((T \text{ is the temperature)}\), \( \mu \) is the chemical potential, and \( \hat{d} \) is the dipole operator, \( \hat{d} = e \sum_i \vec{r}_i. \vec{E}a_i^\dagger a_i \). The site vector \( \vec{r}_i \) is defined with respect to an arbitrary origin. \( \phi = 2\pi \frac{e}{\hbar c} S|\vec{B}| \) is the magnetic flux in units of \( \phi_0 = \frac{e}{c} \), where \( S \) is the surface of a benzene ring.

If the size of the nanographite plan is large enough, signatures of the edge-states should appear in its magneto-polarizability for not too large values of the magnetic field. A characteristic result is shown in figure 2 for a nanographite
layer with 78 benzene rings. In this particular case, there are two edge states with quasi-degenerated energies at zero. An appropriate way to measure the localisation of the different wave functions is to evaluate the sum over the square root of their coefficients along the edges, \( W_e = \sum_{i \in \text{edge}} a_i^2 \). This quantity shows us for the chosen example that: (i) the edge states are at 90% localized on the edges, (ii) there is a small diffusion of the wave function from the edges to the interior of the plane induced by the magnetic field.

Figure 2 shows the corresponding polarizability as function of the magnetic flux for two different fillings; a magnetic flux of \( \phi/\phi_0 = 10^{-5} \) corresponds approximately to a field of 1 Tesla. The full curve is for 78 electrons, which corresponds to the half-filling case, and the dotted curve is for 77 electrons. The temperature is very small \( k_B T = 10^{-5} t_{ij} \), which can be reasonably estimated to \( T \approx 0.1K \), a quantity much smaller than the gap between the energies of the edges states and the rest of the spectrum. So one can conclude that the edge states are occupied only at half-filling. Since only the polarizability for the half-filled band is noticeably a function of the magnetic flux, we may conclude that the edge states are responsible for the strong quadratic dependence obtained for a reasonably small magnetic field (about a few Tesla). It should be stressed that the relative variations in the figure 2 for the half-filled case could be detected experimentally nowaday. To conclude, our claim is that it is possible to identify the existence of edge states in activated carbon fibers or amorphous carbon by measurement of the magneto-polarizability of these materials. Moreover, we believe that informations about the effective sizes of the graphite like regions in the carbon fibers can be gained by careful studies of the quadratic behaviour pointed out here. More systematic studies will be published elsewhere.
Before ending this communication, one should stress first, that electron-electron interactions should be incorporated to get better estimate of the absolute value relative of the magneto-polarizability. However, the screening effect should not depend on magnetic field and therefore, should not change its relative variations (figure 2). Second, the Zeeman and spin-orbit coupling should be also incorporated for a complete treatment. However, for the values of the field considered here, these interactions are less important than those discussed in this work. Thus they should not change drastically our results [6]. Finally, it may be difficult in practice to apply the magnetic field perpendicular to the plan. In this case, we should simply replace $H$ by $H \cos \theta$ in our calculations, where $\theta$ is the angle between the magnetic field and the normal to the plan. Moreover, for disordered materials several averaging procedures should be applied: averaging over the size and shape of the nanographites and averaging over $\theta$.

References

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