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Electronic structure of stage-2 $SbCl_5$-intercalated graphite

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The de Haas—van Alphen (dHvA) effect of the stage-2 $SbCl_5$-graphite intercalation compound was measured. With samples cooled quickly between 300 and 77 K in about 1 h many dHvA oscillations were observed. The dHvA spectrum obtained with samples cooled slowly in 24 h consisted of two oscillations coming from the basic graphitic bands and a low-frequency oscillation coming from intercalate-depleted regions near the edges of the samples. The frequencies of the dHvA oscillations and carrier cyclotron masses of the basic graphitic bands were compared to the predictions of two-dimensional energy band models and the value of the Fermi energy of -0.88 eV was obtained. The electron-phonon mass-enhancement parameter of 0.015 was estimated from the measured band parameters and the conductivity data. The charge transfer of 0.0205 elementary charge per carbon atom was also obtained from the values of the dHvA frequencies.

I. INTRODUCTION

The first measurements of quantum oscillatory phenomena of the $SbCl_5$-graphite intercalation compounds were reported by Batallan *et al.*[1] Stages 2 and 4 were investigated and the frequencies of the oscillations were found to be independent of stage. The data were explained by a free-electron model in which carriers from the intercalate were localized on graphite layers adjoining the intercalate. However, the de Haas—van Alphen (dHvA) work of Takahashi *et al.*[2] showed a stage dependence of the dHvA frequencies. A theoretical explanation of the observed oscillations in the stage-2 compound was given by Tanuma *et al.*[3] using the rigid-band model of Blinowski *et al.*[4] Since the number of observed frequencies was larger than that expected from the model, the in-plane zone folding technique[5] based on a 7×7 intercalate superstructure was used. However, the value of the charge transfer adjusted to fit the data was not in agreement with the one obtained from optical reflectance data of Blinowski *et al.*[4] and Eklund *et al.*[6] Furthermore, x-ray diffraction studies showed that at 220 K the intercalate undergoes a transition to an incommensurate phase.[7]

More recently, Yosida and Tanuma repeated the measurements of the dHvA effect of the stage-2 $SbCl_5$ graphite[8] and found a number of oscillations whose amplitudes increased with increasing cooling rate between room temperature and liquid-nitrogen temperature. The relation of the dHvA amplitudes to the intercalate structure was shown with electron diffraction studies. However, because the spectrum was complex, no attempt was made to explain it in terms of the electronic structure of the compound.

In order to resolve discrepancies between previous works, we have carried out measurements of the de Haas—van Alphen effect in the lowest stages of antimony pentachloride graphite compounds. In the stage-1 compound, we observed a single dHvA oscillation,[9] as predicted by theoretical models. We also mentioned that the spectrum of the stage-2 compound depends on the cooling rate between room temperature and liquid-nitrogen temperature.[9] In this paper, we present detailed results of our investigation of the stage-2 compound that show the existence of two types of dHvA spectra. With fast-cooled samples, we observe a complex spectrum similar to that of Yosida and Tanuma.[8] With slowly cooled samples, we observe only two dHvA oscillations, which are interpreted as coming from the basic graphitic bands. The values of the frequencies and corresponding carrier cyclotron masses are compared with predictions of the rigid-band models[4,10] and a very good agreement is found with the model of Holzwarth.[10]

II. EXPERIMENTAL DETAILS

Although properties of the graphite-$SbCl_5$ compound have been investigated for a number of years, the results obtained by different groups are sometimes contradictory. A possible source of discrepancy is the method of preparation. Therefore, we describe details of the sample preparation method used in this work.

The samples were prepared from highly oriented pyrolitic graphite (HOPG) supplied by Dr. A. W. Moore of Union Carbide. Slabs of HOPG were cut into pieces with a cross section of about 3×3 mm^2 which were cleaved to a thickness of about 0.5 mm. The pieces were washed in an ultrasonic cleaner and vacuum dried for about an hour. A few samples were also made from natural graphite obtained from a quarry near Harrisville, New York. The flakes of natural graphite were washed in boiling distilled water. Antimony pentachloride obtained from Alfa-Ventron was purified by three successive trap-to-trap vacuum distillations. The pure $SbCl_5$ was pale yellow in color and was stored in a dry box with a nitrogen atmosphere.

Some stage-2 graphite-$SbCl_5$ samples were synthesized in a vapor of $SbCl_5$ by the two-temperature technique in a manner similar to that used by Takahashi *et al.*[2] Most of the samples were prepared by the following more convenient method. A piece of Pyrex tube was sealed at one end and was dried under vacuum at an elevated temperature. Pieces of graphite and $SbCl_5$ were put into it. The tube was then evacuated and dissolved nitrogen was removed by pumping and periodically freezing the $SbCl_5$ with liquid nitrogen. Next, the tube was sealed and put into an oven. The reaction lasted four days at 100 °C.

The staging of samples was checked by measuring the $(00l)$ x-ray pattern with a powder diffractometer using Cu $K\alpha$ radiation. The diffractogram consisted of narrow peaks with no discernible shoulders and indicated that the samples were single stage. The c-axis repeat distance of 12.72 ± 0.02 Å was in good agreement with the accepted value for the stage-2 $SbCl_5$ compound.

The dHvA effect measured by the modulation technique was performed with each sample's c axis parallel to the direction of magnetic field to within 2°. The magnetic field was provided by a 5.5-T superconducting solenoid. A minicomputer equipped with two 16-bit analog-to-digital converters was used for acquisition and Fourier analysis of the data.

Cyclotron mass values were determined from the temperature dependence of the dHvA amplitudes between 1.3 and 4.2 K. Two methods of measuring amplitude were used in the present work. The first used the amplitude of a dominant oscillation read off a recorder chart. The second method used fitted amplitudes of oscillations in a small magnetic field range of the digitally recorded data. The results of both methods were consistent to within the limits of error.

III. RESULTS

The dHvA spectrum depended on the cooling rate of a new stage-2 $SbCl_5$ sample between room temperature and 77 K. Figure 1 shows a typical Fourier transform of dHvA data obtained with a sample that was cooled in about one hour. The spectrum is complex with many fundamental oscillations with frequencies up to 800 T. When the cooling time was increased to 24 h or more, the dHvA spectrum consisted basically of two fundamental frequencies and only weak remains of the frequencies observed with fast-cooled samples (Fig. 2). In addition, a strong oscillation of frequency 13 T was observed at low magnetic fields with all slowly cooled samples.

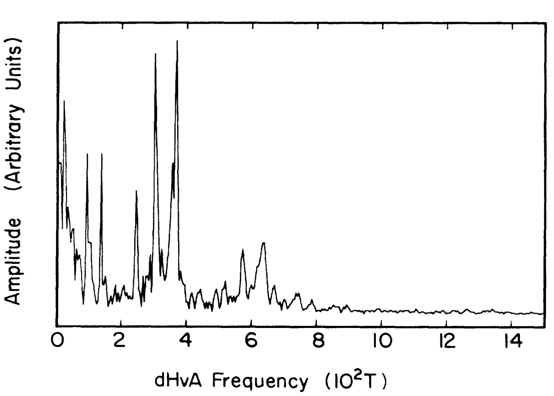

FIG. 1. Fourier transform of the de Haas—van Alphen oscillations of a fast-cooled sample. The analyzed data were in the magnetic field range of 2—5 T.

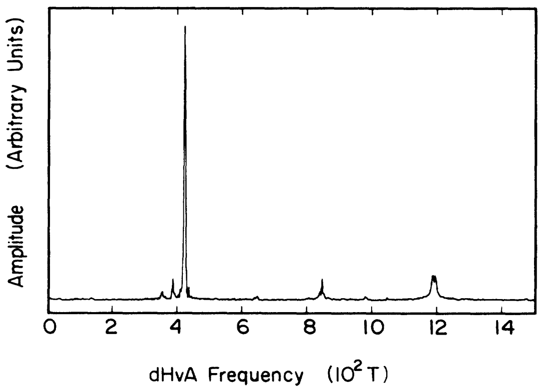

FIG. 2. Typical dHvA spectrum of a slowly cooled sample. The magnetic field range of the analyzed data was 2—5.2 T.

The two spectra presented above are the extreme cases observed in this work. With samples cooled with rates intermediate between 1 and 24 h, we observed both sets of oscillations whose frequencies remain constant, but the amplitudes of the oscillations shown in Fig. 1 decreased with increasing cooling time, while the amplitudes of the oscillations shown in Fig. 2 increased with cooling time.

The frequencies observed in this work with slowly cooled samples agree with some of the frequencies reported by Takahashi *et al.*[2] Other frequencies observed by Takahashi *et al.*[2] and most of the frequencies reported by Batallan *et al.*[1] were also observed in this work with samples cooled fast. The data of this work confirm both previous results and indicate that cooling-rate effects account for the discrepancy between them. The observation of the dependence of the dHvA spectrum on the cooling rate in this work is consistent with the results of Yosida and Tanuma[8] who showed that dHvA amplitudes increased with increasing cooling rate and found that, on fast cool down, a substantial portion of the sample retained the high-temperature structure. Furthermore, the amplitudes of dHvA frequencies were correlated with the amount of the high-temperature phase that was present within samples.[8] With our samples we observed, by x-ray diffraction, a $\sqrt{7}\times\sqrt{7}\pm R$ 19° coexisting with $\sqrt{39}\times\sqrt{39}\pm R$ 17° in-plane intercalate ordering at room temperature and we believe that the combined periodicities produce the complex spectrum observed with fast-cooled samples. Additionally, there is a possibility of strained regions that may produce other dHvA frequencies.

In this work the spectrum of the slowly cooled stage-2 $SbCl_5$ compound is analyzed in detail. The strongest dHvA oscillation of slowly cooled samples has the frequency $f_1=422\pm2$ T, its second harmonic is observed at 845 ± 2 T. The second fundamental frequency has the value of $f_2=1190\pm5$ T. Sometimes a combination of $f_1+f_2=1610$ T was also observed. The carrier effective masses corresponding to f_1 and f_2 are $m_{c1}=(0.146\pm0.002)m_0$ and $m_{c2}=(0.267\pm0.003)m_0$, respectively. The carrier effective mass corresponding to the 13-T frequency is $(0.040\pm0.001)m_0$.

With slowly cooled samples Yosida and Tanuma[8] did not observe the f_1 and f_2 frequencies reported above. This comes from the fact that they used a torque magnetometer, which is more sensitive to low-frequency oscillations, while a modulation technique, more sensitive to high-frequency oscillations, was used in this work. Their structure investigation showed that the intercalate was in a glassy state by an electron diffraction study. However, it has been discovered recently that the transition to the glassy state is induced by the electron beam[11] and at low temperature the intercalate structure is actually incommensurate with the graphite lattice, as observed in x-ray diffraction.[7] In this case, one expects that there is no splitting of the Fermi surface of the basic graphitic bands. This situation is similar to that of the stage-1 $SbCl_5$ compound which has incommensurate intercalate structure,[7] and a single dHvA oscillation of the basic graphitic band is observed.[9] In the case of the stage-2 compound, one expects two basic bands and we identify the f_1 and f_2 frequencies with these bands. This interpretation is different from that of Tanuma *et al.*[3] who tried to fit four of the dHvA oscillations to a more complex model that involved the splitting of the bands by an intercalate superlattice.

IV. DISCUSSION

Having identified the oscillations of the basic graphitic bands we can now compare the measured Fermi surface parameters with the predictions of the electronic structure models and verify their validity in the case of the stage-2 $SbCl_5$ compound. We use the fact that the frequency of a dHvA oscillation is directly proportional to the extreme cross section of the Fermi surface that creates it:[12]

$$f = \frac{2\pi e}{\hbar} A \,, \tag{1}$$

and the cyclotron mass is proportional to the derivative of the area with respect to energy:

$$m_c = \frac{\hbar^2}{2\pi} \left[\frac{\partial A}{\partial E} \right]_{E_F} . \tag{2}$$

Several band models which are based on modified graphitic π bands have been proposed.[4,10,13] We would like to examine two two-dimensional models: a simple tight-binding model proposed by Blinowski *et al.*[4] and a more elaborate model of Holzwarth.[10] These models assume that the in-plane unit vectors are the same as in graphite and the c-axis unit vector is equal to the intercalate-intercalate spacing. This gives n valence-conduction pairs of bands for a stage-n compound with little or no overlap between valence and conduction bands. The top of the valence bands is unoccupied because some electrons are transferred to the acceptor intercalate species. The electron dispersion is assumed to be independent of the number of electrons transferred and is calculated using the tight-binding formalism. In the case of the Blinowski *et al.*[4] model, only the nearest-neighbor interactions are included; γ_0, which describes the in-plane interaction, and γ_1, the intralayer interaction. The valence-band energies are given by

$$E = -\tfrac{1}{2}[(\gamma_1^2 + 9\gamma_0^2 a^2 |k|^2)^{1/2} \pm \gamma_1] \,, \tag{3}$$

where k is the electron momentum measured from the corner of the Brillouin zone and a is the in-plane carbon-carbon distance. In our calculations we used the values of the parameters γ_0 and γ_1 of 2.4 eV and 0.377, respectively.

The model proposed by Holzwarth[10] includes four in-plane and four interplanar interactions and a difference in energy for nonequivalent carbon sites. The extra terms modify slightly the electron dispersion but retain the qualitative features of the bands. In our calculations, we have made two modifications to the Hamiltonian as compared to the original work. Firstly, we have used $\frac{1}{2}$ of the suggested value of the difference in energy of nonequivalent carbon sites because there is only one neighboring layer in a stage-2 compound, i.e., the value used here is -0.01 eV for the element M_{BB}^{000} of Ref. 10. Secondly, the B-atom sublattice is not invariant with respect to the in-plane inversion and the corresponding matrix element does not have to be real as was suggested in the original work. The remaining values of the interaction parameters were the same as those in the original work[10] and are the same as in pristine graphite.

The comparison to the theory is done in the following way. From the theory, the areas of the two bands are calculated as a function of energy. The value of the Fermi energy is adjusted to fit the sum of the experimental Fermi areas obtained from the values of frequencies using Eq. (1). Then, the fitted Fermi energy is used to calculate Fermi areas and cyclotron masses of both bands, which are compared to the experimental values. The results are shown in Table I.

The model of Blinowski *et al.*[4] predicts both areas accurately but overestimates the cyclotron masses. In the case of the Holzwarth model, all predicted values are within 2% of the experimentally observed ones. Furthermore, we can compare our fitted value of the Fermi energy to that determined in the most recent optical reflec-

TABLE I. Comparison of measured and calculated Fermi surface parameters. The value of the Fermi energy was adjusted to match observed and calculated sums of the Fermi areas.

	Experimental		Blinowski model ($E_F = -0.80$ eV)		Holzwarth model ($E_F = -0.88$ eV)	
	Fermi area (Å^{-2})	Cyclotron mass (m_0)	Fermi area (Å^{-2})	Cyclotron mass (m_0)	Fermi area (Å^{-2})	Cyclotron mass (m_0)
f_1	0.0403	0.146	0.0394	0.176	0.0396	0.144
f_2	0.1136	0.267	0.1144	0.289	0.1139	0.271

tance studies by Hoffman *et al.*[14] The value of the Fermi energy of -0.89 ± 0.01 eV was obtained directly from the measurements of the valence—conduction-band transition. This is in an excellent agreement with our value of -0.88 eV fitted to the model of Holzwarth. This shows that the model describes the electronic structure of the compound studied very accurately. The model of Blinowski *et al.*[4] is less accurate; its predictions differ from the experimental results by about 10%.

The model of Blinowski *et al.*[4] is a first-order expansion of energy versus momentum near the corner of the Brillouin zone and the accuracy it provides seems reasonable. The good agreement of the Holzwarth model[10] with the data is remarkable considering the fact that it uses the band parameters determined for pristine graphite, which has a much smaller Fermi surface than that of the intercalation compound studied. However, similar accuracy has been found with the dHvA results of other acceptor compounds.[9,15,16] This suggests that the rigid-band model is general enough to be applicable to most of the acceptor compounds of graphite.

Another point that should be discussed is the effect of the electron-phonon interaction on the cyclotron mass. The values used in Table I are "bare" masses calculated from the band models. In metals and semimetals there is an interaction of a moving electron with phonons that results in an increase of energy required to accelerate the electron by the amount needed to create a cloud of phonons that follow it. This leads to an increase of the measured electron effective mass by a factor of $1+\lambda$ where λ is the mass enhancement parameter.[17] We would like to estimate this parameter in the stage-2 $SbCl_5$ compound from transport measurements.

The electrical conductivity tensor element is given by

$$\sigma_i = \frac{e^2\tau}{4\pi^3} \int \frac{dS_k}{|\nabla_k E|} v_i^2 \; . \tag{4}$$

Using the simplified electron dispersion given by the Blinowski *et al.* model and the room-temperature in-plane conductivity[18] value of $\sigma_a = 2\times10^7 \; \Omega^{-1}\,\mathrm{m}^{-1}$, one gets a scattering time of $\tau = 2.6\times10^{-13}$ s. The low-temperature value of the λ parameter is related to the phonon scattering rate at high temperatures by[17]

$$1/\tau = 2\pi\lambda k_B T/h \; . \tag{5}$$

Assuming that the scattering is phonon-dominated at room temperature and substituting the estimated scattering time in Eq. (5), one gets the value of $\lambda = 0.015$. Thus, the correction of the electron-phonon interaction to the cyclotron mass is of the order of 1.5% and is within the limits of expected accuracy of the band model.

The 13-T oscillation cannot be accounted for within the rigid-band model. Recently, Campagnoli and Tosatti[19] suggested that with some intercalate superlattices one might obtain a low-frequency oscillation as a result of an interference between two trigonally warped orbits rotated by 60°. However, this oscillation is observed with samples cooled slowly, which have incommensurate intercalate structure, and this mechanism is not a likely cause. Instead, thermal contraction of the intercalate can be a source of this frequency. Antimony pentachloride and graphite have different thermal expansion coefficients. On cooling, the intercalate contracts faster than graphite and leaves macroscopic-size regions near the edges of samples with charge transfer much lower than that in the bulk.[20] We postulate that the 13-T oscillation comes from these regions. Although the regions are very small compared to the sample size, the dHvA signal from them would be strong, because of low effective mass of carriers, and preferentially detected with the apparatus used in this work. The frequency of the oscillation and the corresponding effective mass differ from those of pristine graphite, which indicates that these regions resemble the residual compound rather than pure graphite.

Finally, we would like to address the problem of charge transfer in the stage-2 $SbCl_5$ compound. The mechanism of the charge transfer proposed by Boolchand *et al.*[21] is due to a disproportionation reaction

$$3SbCl_5 + 2e \rightarrow SbCl_3 + 2SbCl_6{}^- \; ,$$

which gives 0.66 elementary charge per intercalate molecule. The charge transfer per carbon atom x, in a stage-2 compound, is directly proportional to the sum of the fundamental dHvA frequencies[15]

$$x = (f_1 + f_2)/789\,14 \; ,$$

where f_1 and f_2 are in tesla. Substituting the values for f_1 and f_2 of the stage-2 $SbCl_5$ compound of this work, one gets $x = 0.0205$. With the stoichiometry of the compound in the range $C_{24}SbCl_5$ to $C_{28}SbCl_5$, one gets the charge per intercalated molecule of 0.49 to 0.57 elementary charge which is lower than that expected from the above reaction and indicates that the disproportionation reaction is not complete, with only 74—86% of the intercalate disproportionating.

V. CONCLUSIONS

In this work the de Haas—van Alphen effect of the stage-2 $SbCl_5$ graphite intercalation compound was measured and the results showed a dependence of the dHvA spectrum on the cooling rate between room temperature and liquid-nitrogen temperature. That dependence can account for the apparent discrepancy between previously published results. With quickly-cooled samples, the high-temperature structure of the intercalate is frozen and produces a complex dHvA spectrum which is not fully understood yet. Slowly cooled samples produce a simple dHvA spectrum consisting of two oscillations coming from the basic graphitic bands. The frequencies of the oscillations and the corresponding cyclotron masses of slowly cooled samples are in a very good agreement with the prediction of the rigid-band model of Holzwart[10] with the Fermi energy as the only adjustable parameter. The fitted value of the Fermi energy agrees with that obtained from optical reflectance studies of Hoffman *et al.*[14] The simpler model of Blinowski *et al.*[4] was found to be less accurate. Its predictions were about 10% different from the measured values. The effect of the electron-phonon mass enhancement was estimated and it was found that the value of the λ parameter is of the order of 0.015. A low-frequency oscillation observed at low magnetic field values is interpreted as coming from intercalate-depleted regions near the edges of a sample. From the values of the basic dHvA frequencies, the charge transfer was determined accurately. Its value suggests that the disproportionation of antimony pentachloride is not complete.

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