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Magnetic interferometer effect in a graphite intercalation compound

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We report the first observation of the magnetic interferometer effect in a graphite intercalation compound. This effect allows the first precise measurement of trigonal warping in these compounds. The warping cannot be described simply in terms of the standard band model of graphite developed for the Brillouin-zone edges, but can be explained by "nonparabolic" effects, including the momentum dependence of the band parameters. We observe a strong dependence of the warping on the carrier concentration.

Recently, it has been shown[1,2] that the shape of the π bands in graphite remains virtually unchanged during intercalation by acceptors, with the Fermi surface shifting smoothly within the band as charge transfer is increased. This allows the charge transfer to be found from magneto-oscillatory measurements of the Fermi surface. The values of charge transfer so determined were shown[2] to be in good agreement with other estimates.

Experimental magneto-oscillatory spectra are generally found to contain a number of frequencies in addition to the n values expected for a stage-n surface. These extra frequencies are probably produced by a variety of different effects, including magnetic interaction[2,3] and the presence of superlattices.[4] In this paper, we show that a particular frequency observed in AsF_5-graphites can be ascribed to the magnetic interferometer effect.[2,5] Such effects are expected to be quite strong in intercalation compounds because of the two-dimensional nature of the Fermi surface. Interpretation of this effect allows the first direct measurement of trigonal warping in an intercalation compound. The observed warping cannot be explained on the basis of the usual rigid-band model of graphite (Slonczewski-Weiss-McClure model)[6] but can be understood by taking nonparabolic effects[7,8] into account. We observe a variation of the trigonal warping with charge transfer which cannot be simply explained.

The Fermi surfaces in acceptor intercalation compounds are cylinders situated at the corners of the Brillouin zone (K points). In Ref. 2, it was postulated that when the charge transfer is exactly $f=\frac{4}{9}$ per intercalant atom, the ionized molecules (AsF_6^-) form a hexagonal 3×3 superlattice [Fig. 1(a)]. For this particular lattice, the K point is folded into the Γ point, and each trigonally warped cylindrical Fermi surface is rearranged to give two concentric cylinders with hexagonal symmetry. Figure 1(b) shows the two new surfaces, BI (dashed line) and BII (solid), produced from the smaller stage-2 Fermi surface. The small superlattice gaps, produced at the points where these two cylinders nearly touch, are easily broken down in a field of about 1 T, leading to the observed magnetic interferences. As shown in Fig. 1(b), an electron may travel from point A to point B either by staying on the BI orbit or, via a double magnetic breakdown, by following a section of the BII orbit. The resulting interference of the electronic waves is exactly analogous to the two-slit interference of light; it leads to a magnetic-field-dependent oscillation in transport properties at the frequency β which corresponds to the area surrounded by the two paths [shaded region of Fig. 1(b)]. In the absence of trigonal warping, the BI and BII orbits would coincide, and the interference effect would be absent.

In both stage-1 and stage-2 compounds of AsF_5-graphite, we observe a low-frequency oscillation (denoted β) which we identify as a magnetic interferometer orbit for the following reasons: (1) It is

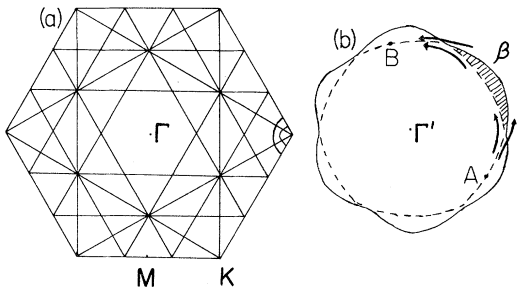

FIG. 1. (a) Two-dimensional Brillouin zone of graphite, showing stage-2 AsF_5-graphite Fermi surfaces at one K point, and the new zone boundaries introduced by a 3×3 superlattice. (b) Solid and dashed curves show the two Fermi surfaces generated from the smaller stage-2 Fermi surface by the superlattice potential. Magnetic breakdown occurs at the points of closest approach of the two surfaces, causing an interferometer orbit corresponding to the area between two breakdown points (shaded). Arrows show the interfering paths.

found only in transport measurements (magnetoresistance), and is absent in the magnetization spectrum (de Haas–van Alphen effect), in accordance with prediction.[5] (2) The effective mass of the oscillation is quite low, as expected. By contrast, a magnetic interaction effect would show a mass equal to the sum of the two separate masses. (3) The β frequency produces a strong modulation of the fundamental frequency associated with the large Fermi surface. All orbits of frequency $B\mathrm{I}+n\beta$, where n is any integer, can occur. Figure 2 shows Fourier transforms of the magnetoresistance spectra for both stages 1 and 2. The fundamental frequency shows a series of equally spaced sidebands with the spacing equal to the β frequency.

In the rigid-band model of Slonczewski, Weiss, and McClure[6] (SWM), trigonal warping is determined by the parameter γ_3, which is produced via the interaction of carbons on adjacent layers. In applying this model to a stage-n intercalation compound, only the n graphite layers between a pair of intercalant layers are assumed to contribute to the interaction. In particular, for a stage-1 compound, all interlayer interactions are absent—hence no trigonal warping is expected. While some warping is present in stage 2, it is too small to account for observation. The value of γ_3 would have to be nearly doubled to reproduce the correct β frequency— in contrast to the other band parameters, which are practically unchanged from their graphitic values.

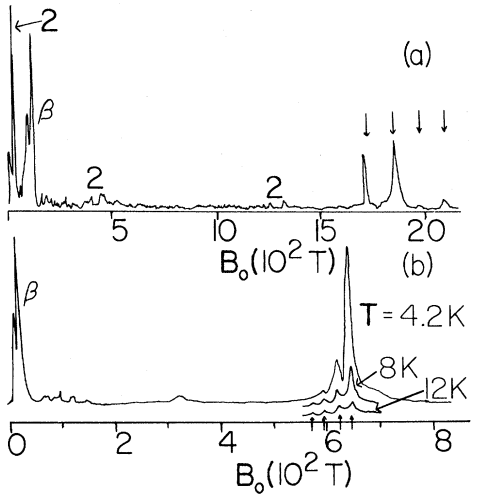

FIG. 2. (a) Fourier transform of Shubnikov–de Haas spectrum for stage-1 AsF_5-graphite showing the β frequency and the resulting modulation of the principal frequency (vertical arrows are spaced by the β frequency). Peaks marked 2 are probably due to regions of stage 2 in the sample. (b) Similar spectrum for stage 2. Note that as the temperature is increased, the modulations become more prominent.

To resolve these discrepancies, we have looked at rigid-band models which generalize the SWM result. The SWM result is valid only near the K point of the Brillouin zone, while others[7,8] have produced models of the full π bands. We have studied how these corrections modify the bands near the Fermi surface. We find that the *areas* of the Fermi surfaces are essentially unchanged, but *trigonal warping* is greatly enhanced and should be present in stage 1 as well. The former result is consistent with the experimental result that the SWM parameters describe the areas of the Fermi surfaces of intercalation compounds,[1,2] while the latter result allows us to explain the frequencies of the β oscillations. The lowest-order correction to the SWM results consists of replacing the parameter γ_0 by γ_0', where

$$\gamma_0'^2=\gamma_0^2\left(1-\frac{\alpha k_F a}{2\sqrt{3}\gamma_0}\cos 3\theta\right) ,$$

where $a=2.46$ Å, k_F is the Fermi momentum, and θ is the angle between k and the [100] axis. In a stage-1 sample with $f=0.37$ we find $\alpha=-0.89\gamma_0$; in stage 2, the β frequency is about three times smaller, but the same value of α gives agreement with the data near the commensurate composition, $f=0.44$. (In stage 2 we include the effect of ordinary trigonal warping, with γ_3=0.3 eV.)

As f is varied, the β frequency remains present over the range $0.36<f<0.46$, but is absent for $f<0.36$. In stage-2 samples,[9] the frequency of the β oscillation is found to decrease as f increases (Fig. 3). This is in contrast to the simple prediction based on band filling with fixed γ_3, α, but is consistent with magnetoreflection studies[10] which find that intercalation seems to decrease trigonal warping. This behavior may be related to modifications of the Fermi-surface shape produced by in-plane charge-density oscillation. These have been predicted[11,12] to occur in order to screen the ionic potential produced in the intercalant layer.

In terms of the Fourier coefficients introduced by Johnson and Dresselhaus,[7] the parameters γ_0 and α may be rewritten[13]:

$$\gamma_0=-a_{010}+2a_{0\bar{2}0}+a_{1\bar{2}0} ,$$

$$\alpha=a_{010}+4a_{0\bar{2}0}-13a_{1\bar{2}0} .$$

In a linear combination of atomic orbitals model, a_{010} is a matrix element for nearest-neighbor interactions, and the other terms refer to more distant neighbors. The higher-order terms were introduced to explain the optical spectra of graphite: if only a_{010} is nonzero, there should be a strong interband transition at $h\nu\simeq 2\gamma_0=6.4$ eV, whereas it is observed to be close to 4.9 eV. while our data cannot specify all three Fourier coefficients, the ratio $\alpha/\gamma_0\simeq -0.89$ is close

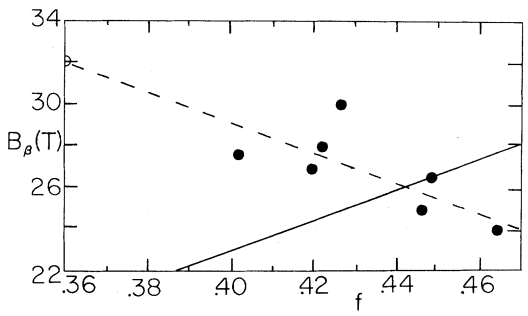

FIG. 3. Circles are the observed β frequency as a function of change transfer f. [The open circle is the stage-2 data of Fig. 2(a).] The solid line is the theoretical curve, assuming trigonal warping is independent of f (constant γ_3, α). Dashed line is a guide to the eye.

to the value -1 expected if only a_{010} were nonzero. It is possible to adjust the a's to give γ_0, α and the correct optical gap, but then a_{010} is smaller than the other parameters.[14] Alternatively, Fig. 3 suggests that α has a larger value in pure graphite and is reduced by intercalation.

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[12]G. Campagnoli and E. Tosatti, Ref. 4, p. 144.
[13]The expression for γ_0 in Ref. 7 is incorrect. Consequently, so is the dashed curve of Fig. 1 in Ref. 1—the corrected curve would be nearly indistinguishable from the solid (SWM) curve.
[14]We do not measure the sign of α in our experiments; however, choosing the positive sign does not improve agreement with optical results.