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Intercalant ordering in the stage-1 indium chloride graphite intercalation compound

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Abstract. The stage-1 InCl_3 graphite intercalation compound (GIC) was studied by the de Haas–van Alphen (dHvA) effect in the temperature range 1.4 to 4.2 K with magnetic fields from 3 to 5 T. The observed dHvA oscillations possess frequencies of $f_1 = 263$ T, $f_2 = 458$ T, $f_3 = 705$ T and $f_4 = 878$ T. They are shown to result from Fermi surface pieces which are constructed from the zone folding of the two-dimensional free electron Fermi surface. The fragmentation of the Fermi surface is shown to be a consequence of the additional periodicity of a commensurate $(8\sqrt{3} \times 8\sqrt{3})R30^\circ$ in-plane superlattice formed by the InCl_3 molecules. This ordering of InCl_3 molecules is a result of a phase transition which occurs upon cooling at approximately 260 K. This transition was identified by temperature dependent resistivity studies and by differential thermal analysis (DTA) of the stage-1 InCl_3 GIC sample.

1. Introduction

Graphite intercalation compounds (GICs) are formed by incorporating a layer of guest atoms or molecules, the intercalant, between layers of the graphite host. These compounds exhibit a unique staging phenomenon in which a constant number of graphite layers are separated by an intercalant layer. A stage- n GIC is composed of a series of n graphite layers separated by successive intercalant layers. The GIC is a highly anisotropic layered structure possessing strong intraplanar binding forces relative to the weak interplanar binding.

The metal chloride intercalants such as InCl_3 are electron acceptors which introduce delocalized holes in the graphite π band. In many graphite acceptor compounds the intercalant molecules do not arrange periodically with respect to the carbon atoms in the graphite plane. In the present case, the stage-1 InCl_3 GIC, the InCl_3 molecules form a commensurate in-plane superlattice when cooled below 260 K.

The stage-2 InCl_3 GIC has been made previously [1, 2] by reacting highly oriented pyrolytic graphite (HOPG) and InCl_3 in a Cl_2 atmosphere at a temperature of 480 K. There is an ordering transition at 155 K the first time a sample is cooled. It remains in an ordered state at room temperature after it has been cooled. X-ray diffraction measurements showed that the ordering attributed to the intercalant InCl_3 is $\sqrt{3} \times \sqrt{3} R30^\circ$ with respect to the hexagonal graphite lattice. The periodicities of the intercalant and the lattice provide for zone folding of the Brillouin zone which results in overlaps of the Fermi surface of the graphite bands. This produces many pieces of the Fermi surface which were detected by the de Haas–van Alphen (dHvA) effect. From the observed frequencies we were able to determine that the magnitudes of the intercalant lattice vectors were $8\sqrt{3}$ times those of the graphite lattice vectors.

The stage-1 InCl_3 GIC has not been reported previously. However there were traces of the stage 1 in some samples that were prepared for the stage-2 studies. This directed us to search for the conditions for the preparation of the stage-1 GIC. In this paper we present the reaction conditions and the results of dHvA, resistivity and differential thermal analysis (DTA) measurements performed on the stage-1 InCl_3 GIC.

2. Experimental details

The preparation of the stage-1 GIC was very difficult because mixed stages of 1 and 2 and unreacted graphite resulted from many preparations. The conditions with a temperature of 480°C for the InCl_3 and HOPG, a Cl_2 pressure of 2 atm and a time of 18 d used for the stage-2 GIC were not suitable. The use of 500°C , 2 atm of Cl_2 and a time of 20 d resulted in a mixture of stages 1 and 2 and no stage 3. The proportion of stage 1 to stage 2 determined by x-ray diffraction analysis was about 5:3. After many attempts, the stage-1 samples were made from HOPG in 9 weeks with a temperature of 490°C and a Cl_2 pressure of 800 Torr.

InCl_3 (99.999% pure) was purified by repeated sublimation under vacuum at 498°C . The intercalation was carried out with cleaved pieces of HOPG that were cleaned ultrasonically in anhydrous methanol. The HOPG and InCl_3 were reacted in a sealed Pyrex tube under the conditions described above. (00 l) x-ray diffraction using Cu $K\alpha$ radiation was performed on the stage-1 InCl_3 GIC. The c -axis repeat distance, $I_c = 9.53 \text{ \AA}$, was determined from the slope of the straight line given by the reflection order l versus $1/d_l$. The expected value of I_c is 9.51 \AA which is determined by subtracting the graphite layer spacing of 3.35 \AA from the $I_c = 12.86 \text{ \AA}$ value for the stage-2 InCl_3 GIC [3]. The x-ray diffraction spectrum showed a well staged sample with reflection orders indexed from (001) to (007) and a small amount of stage 2. However, the dHvA effect did not show any signal from the small amount of the second stage.

The dHvA oscillations were observed with the low-frequency field modulation technique with a modulation frequency of 47 Hz along the magnetic field direction. The sample was put inside a set of coils which consisted of a modulation coil and a rotatable pick-up coil and balance coil. The balancing coil was wound in an antiparallel fashion above the pick-up coil in order to maximize the signal from the sample's oscillating magnetization. This set of coils was placed inside a 5.5 T superconducting solenoid. Both the dHvA frequency spectrum and the temperature dependence of the amplitude between 1.4 K and 4.2 K were measured with the c -axis of the sample parallel to the direction of the magnetic field.

The resistance as a function of temperature of the samples was determined with both the classical four-probe method and the van der Pauw method [4] with contacts at each of the corners of the rectangular sample. Electrical contacts were made to the sample with silver paste. Experiments were carried out in a cryostat cooled with both liquid N_2 and He to take data over the temperature range 4.2–300 K. The current direction through the sample was switched at every data point and the measured voltage drops were averaged. The sample thickness was $240 \mu\text{m}$ as determined by a micrometer measurement.

For DTA measurements, a copper–constantan thermocouple was mounted on a sample using silver paste and a second similar thermocouple was placed in copper powder. Both were contained in Pyrex tubes which were inserted in holes in a copper block. The constantan wire was connected between the two thermocouples and the copper wire was connected to the instrumentation. The unit was placed in a cryostat which could be cooled slowly with liquid nitrogen and liquid helium. Data were taken during cooling and warming cycles.

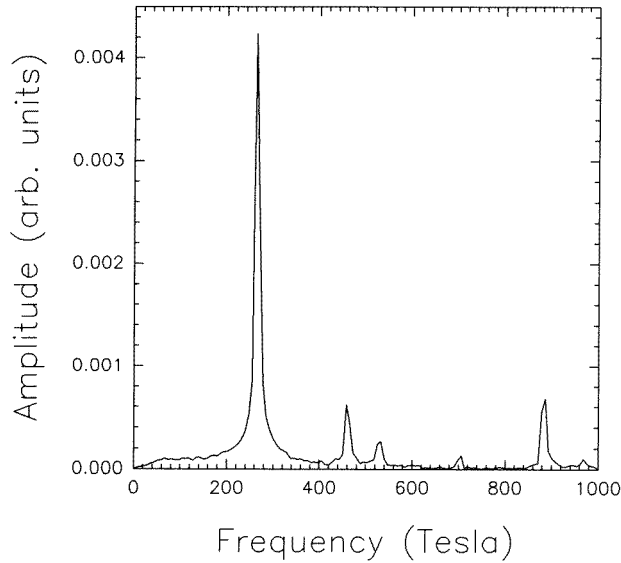


Figure 1. Fourier transform spectrum of the dHvA oscillations of the stage-1 InCl_3 GIC.

3. Results and analysis

The Fourier transform frequency spectrum of the dHvA oscillations between 3 and 5 T is shown in figure 1. The observed frequencies are $f_1 = 263$ T, $f_2 = 458$ T, $f_3 = 705$ T and $f_4 = 878$ T. The peak at 526 T is the second harmonic of f_1 . The cross-sectional Fermi areas are determined by the relation $A_f = (4\pi^2 e/h)f$ yielding $A_1 = 0.0251 \text{ \AA}^{-2}$, $A_2 = 0.0437 \text{ \AA}^{-2}$, $A_3 = 0.0673 \text{ \AA}^{-2}$ and $A_4 = 0.0839 \text{ \AA}^{-2}$.

A stage-1 GIC is expected to possess one oscillation arising from the modified graphite π band. The stage-1 InCl_3 GIC however possesses four oscillations which are attributable to composite pieces of the free electron cylindrical Fermi surface. Thus, the dHvA results indicate that the Fermi surface has been divided into smaller pieces due to zone folding effects introduced by an InCl_3 superlattice. The ordering of the InCl_3 superlattice allows the Brillouin zone (BZ) of graphite to be translated onto the centre (O point) or the corner points (U and U' points) of the InCl_3 BZ depending on the orientation of the InCl_3 lattice with respect to the graphite lattice. In the absence of an intercalant superlattice the expected result for a stage-1 GIC is a cylindrical Fermi surface centred at the U and U' points of the graphite hexagonal BZ with the axis of the cylinder along the c -axis. The effect of the intercalant superlattice is to translate these 2D circular Fermi surface cross-sectional areas with radius k_f into the intercalant BZ resulting in additional orbits formed by the intersection of the hole Fermi surfaces [5].

The crucial parameter is the ratio k_f/l where l is the length of a side of the intercalant hexagonal BZ. The analysis involved the selection of different k_f/l ratios and translation to the U and U' points and the O point of the intercalant BZ in order to find the Fermi surface construction which agrees with the experimentally determined Fermi surface pieces.

The ratio $k_F/l = 1.63$ provides the construction shown in figure 2. This figure shows the first BZ of the intercalant along with its six nearest neighbours. A free hole Fermi surface circle is drawn at each BZ centre with a k_F to l ratio of 1.63. The intersection of

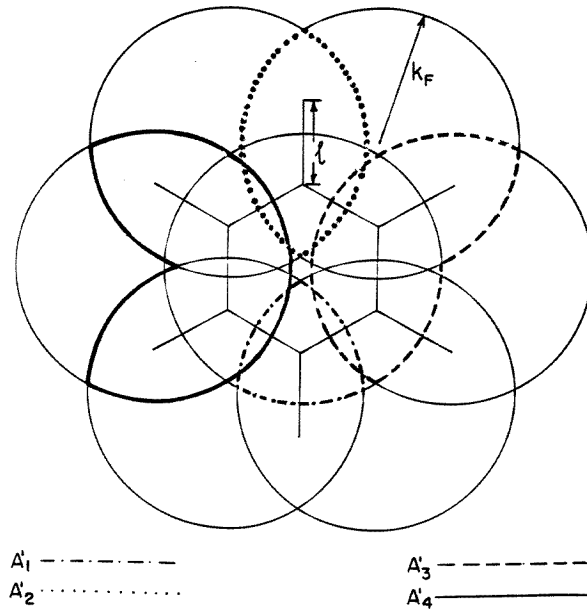


Figure 2. Fermi surface construction by zone folding effects for the stage-1 InCl_3 GIC.

these surfaces produces the five new orbits that are highlighted. The dHvA frequency (f') represented by each orbit is calculated using $f' = (A'/A_F) \times 1320$ T where A' is the area of the orbit and A_F is the free hole Fermi surface area of radius $k_F = 0.200 \text{ \AA}^{-1}$ which has a corresponding dHvA frequency of 1320 T. This value is typical for a stage-1 acceptor GIC. The uncertainty in the frequency calculations from the Fermi surface construction is approximately $\pm 1\%$, determined from repeated trials.

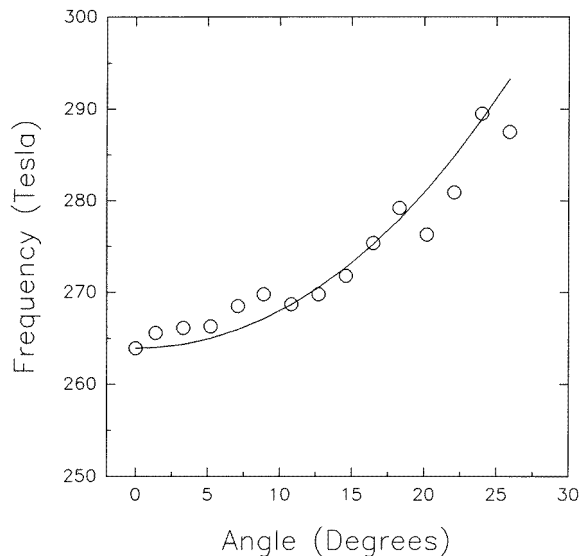
The small lens shaped orbit formed by the intersection of two free Fermi surfaces has a calculated dHvA frequency of $f'_0 = 33$ T. This low-frequency oscillation was not observable in the dHvA measurements taken in a magnetic field range of 3–5 T. The A'_1 section is indicated by a dashed–dotted line and corresponds to a calculated frequency of $f'_1 = 257$ T. The A'_2 orbit (dotted line) possesses a calculated frequency of $f'_2 = 478$ T. Sections A'_3 with a frequency of $f'_3 = 697$ T and A'_4 with a frequency of $f'_4 = 914$ T are formed by different couplings of two A'_2 orbits. They are indicated by the dashed line and the solid line, respectively.

A dHvA oscillation with a frequency of 968 T with a small amplitude was experimentally observed. There is no simple hole construction that agrees with this observation, although this oscillation at 968 T may result from the combination of two Fermi surface sections, namely the sum of 914 T and 33 T, yielding 947 T. This value agrees within approximately 2% of the observed frequency.

The frequencies of the Fermi surface constructions comply with the experimentally determined dHvA frequencies with an average discrepancy of approximately 2.5%. The comparison of the experimental and calculated frequencies is given in table 1. The calculated frequency values are sensitive to the ratio k_F/l . The average difference between the dHvA frequencies and the calculated frequencies is approximately 11% and 4% for the k_F/l ratios 1.61 and 1.65, respectively. Thus, the ratio $k_F/l = 1.63$ chosen represents a minimum in the average difference between the experimental and calculated values.

Table 1. A comparison of experimental and calculated dHvA frequencies for the stage-1 InCl_3 GIC.

	dHvA frequency (T)	Calculated frequency (T)	% difference
f_0	—	33	—
f_1	263	257	-2.3
f_2	458	478	4.4
f_3	705	697	-1.1
f_4	886	914	3.2
f_5	968	947	-2.2

**Figure 3.** Angular dependence of the 263 T dHvA frequency of the stage-1 InCl_3 GIC.

In order to provide a commensurate superlattice that facilitates the mapping of the U and U' points of the graphite BZ to the O point of the intercalant BZ an l value of 0.123 \AA^{-1} was chosen to give a Fermi surface construction that is consistent with the Fermi surface pieces determined from the dHvA measurements. If the intercalant in-plane structure is commensurate (i.e. each superlattice point is in the same registry with the graphite lattice) a straightforward mapping into the reduced zone scheme can be made. This analysis requires the InCl_3 molecules to lie on an $(8\sqrt{3} \times 8\sqrt{3})$ tetragonal in-plane superlattice whose primitive lattice vector is rotated by 30° with respect to the lattice vector of the hexagonal graphite lattice. Unfortunately we were unable to obtain a single crystal of InCl_3 stage-1 GIC to perform $(hk0)$ x-ray diffraction measurements to verify the ordered structure.

The angular dependence of f_1 was monitored from $\theta = 0^\circ$ to 28° where θ is the angle between the c -axis and the magnetic field direction. This dependence is shown in figure 3 and reveals the $f(\theta) = f \sec \theta$ behaviour expected for a cylindrical Fermi surface. The remaining frequencies could not be monitored beyond 6° since the magnitude of these oscillations diminished rapidly as the angle was increased.

The carrier effective masses corresponding to the dHvA frequencies were determined from the temperature dependence of the dHvA amplitude between 1.4 K and 4.2 K. The

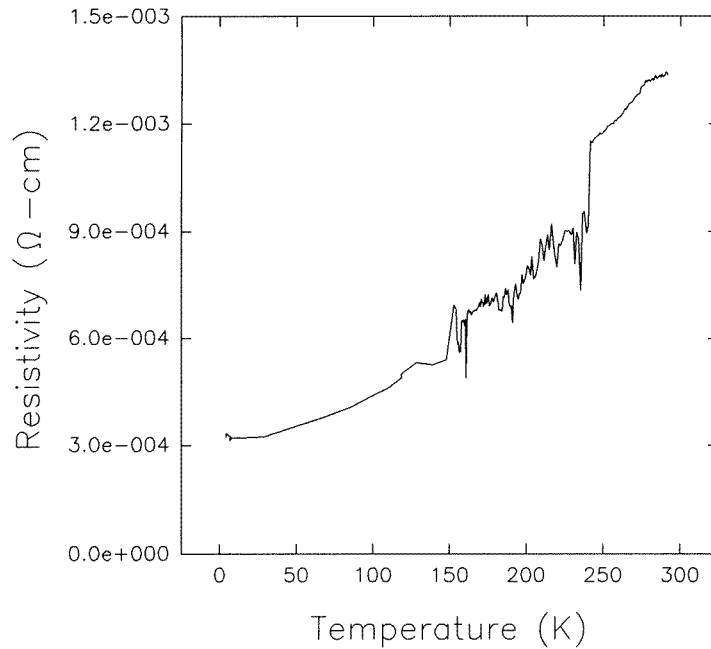


Figure 4. The temperature dependence of the resistivity of the stage-1 InCl_3 GIC.

dHvA amplitude is related to the sample temperature by the proportionality [6]

$$A \propto T / \sinh(bm^*T/Bm_0) \quad (1)$$

where A is the dHvA amplitude at temperature T and magnetic field B , m_c and m_0 are the cyclotron mass and free electron mass respectively, and $b = 14.69 \text{ T K}^{-1}$. The measured cyclotron effective masses are $m_1^* = 0.11 m_0$, $m_2^* = 0.14 m_0$, $m_3^* = 0.22 m_0$ and $m_4^* = 0.20 m_0$.

The room-temperature resistances of the samples prior to cooling ranged between $2.5 \text{ m}\Omega$ and $6.8 \text{ m}\Omega$. As the sample was cooled there was a sudden drop in the resistance at approximately 260 K decreasing the resistance on average by a factor of 1.4. Upon further cooling to 4.2 K the sample obeyed a typical metallic curve, gradually decreasing to a minimum value of approximately $1.2 \text{ m}\Omega$ at 4.2 K (see figure 4). The warming curve of the sample was similar to the cooling curve with a sudden increase in resistance at approximately 250 K and the same room-temperature resistance as was initially observed, thus indicating no hysteresis in the resistance jump. The resistivities of the samples that were completely cooled to 4.2 K varied between $1.8 \times 10^{-3} \Omega \text{ cm}$ at room temperature and $3.2 \times 10^{-4} \Omega \text{ cm}$ at 4.2 K . The sample measured with the four-probe method had a room-temperature resistivity of $1.2 \times 10^{-4} \Omega \text{ cm}$.

The results of DTA measurements showed an exothermic peak on cooling at approximately 260 K and an endothermic peak on warming at the same value. These peaks were evident on subsequent thermal cycles with only slight changes in the position and magnitude of the peaks.

The resistivity data for the samples exhibit a typical metallic behaviour on cooling and warming except for the sudden change in the resistivity at approximately 260 K . The sudden change in the resistance indicates a change in the ordering within the sample that alters

the electron–phonon interaction. This ordering transition is responsible for the intercalant superlattice seen at low temperatures. The peak in the DTA data also confirms this ordering transition at approximately 260 K as it shows an exothermic peak on cooling. This indicates that the intercalant layer is in a lower-energy or more ordered state at temperatures below 260 K than above it. Both the temperature dependent resistivity and DTA data for the samples were reversible on cooling–warming cycles and showed little or no hysteresis, indicating that the intercalant layer returns to its less ordered state on warming above 260 K.

A comparison of stage-1 and stage-2 InCl_3 GIC shows similarities in their properties. The $(8\sqrt{3} \times 8\sqrt{3}) R30^\circ$ intercalant superlattice was seen in $(hk0)$ x-ray diffraction of the stage-2 compound and was the calculated superlattice for the stage-1 compound. Both compounds showed ordering transitions on cooling with the differences being the onset temperature (stage 1 ordered at 260 K and stage 2 ordered at 155 K). However, the stage-1 ordering was reversible on warming and the stage 2 was not.

4. Conclusions

The stage-1 InCl_3 GIC was determined to have dHvA oscillations at frequencies of $f_1 = 263$ T, $f_2 = 458$ T, $f_3 = 705$ T and $f_4 = 878$ T. These frequencies result from the fragmentation of the expected stage-1 single band by zone folding due to an intercalant superlattice. By a comparison of expected and observed frequencies it was determined from the dHvA data that the InCl_3 molecules form an in-plane superlattice commensurate to the graphite host lattice with a periodicity of $(8\sqrt{3} \times 8\sqrt{3}) R30^\circ$. There is agreement to within 2% between the observed and calculated Fermi surface area. This superlattice results from ordering within the intercalant layer and this ordering was determined to have occurred at 260 K by the temperature dependent of the resistivity and DTA. Both of these methods show a reversible transition at approximately 260 K consistent with ordering taking place within the intercalant layer.

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