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THE INTERRELATION OF SHUBNIKOV-DE HAAS, MAGNETOREFLECTION AND TRANSPORT PROPERTIES OF ALKALI METAL DONOR INTERCALATION COMPOUNDS

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The k_z-axis zone folded Hamiltonian based on pristine graphite energy bands with an empty intercalate layer accounts for both observations of the Fermi surface made by the Shubnikov-de Haas technique, which show large changes with intercalation, and of the magnetic energy level structure by the magnetoreflection technique, where very small changes are found. This model has implications for transport and optical properties for donor intercalation compounds.

Because of the unusual properties of graphite intercalation compounds and their close connection to the semiconductor superlattice structures now being fabricated by molecular beam epitaxy, graphite intercalation compounds have attracted attention in the semiconductor community. Analogous to the transport behavior observed for the semiconductor superlattice structures, the high electrical conductivity of graphite intercalation compounds is achieved by charge transfer from the intercalate layers where the mobility is low to the graphite layers where the mobility is very high. The superlattice structure created by molecular beam epitaxy growth is achieved in graphite intercalation compounds by the staging mechanism which results in intercalated graphite with sequential intercalant layers separated by n graphite layers where n denotes the stage. For intercalated graphite the staging periodicity is long range and is a dominant symmetry.

The electronic structure is determined by the basic symmetry of graphite as modified by the staging periodicity. This structure is here studied by the Shubnikov-de Haas effect for a determination of the Fermi surface and by the magnetoreflection technique which is sensitive to the quantized electronic energy levels in a magnetic field. A phenomenological model based on crystal symmetry is used to interpret and to interrelate the experimental observations made by the two techniques. Application of the calculational techniques developed for the intercalated graphite superlattice structures to the semiconductor superlattice structures could be of significance.

Observation of only small changes in the electronic band parameters due to intercalation suggests a theory for the electronic structure based on perturbed pristine graphite. The staging periodicity is treated by a k_z-folding of the energy bands and a replacement of a graphite layer by intercalant at the proper periodicity [1,2]. The interaction between the intercalant and the graphite bounding layer is treated in perturbation theory. Results for the graphite π-bands for a stage 5 compound are shown in Fig. 1 for an "empty lattice intercalate model", where the intercalate layer is assumed to be empty and the intercalate-graphite bounding layer

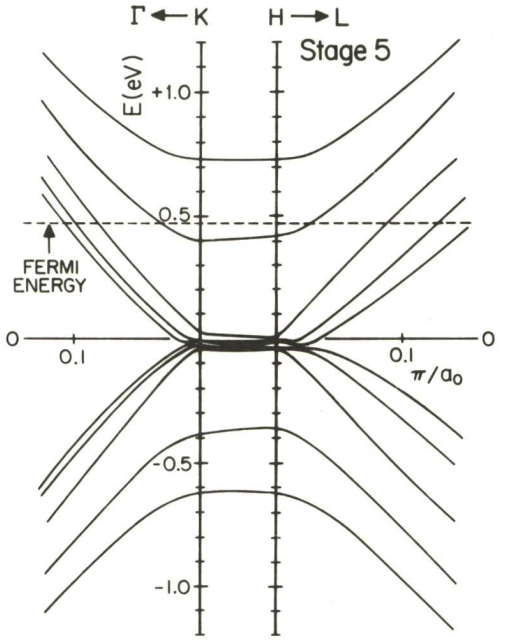

Fig. 1 Electronic band structure in the vicinity of the HK axis for a stage 5 "empty intercalate layer" model for a graphite intercalation compound: The Fermi energy is determined to fit the observed SdH frequencies. For the indicated Fermi level, four of the conduction bands are partially occupied and give rise to Fermi surfaces and carrier pockets.

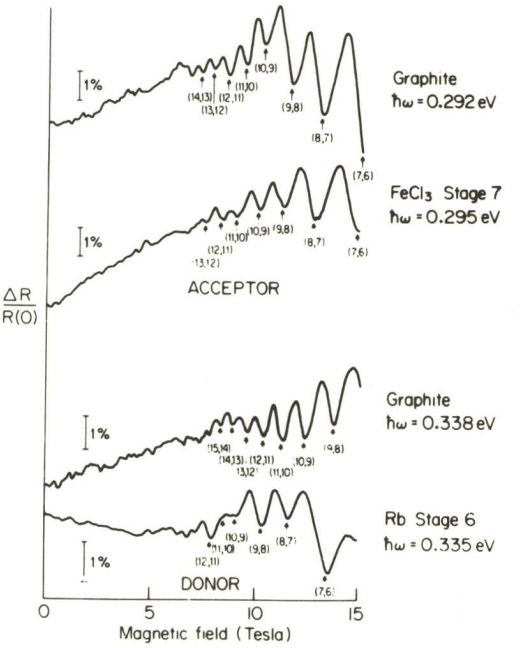

Fig. 2 Magnetoreflection spectra using (+) circular polarization for an acceptor ($FeCl_3$ stage 7) and for a donor compound (Rb stage 6) at the indicated photon energies: For comparison, traces for graphite are shown. The resonances are specified by quantum numbers for the initial and final states (Ref. 3).

interaction is neglected [2]. These results, shown for the 5 conduction and 5 valence bands near the H-K zone edge, demonstrate that intercalation greatly decreases the k_z dispersion. The placement of the Fermi level in Fig. 1 results in a partial occupation of the π-bands which gives rise to a z-dependent charge distribution.

Detailed information on the form of these energy bands is provided by the magnetoreflection experiment which probes resonant transitions from occupied magnetic energy levels below the Fermi level E_F to unoccupied levels above E_F. Measurements have been made on well-staged donor (stages $n \gtrsim 6$) and acceptor (stage $n \gtrsim 4$) compounds [3], characterized by (00ℓ) diffractograms to establish their stage index and staging fidelity. Resonant structures observed in the magnetoreflection spectra are identified with Landau level transitions between magnetic energy levels associated with the E_3 bands which in graphite are degenerate at the K-point. The close similarity of the magnetoreflection spectra in pristine graphite and in these donor and acceptor compounds indicates that the electronic structure of the π-bands near E_F remains highly graphitic upon intercalation.

Table 1 Results of analysis of magnetoreflection experiments

Intercalant	Stage	m_c^*	m_v^*	(γ_0^2/γ_1)
(HOPG)	∞	0.056	0.084	25.1
$AlCl_3$	8	0.056	0.076	26.0
	6	0.054	0.076	26.6
$FeCl_3$	7	0.055	0.079	26.1
	5	0.054	0.075	26.6
Rb	6	0.045	0.065	31.7

Analysis of the observed spectra on the basis of a two-band model for the K-point valence and conduction bands yields the valence and conduction band effective masses m_v^* and m_c^*. Since the observed magnetoreflection spectra in the intercalation compounds are well satisfied by the form of the Slonczewski-Weiss-McClure (SWMcC) energy level model for graphite, analysis of these data yields the SWMcC band parameter combination (γ_0^2/γ_1) which determines the Landau level separation. A summary of typical results is given in Table 1, giving strong support for the close relation between the graphite π-bands in the intercalation compounds and in pristine graphite.

To study the Fermi surface, Shubnikov-de Haas (SdH) measurements of the transverse magnetoresistance have been made. Particular emphasis was given to measurements on encapsulated, well-staged alkali metal donor compounds [2]. The four-point method was used to study the a-plane transverse magnetoresistance in the temperature range $1.4<T<4.2K$ and in magnetic fields up to 15 Tesla. Data acquisition was by computer, and the data were manipulated to obtain a Fourier power spectrum of resistance vs 1/H, thereby yielding the frequencies of SdH oscillations, which are related to the extremal cross sections of the Fermi surface [2]. The Fourier power spectra for the SdH frequencies for potassium stages 2,5 and 8 are shown in Fig. 3. Of particular significance is the stage dependence of the observed spectra, in agreement with results by Suematsu et al. [4]. A detailed study was made for several stage 5 samples and the observed SdH frequencies compared with predictions of the empty intercalate layer model of Fig. 1, with the Fermi level placed to fit the SdH frequencies. It should be noted that the empty intercalate layer model uses only graphite band parameters, which have been determined previously. Thus the good agreement obtained between the calculated and observed SdH frequencies in Table 2 gives strong support that the energy levels close to E_F are very similar to the basic π-bands of pristine graphite in agreement with the magnetoreflection results discussed above. The large change in the SdH frequencies and their stage dependence is due to the stage dependence of the number of conduction and valence bands, of the k_z-axis zone-folding procedure and of the position of the Fermi level relative to the K-point band edge. It is of interest to note that light masses similar to those in pristine graphite are found for the small carrier pockets, with significantly larger masses for the larger carrier pockets which probably contribute more significantly to transport properties. It is furthermore likely that other carrier pockets of lower mobility occur elsewhere in the zone, thereby accounting for the proper charge transfer.

From the Shubnikov-de Haas results and the model for the energy bands we conclude that the transport properties of graphite intercalation compounds must be interpreted in terms of a multi-pocket model, with contributions from each of the occupied carrier pockets (see Fig. 1 and Table 2). Explicit use of an energy band model which can be applied to any stage and intercalant provides a basis for calculations of the transport properties for intercalated graphite.

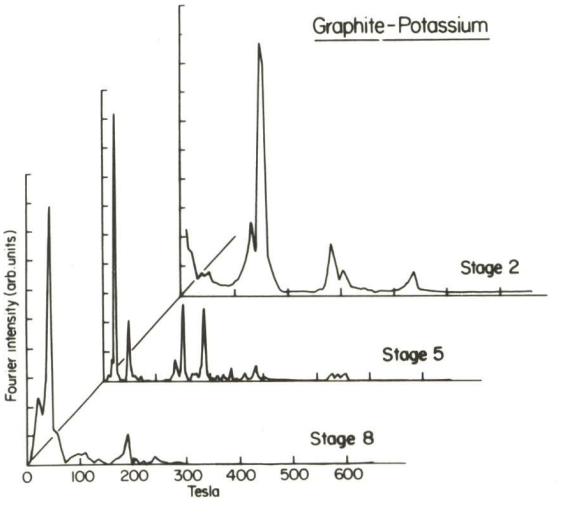

Fig. 3 Shubnikov-de Haas Fourier transform power spectra for stages 2,5 and 8 graphite-K: These power spectra were obtained by a Fourier transform of an experimental resistivity vs 1/H trace for magnetic fields H<15 Tesla. The peaks in the power spectra correspond to SdH frequencies, which are given in Tesla and the same scale is used for each stage.

Table 2 Fermi surface parameters associated with stage 5 graphite-K

	K-point Band Designation			
Fermi Surface Parameters	K_1	K_2	K_3	K_4
m^*/m_o	0.143	0.115	0.0828	0.0511
n_i ($\times 10^{20}$ cm^{-3})	2.36	1.76	0.975	0.138
SdH Frequencies Calculated (Tesla)	401	300	163	26.7
Observed (Tesla)	453 430	290 267 243	191 152 135	24 18

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