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## ELECTRONIC PROPERTIES OF METAL CHLORIDE INTERCALANTS OF GRAPHITE\*, \*\*

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### Summary

The Shubnikov-deHaas (SdH) effect has been used to study the electronic properties of graphite intercalated with PdCl<sub>2</sub> (stage 3), FeCl<sub>3</sub> (stages 2, 4, 6, and 11), CuCl<sub>2</sub> (stage 1), and WCl<sub>6</sub> (stage 5). For the palladium chloride, ferric chloride, and copper chloride intercalants the SdH spectra are similar: these show frequencies of approximately, 27, 80, 380, and 550 Tesla for fields parallel to the *c*-axis. The effective masses have been measured for each of these carriers, and are of the order of 0.1  $m_0$ , where  $m_0$  is the free electron mass. These carriers have mobilities of the order of 10<sup>4</sup> cm<sup>2</sup>/V s at 4 Kelvin. No graphite frequencies (4.7 and 6.3 Tesla) were observed. The similarity of data for these compounds suggests comparable charge transfer and Fermi surfaces. Data from the tungsten chloride compound are somewhat different: the majority carrier electron frequency for pure graphite was observed, as well as frequencies of 76 and 540 Tesla. Air stability of all compounds was studied. In addition, we have used differential thermal analysis, X-ray diffraction, and scanning and transmission electron microscopy to characterize the material.

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## Introduction

For years quantum oscillatory phenomena such as the deHaas–van Alphen and Shubnikov–deHaas effects have been used to determine Fermi surface parameters for metals, dilute alloys, and a few compounds [1]. Included was work on pure graphite, with the resultant determination of many of the parameters of the Slonczewski–Weiss–McClure energy band model.

The process of intercalation involves charge transfer to, or from, the intercalant layer. To a first approximation one can consider that this moves the Fermi energy up or down in an otherwise rigid band of the electron energy states of graphite. Since the density of states at the Fermi energy is near a minimum for pure graphite, the intercalation by either donors or acceptors rapidly increases the density of states. In most three dimensional metals the analogous operation to intercalation would be alloying. Alloying usually reduces the carrier mobility so that quantum oscillatory effects are very difficult to observe for even a few percent. of a “foreign” element. Since the host layers of carbon atoms remain relatively undisturbed by intercalation (some evidence to the contrary was reported recently by Moss) [2], the carrier mobilities decrease only by about an order of magnitude. Thus quantum oscillatory phenomena are remarkably easy to observe. Bender and Young [3] were the first to see these effects in intercalated graphite. They made a fairly complete study of bromine intercalated graphite using the Shubnikov–deHaas effect, found the simultaneous presence of pure graphite frequencies, and up to four frequencies due to intercalation.

Recently, Batallon *et al.*, [4] and Tanuma *et al.* [5] have reported results from magneto thermal oscillation experiments on  $C_{12n}(SbCl_5)$  (acceptor compounds) for stages 2 and 4. Their results were interpreted by assuming that the compounds were composed of two phases: pure graphite, and intercalated sandwiches which behave like two-dimensional metals. To analyze their data a nearly free electron Fermi surface of two dimensions was constructed which explained two of the observed frequencies. The presence of additional frequencies was attributed to the presence of charge density waves and to magnetic breakdown. A major observation was the lack of stage dependence of frequencies.

Tanuma *et al.* [5] observed the deHaas–van Alphen effect in potassium intercalated graphite (a donor compound) for  $C_{48}K$ ,  $C_{36}K$ , and  $C_8K$  (stages 4, 3 and 1). To explain their data Tanuma *et al.* used a rigid band model in which the new *c*-axis periodicity introduced by staging produced new Brillouin Zone boundaries which broke up the original Fermi surface into sections having different frequencies. For  $C_8K$  they compared their results with a tight binding calculation of Inoshita *et al.* [6]. The latter calculation had two Fermi surface parts. One part was similar to a rigid band extension of the graphite Fermi surface. The other (located at the  $\Gamma$  point of the Brillouin Zone) had features like a pure alkali metal Fermi surface.

At the March, 1980, American Physical Society Meeting deHaas-van Alphen data for  $C_{8n}AsF_5$  stages 1 and 2 were reported [7], and interpretation was based on a two-dimensional Brillouin Zone. An important result of this work was the observation of a very strong dependence of frequency and amplitude on air exposure. Shubnikov-deHaas work on the alkali-metal compounds was also reported at the March meeting [8]. Interpretation of these data was based on modifications of the graphite rigid bands: zone folding due to *c*-axis periodicity, and a reduced  $k_z$  dispersion due to intercalant layers. Also reported by Markiewicz *et al.* [9] at that meeting (in a post deadline paper) were results on stages 1, 2, and 3,  $AsF_5$  compounds.

In this paper we report on Shubnikov-deHaas studies in a series of chloride intercalation compounds [10]. In addition to reporting SdH frequencies we have determined effective masses, and in a few cases have found mean carrier scattering times. When both scattering times and effective masses were determined, the mobility for individual carriers (not just averages over all carriers) was found. In addition, differential thermal analysis and electron microscopy were used to characterize materials.

## Experimental

Two techniques for sample preparation were used: two zone [11], and transport. The two-zone method was used for preparation of  $C_xFeCl_3$  by sublimating  $FeCl_3$  from one chamber at 300 °C to another chamber containing the sample at 310 °C. This preparation was described in more detail earlier [10, 11]. Since details of the vapor transport preparation of  $PdCl_2$ -graphite have not been published in complete detail, these are presented in Appendix A.

The  $CuCl_2$  and  $WCl_6$  compounds were prepared in a transport tube with argon or chlorine gas flow. Reactions with graphite were very slow since the vapor pressures above  $CuCl_2$ , solid at high temperatures, are very low. The presence of added chlorine gas in the transport tube aided the intercalation reaction with  $CuCl_2$ . In order better to understand  $CuCl_2$  intercalation, the vapor pressures of  $Cu_3Cl$  and of  $Cl_2$  over solid  $CuCl_2$  were calculated. The results are shown in Appendix B.

Shubnikov-deHaas data were taken with two probes, one having double chambers, one filled with helium gas, so that temperatures could be easily and accurately changed or held constant. Data up to 55 K were taken. The second probe had a rotating platform so data at 1.2 - 4 K could be taken as a function of the angle between field and the *c*-axis. Two different magnets were used. One was a superconducting solenoid with a maximum field of 14 T, and a 2-in. dia. liquid helium insert dewar. The second was water cooled and had a maximum field of 23 T (at the National Magnet Laboratory) in which data were taken only at 4 K. In both cases, data were digitized and a Fourier analysis of frequencies was made. Data were taken both d.c., and with field modulation and lock-in amplifier detection.

Five samples of  $C_x\text{FeCl}_3$  intercalated graphite were studied, two of stage 4, and one each of stages 2, 6, and 11. Shubnikov-deHaas experiments were also done on four samples of  $C_x\text{PdCl}_2$  (stage 3) three of  $\text{CuCl}_2$  (stage 1), and one of  $\text{WCl}_6$  (stage 5). Since only one sample of  $\text{WCl}_6$  intercalated graphite was used, the results from this compound may be considered preliminary.

### Shubnikov-deHaas results

Figure 1 is a plot of the field modulated resistivity as a function of field to 14 T for a sample of  $\text{CuCl}_2$  intercalated graphite at 4.2 K. Similar data were found for  $\text{PdCl}_2$  and  $\text{FeCl}_3$  intercalated samples. The squared Fourier transform amplitudes are displayed as a function of frequency to 480 T in Fig. 2. Figure 3 shows details of the low frequency region of Fig. 2. The dominant frequencies for  $\text{CuCl}_2$  intercalants are obviously at 22, 70, 92, and 380 T. Double checks on values of the strongest frequencies were made for both d.c. and field modulated data by hand plots of integers *vs.* inverse field. Good agreement was found.

From studies of amplitude at various temperatures, the effective masses were determined using the relation [1]

$$m^* = \frac{m_0 \hbar \omega_0}{2\pi^2 k} \frac{d \ln A/T}{dT} \quad (1)$$

where  $m_0$  is the free electron mass,  $\omega_0$  the cyclation frequency,  $k$  the Boltzmann constant,  $T$  the temperature, and  $A$  the oscillatory amplitude. Plots of  $\ln A/T$  *vs.*  $T$  were straight lines with slopes related to  $m^*$  through eqn. (1). Figure 4 shows such plots for the 70 and 380 T frequencies in  $C_x\text{CuCl}_2$ . When

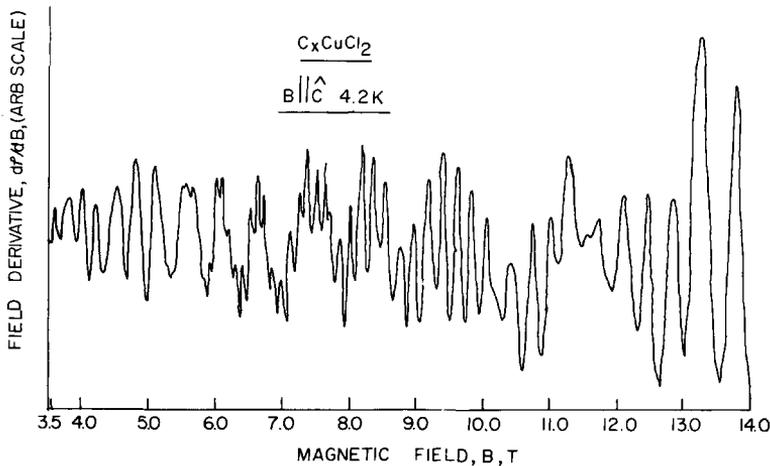


Fig. 1. Field derivative Shubnikov-deHaas data in copper chloride-graphite as a function of magnetic field to 14 T at 4.2 K with field parallel to the  $\bar{c}$  axis.

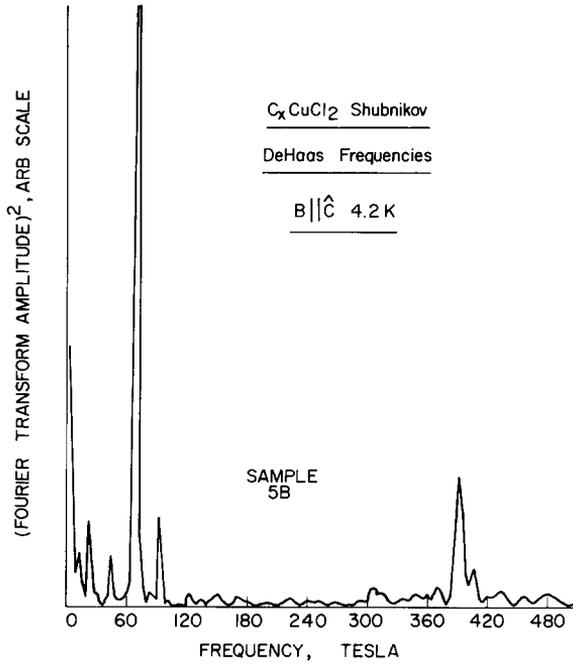


Fig. 2. Fourier transform amplitude squared as a function of frequency, from analysis of the copper chloride-graphite data of Fig. 1.

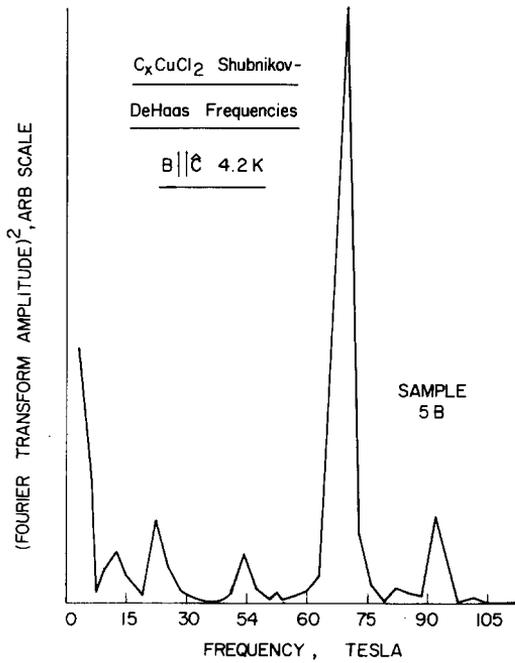


Fig. 3. Expanded scale of the low frequency data of Fig. 2.

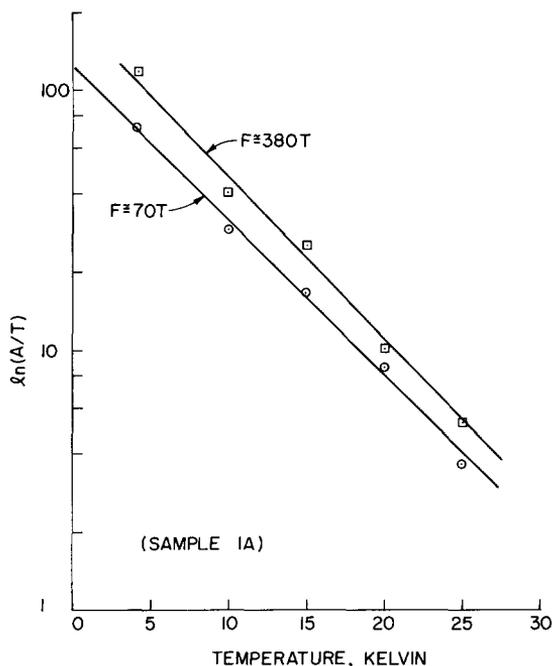


Fig. 4. Effective mass determinations for the  $F = 70$  and  $380$  T frequencies in copper chloride intercalated graphite.

possible, amplitudes at several field values were used, and good agreement between mass values was found.

Table 1 summarizes the frequency data on  $\text{PdCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{CuCl}_2$ , and  $\text{WCl}_6$  intercalation compounds. Notice that there are groupings of frequencies for each compound ranging from 22 to 550 T, with some exceptions. The greatest differences come with the  $\text{WCl}_6$  compound where one of the graphite frequencies is present, as well as one of the frequencies (at 75 T) of the group shown in the Table.

In Table 2 the effective masses are shown, corresponding to the frequencies  $F_1$ ,  $F_2$ ,  $F_3$  and  $F_4$  from Table 1.

From amplitude *vs.* field plots from d.c. data, the carrier scattering time  $\tau$  is determined. Once both  $\tau_i$  and  $m_i$  are determined for the  $i$ th carrier, the mobility of that carrier can be determined from

$$\mu_i = e\tau_i/m_i. \quad (2)$$

Results for several carriers are shown in Table 2.

### Differential thermal analysis

Thermal anomalies were looked for in  $\text{PdCl}_2$  and stage 6  $\text{FeCl}_3$  compounds, using a DuPont Model 910 differential scanning calorimeter with

TABLE 1

Measured Shubnikov-deHaas frequencies for metal chloride intercalants of graphite

Numbers were obtained from plots of Fourier transform amplitudes squared as a function of field, such as shown in Figs. 2 and 3. Frequencies for pure graphite are 6.6, 4.8, and 0.33 T for majority electron, majority hole, and minority hole, respectively.

| Intercalant<br>(stage) | Frequency (T) |        |        |         |       |
|------------------------|---------------|--------|--------|---------|-------|
|                        | $F_0$         | $F_1$  | $F_2$  | $F_3$   | $F_4$ |
| PdCl <sub>2</sub> (3)  | —             | 22 ± 8 | 85 ± 7 | 373 ± 5 | —     |
| FeCl <sub>3</sub> (2)  | —             | 26     | 80     | —       | 550   |
| FeCl <sub>3</sub> (4)  | —             | 24     | 125    | —       | 630   |
| FeCl <sub>3</sub> (6)  | —             | 22     | 90     | —       | 580   |
| FeCl <sub>3</sub> (11) | —             | 20     | 90     | —       | 560   |
| CuCl <sub>2</sub> (1)  | 7*            | 22     | 70     | 380     | 550   |
|                        |               |        | 92     |         |       |
| WCl <sub>6</sub> (5)   |               |        | 76     |         | 540   |

\*This frequency is *not* the graphite majority electron frequency since the associated effective mass is 0.01 - 0.02, a factor of 3 - 6 times too small.

TABLE 2

Effective masses  $m^*/m_0$ , carrier scattering times  $\tau$ , and mobilities  $\mu$ , corresponding to the frequencies  $F_i$  in Table 1.

In pure HOPG at 4 K,  $\mu \approx 10^5$  cm<sup>2</sup>/V s, and effective masses are 0.055  $m_0$ , 0.04  $m_0$ , and 0.005  $m_0$ , for majority electron, majority hole, and minority hole, respectively.

| Intercalant<br>(stage)            | Parameter                    | $F_0$       | $F_1$           | $F_2$               | $F_3$               | $F_4$ |
|-----------------------------------|------------------------------|-------------|-----------------|---------------------|---------------------|-------|
| PdCl <sub>2</sub> (3)             | $m^*/m_0$                    |             | 0.12            | 0.08                | 0.15                |       |
|                                   | $\tau$ (s)                   |             | —               | $5 \times 10^{-13}$ | $5 \times 10^{-13}$ |       |
|                                   | $\mu$ (cm <sup>2</sup> /V s) |             | —               | $1 \times 10^4$     | $6 \times 10^3$     |       |
| FeCl <sub>3</sub> (4)             | $m^*/m_0$                    |             | 0.016           | 0.10                | —                   | 0.16  |
|                                   | $\tau$ (s)                   |             | $10^{-13}$      | —                   | —                   | —     |
|                                   | $\mu$ (cm <sup>2</sup> /V s) |             | $2 \times 10^4$ | —                   | —                   | —     |
| CuCl <sub>2</sub> (1)             | $m^*/m_0$                    | 0.01 - 0.02 | —               | 0.07                | 0.15                | —     |
| WCl <sub>6</sub> (5) <sup>†</sup> | $m^*/m_0$                    | —           | —               | 0.1                 |                     |       |

<sup>†</sup>The graphite majority electron frequency of 6.6 T with a mass of 0.06  $m_0$  was observed for this material only.

better than 0.02 cal/g sensitivity. No thermal anomalies were seen for the PdCl<sub>2</sub> compound over the range 0 - 220 °C. The ferric chloride compound was heated from -90 to +120 °C, and an endotherm of 0.10 cal/g was observed at 22 K. A second endotherm, of 0.06 cal/g was found at 238 K. If these heats are attributed to intercalated FeCl<sub>3</sub>,  $\Delta H_{229} = 80$  cal/mole FeCl<sub>3</sub>,  $\Delta S_{229} = 0.35$  eu/FeCl<sub>3</sub>, and  $\Delta H_{238} = 48$  cal/mole FeCl<sub>3</sub>,  $\Delta S_{238} = 0.20$  eu. These enthalpies are similar in magnitude and temperature of occurrence to those of intercalant layer order-disorder transformations in graphite bro-

mides [12], where  $\Delta H_{278} \cong 125$  cal/mole  $\text{Br}_2$  and  $\Delta H_{298} \cong 13$  cal/mole  $\text{Br}_2$ , and in graphite nitrates, where  $\Delta H_{252} = 370$  cal/mole and  $\Delta H_{261} = 46$  cal/mole.

## Discussion

Tables 1 and 2 suggest that the Fermi surfaces of the palladium chloride, ferric chloride and copper chloride intercalation compounds of graphite are similar. There seem to be four groupings of frequencies: those near 22, 90, 380, and 550 Tesla, with some obvious small differences between compounds and stages. There is some evidence for additional frequencies with too low signal to noise ratio to be positively identified. In bromine-graphite there were seven frequencies [5], and these ranged from 15 to 540 T, that is, they had the same range of values. In  $\text{SbCl}_5$ -graphite there were three frequencies observed, and these were stage independent and, similarly, ranged from 50 to 550 T.

In copper chloride we observed a 7 T frequency having a mass of 0.01 - 0.02  $m_0$ . This cannot be attributed to the pure graphite majority electrons, because of the low mass. We speculate that this frequency comes from the H point of the Brillouin Zone, and has the same origin as the minority carrier holes in pure graphite but of higher frequency (due to the Fermi energy shift from intercalation). This frequency is difficult to observe at 4 K, and was best seen at higher temperatures where there was less interference from other frequencies. It is probably present in many acceptor compounds but has just not been observed until now. If it is from the H point, then it is a unique frequency to study as a function of stage, because it should not be affected by c-axis zone folding.

Effective mass measurements provide powerful additional data to aid the eventual identification of frequencies. Note that masses are generally only somewhat higher than those in pure graphite. This suggests the reasonableness of models for acceptor compounds which start with the rigid bands of graphite and add effects such as new Brillouin Zone boundaries due to new periodicities [14]. Models proposed so far have not been able to explain the origins of all frequencies found in the acceptor compounds. The two-dimensional Harrison models proposed so far must rely on such "refinements" as magnetic breakdown and charge density waves to explain frequency data. These do explain the lack of stage dependence of observed frequencies, however. At the moment there is need for both more theoretical work, as well as careful experiments to be done on the acceptor compounds. Much progress is being made, and the use of quantum oscillatory effects in the study of graphite intercalation compounds is adding valuable quantitative information.

## Acknowledgment

We thank Dr. G. Dresselhaus for use of his computer program to do Fourier transform analysis of data.

## Appendix A

### *C<sub>x</sub>PdCl<sub>2</sub> preparation*

Wafers of palladium chloride-graphite were prepared by a method described previously [15]. The pristine graphite wafer, a disc of Union Carbide highly oriented pyrolytic graphite, Grade ZYA, having a diameter of 0.72 cm, was cut from a specimen having an average basal plane misalignment or "mosaic spread" of approximately 0.5 deg (full width of half maximum intensity) and lattice spacings closely approximating theoretical values for graphite. The wafer was placed in a packed bed of anhydrous PdCl<sub>2</sub> in a quartz boat and heated for 21 h at 590 °C under Cl<sub>2</sub> flowing at 8 cm<sup>3</sup>/s through a quartz tube having a volume of 680 cm<sup>3</sup>. Comparison of initial and final weights yields an empirical formula C<sub>12.81</sub>PdCl<sub>2</sub>, corresponding to a reaction which is 84.4% complete based on the reported [16] formula C<sub>10.8</sub>PdCl<sub>2</sub>.

The specimen of palladium chloride-graphite thus prepared was cleaved into two nearly equal parts along the basal plane. One part was reserved for measurements of electronic properties, and the matching part was used for the additional physical characterizations now to be described. These characterizations are expected to apply equally well to the part of the specimen reserved for measurements of electronic properties.

Uniformity of reaction over the highly reflective cleaved surface was assessed by electron microprobe analysis using a Kevex energy dispersive detector. Backscattered Cl K $\alpha$  radiation was constant within a counting error  $\pm 3.3\%$  over the entire surface, consistent with the observed close approach to complete reaction. Comparable results were obtained by counting the overlapping (Pd L $\alpha$ , Cl K $\beta$ ) radiation. Energy dispersive analysis detected no other elements.

The X-ray diffraction pattern of this PdCl<sub>2</sub>-intercalated highly oriented pyrolytic graphite consists of a series of strong diffraction peaks which can be indexed as (00*l*) reflections of a third-stage compound with C<sub>0</sub> = 16.6 Å, compared with 16.7 Å as reported for the fully-reacted compound. Only 00*l* lines which are multiples of *l* = 5 are observed, presumably because the filled layer thickness, 6.65 Å, is a near-multiple of the graphite identity period; a similar selection rule operates in graphite bromides [17]. No diffraction peaks attributable to unreacted graphite were observed. Diffraction peaks due to Cu K $\alpha$ <sub>2</sub> radiation could clearly be distinguished from peaks due to Cu K $\alpha$ <sub>1</sub> at Bragg angles as small as 27 deg  $\theta$ , since pristine ZYA highly oriented pyrolytic graphite is an excellent monochromator and is little affected by the intercalation process. Rocking curve, or twice root-mean-square deviation of the C-axes of individual domains from parallelism, of this intercalated specimen was determined as 0.49 deg (full 005 peak width at half maximum intensity). This value is essentially unchanged from that of the pristine graphite.

Average basal plane stack height of PdCl<sub>2</sub>-graphite was determined from broadening of the (005) Bragg peak, treating it as though it were the (002) peak of pristine graphite. The observed peak width, 0.075 deg, com-

bined with an "instrumental" line broadening of 0.052 deg determined by using a silicon single crystal standard, yields an estimated basal plane stack height,  $L_c$ , of 1580 Å.  $L_c$  Values determined from angular breadths of the (002) peak of pristine highly oriented pyrolytic graphite are generally similar.

A somewhat more refined estimate of  $L_c$  can be obtained by separating the component of line broadening attributable to finite crystallite size from that due to lattice strain by using the formula [18]:

$$\beta \cos \theta = \frac{\lambda}{L_c} + 2\pi^2 \frac{\lambda}{C_0} \sigma^2 l^2 \quad (1)$$

where  $\theta$  is the Bragg angle of the (00 $l$ ),  $\beta$  is the full width at half maximum intensity, corrected for instrumental line broadening,  $\lambda = 1.5440$  Å for Cu K $\alpha$  radiation,  $\sigma$  is the lattice strain, and  $C_0$  appears to the inverse first power, not to the inverse second power.

Results in Table 3 yielded  $L_c = 4500$  Å,  $\sigma = 0.9 \times 10^{-3}$  when breadths of the resolved K $\alpha_1$  and K $\alpha_2$  peaks are separately extrapolated to  $l = 1$ . This value of mean strain reported here is somewhat smaller than known values for heat-treated pyrolytic carbons, but appears reasonable in view of the greater crystalline perfection of the highly oriented pyrolytic graphite used as starting material. The large discrepancy between values of  $L_c$  reported by the method of Thrower and Nagle [18] and that obtained by the Sherrer method arises because, in the present experiment, it is possible to separate the Cu K $\alpha_1$  and Cu K $\alpha_2$  reflections of the (00, 10), (00, 15) and (00, 20) planes, but not of the (005) plane. A plot of the combined full widths at half maximum intensity of Cu K $\alpha_1$  and Cu K $\alpha_2$  reflections as a function of  $l^2$  yields  $L_c = 2315$  Å.

These combined results show that the specimen of palladium dichloride-intercalated graphite used in the experiments contains only one crystal structure, that of a third-stage intercalation compound, and has the composition, C<sub>12.81</sub>PdCl<sub>2</sub> uniformly throughout the bulk. This third-stage compound is now known, by comparison with the results of Novikov *et al.* to be non-stoichiometric, and by comparison of its preparation conditions with reported diffusion coefficients and apparent activation energies for diffusion, to be synthesized by the same diffusion process reported previously. Clear separa-

TABLE 3  
Breadths of (00 $l$ ) lines in C<sub>12.81</sub>PdCl<sub>2</sub>

| $\theta$ (deg)         | Index  | $\Delta\theta_{\text{obs}}$ (rad) | $\beta_{\text{corr}}$ (rad) |
|------------------------|--------|-----------------------------------|-----------------------------|
| 13.520                 | 005    | $1.309 \times 10^{-3}$            | $9.409 \times 10^{-4}$      |
| 27.695 (K $\alpha_1$ ) | 00, 10 | $1.082 \times 10^{-3}$            | $5.855 \times 10^{-4}$      |
| 44.060 (K $\alpha_1$ ) | 00, 15 | $1.309 \times 10^{-3}$            | $9.408 \times 10^{-4}$      |
| 44.200 (K $\alpha_2$ ) |        | $1.396 \times 10^{-3}$            | $10.590 \times 10^{-4}$     |
| 70.825 (K $\alpha_1$ ) | 00, 20 | $3.054 \times 10^{-3}$            | $29.156 \times 10^{-4}$     |
| 71.180 (K $\alpha_2$ ) |        | $3.491 \times 10^{-3}$            | $33.699 \times 10^{-4}$     |

tion of  $\text{Cu K}\alpha_1$  from  $\text{Cu K}\alpha_2$  diffraction peaks, small values of mosaic spread, unusually large layer stack heights  $L_c$ , and exceptionally small values of mean strain,  $\sigma$ , parallel to the  $c$ -axis, all demonstrate that intercalation proceeds without introducing significant disorder in the basal plane structure of the pristine highly oriented pyrolytic graphite. Since transport of holes and electrons occurs in bands arising primarily from carbon orbitals, perturbations resulting from distorted bond distances or from misorientations of graphite layer planes are expected to be comparable with perturbations encountered in measurements on pristine highly oriented pyrolytic graphite itself.

## Appendix B

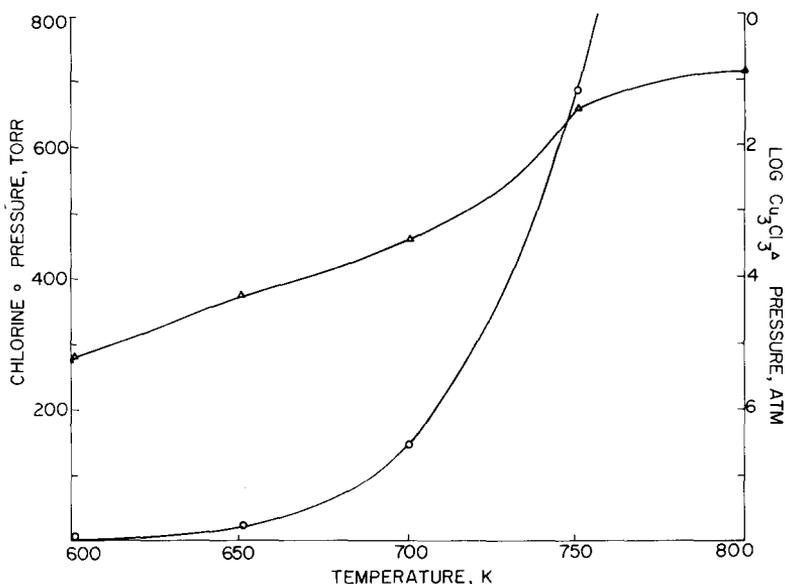


Fig. 5. Calculated vapor pressures over  $\text{CuCl}_2$ .

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