An ordering transition in InCl$_3$ stage 2 intercalated graphite

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Abstract. An ordering transition at 155 K is reported for the stage 2 InCl$_3$ graphite intercalation compound. It was detected as a sharp decrease in the resistivity during the first cooling of a sample. It was observed also by differential thermal analysis during both warming and cooling. X-ray diffraction from intercalated single crystals showed an ordered phase at room temperature after a sample was cooled below the transition temperature. The ordered phase has a $(4\sqrt{3} \times 4\sqrt{3})$R30° unit cell with respect to the hexagonal graphite lattice.

1. Introduction

In some graphite intercalation compounds (GICs), the intercalants have ordered structures which usually form at a temperature below room temperature. The SbCl$_5$ GIC has received a great deal of attention and has several ordered structures which have been examined by x-ray [1] and electron [2–4] diffraction. The change from the unordered state to the ordered state reduces the resistivity by a factor of 2 [5]. Since the review [6] that described the ordering that had been observed up to 1980 in different GICs, ordering has been reported in only a few other compounds.

The intercalation of InCl$_3$ in graphite forms a stage 2 compound [7]. In the stage 2 GIC, there are two graphite layers between single intercalant layers stacked along the c axis. In this paper, we report the temperature dependence of the resistivity and the Hall voltage, differential thermal analysis (DTA) and an examination by (hkl) x-ray diffraction of intercalated single crystals. The purpose is to report an ordering transition at 155 K and the unit cell of the ordered phase.

2. Experimental details

The temperature for intercalation of InCl$_3$ is higher than that required for many other GICs because the sublimation temperature of InCl$_3$ is 489 °C. Also, the intercalation is very sensitive to the choice of sample temperature and an atmosphere of Cl$_2$ gas is required. The InCl$_3$ was purified by sublimating it in vacuum before the intercalation reaction. Highly ordered pyrolytic graphite (HOPG) was used to prepare samples for the transport measurements. The choice of sample temperature was critical and the use of 450 °C, 460 °C and 500 °C in different reactions resulted in samples with mixed stages.

The preparation of a pure stage 2 sample required 480 °C, close to the sublimation temperature of InCl$_3$. It was reacted for 18 d with a Cl$_2$ pressure of 2 atm. The compound was determined to be C$_{17.6}$InCl$_3$ from the change in weight by intercalation and was in
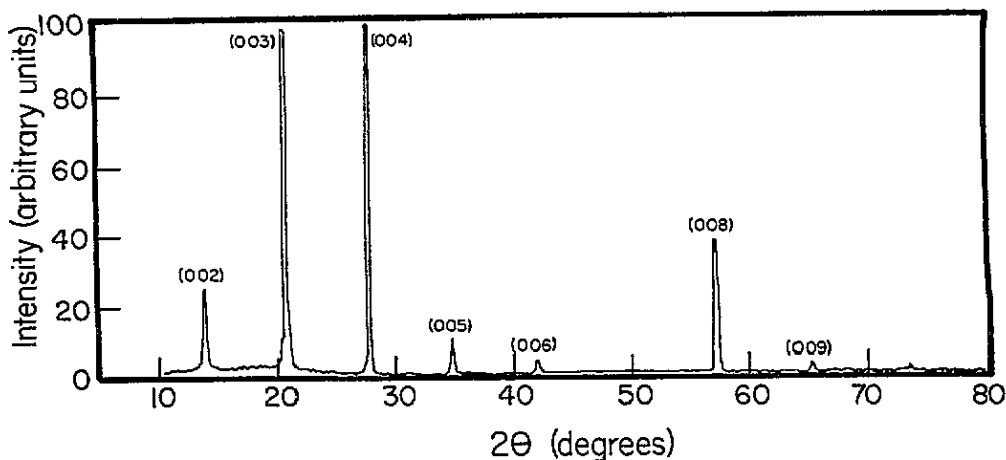
Figure 1. (00*l*) x-ray diffraction of the stage 2 InCl$_3$ GIC with Cu Kα radiation.

stage 2 with a *c* axis repeat distance $I_c = 12.8$ Å. This was determined from the (00*l*) x-ray diffraction shown in figure 1.

The intercalation of single crystals was more difficult. The crystals were obtained from a mine in New York state. Attempts to intercalate single crystals in Cl$_2$ at a pressure of 2 atm and at temperatures of 470 °C and 480 °C for periods of time between 2 and 4 weeks produced samples with a mixture of stages 1 and 2 and unreacted graphite in the interior. Thus, the conditions for HOPG are not suitable to intercalate single crystals with InCl$_3$. Rather, Cl$_2$ at 3 atm pressure and a temperature of 500 °C for 3 weeks were required to prepare good stage 2 intercalated crystals with no unreacted graphite.

Electrical contacts were attached with silver paste to the corners of rectangular, cleaved samples to measure the resistivity by the Montgomery [8] method and along a line of narrow samples for measurement by the four-probe method. Contacts at the midpoints of the sides of thin, cleaved rectangular samples were used to detect the Hall voltage. The voltage for both directions of current of 1 mA was measured with a sensitive voltmeter (Keithley 181) and was stored in a computer for analysis.

For the DTA measurements, a copper–constantan thermocouple was mounted on a sample and a second similar thermocouple was placed in copper powder. Both were in Pyrex tubes which were inserted in holes of a copper block. Constantan wire was between the two thermocouples and copper wire connected them to the measuring instrumentation. The unit was placed in a cryostat which could be cooled slowly with liquid nitrogen and liquid helium.

Cu radiation was used in the diffraction studies. The stage was determined from (00*l*) diffraction with a Nicolet diffractometer. The diffraction from single crystals was examined with a precession camera. The diffractograms were obtained with photographic film and all measurements were made at room temperature.

3. Results

The resistivity measured by the Montgomery method during the first cooling and warming cycle of a sample is shown in figure 2. After a small decrease at 200 K during cooling

there is a large decrease between 160 and 150 K. These changes are not present in the return warming curve. The resistivity during subsequent cooling–warming cycles followed the resistivity of the first warming curve with no sharp changes. The resistivity of the unintercalated HOPG is large and changes slowly with a metallic behaviour as a function of temperature with no sharp transition.
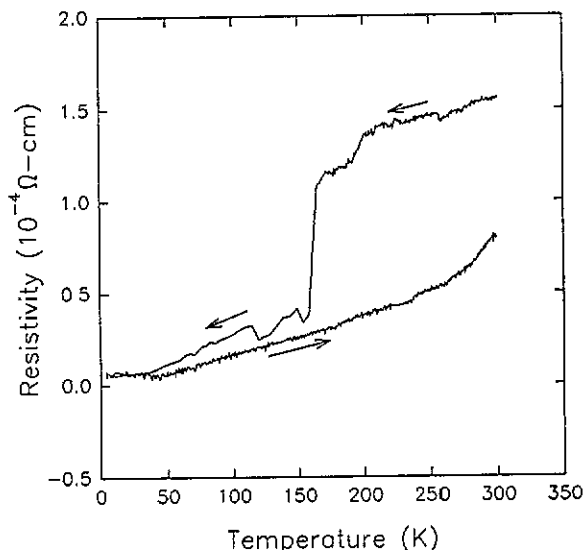

Figure 2. Resistivity versus temperature of a stage 2 InCl₃ GIC sample during its first cooling–warming cycle.

Figure 3 shows the resistivity measured by the four-probe method after the first cooling–warming cycle. The temperature dependence follows $\rho = a + bT + cT^2$. The coefficient of the linear term is $(6.5 \pm 0.3) \times 10^{-8}$ Ω cm K^{-1}. The quadratic term is a small correction with $c = (10 \pm 5) \times 10^{-11}$ Ω cm K^{-1}. The residual resistivity given by the constant a is $(5 \pm 3) \times 10^{-6}$ Ω cm. The uncertainties were determined from measurements of several samples after the first cooling–warming cycle.

The temperature dependence of the Hall voltage shown in figure 4 was the same during the first and subsequent cooling–warming cycles with no indication of the ordering transition. The voltage was measured with a current of 10 mA in a magnetic field of 1.5 T and a sample thickness of 1.5×10^{-4} m. The Hall coefficient changes from 1.5×10^{-8} m^3 C^{-1} at 300 K to 1.3×10^{-8} m^3 C^{-1} at 4.2 K.

The differential voltage of the DTA measurement during warming plotted in figure 5 exhibits an endothermic minimum centred at 155 K. The change is exothermic at the same temperature during cooling. The data of figure 5 were taken during the first cooling–warming cycle of a sample. Similar endothermic and exothermic changes were also observed during subsequent cooling–warming cycles of a sample. Thus, the transition appears the same in DTA during the first and subsequent thermal cycles of a sample.

The (hkl) x-ray diffraction measurements were done first with a graphite single crystal. The measurements of the diffraction agreed with the accepted values of the in-plane lattice constant $a_0 = 2.46$ Å and the c axis lattice constant $c_0 = 3.35$ Å. The diffraction of an intercalated crystal which had not been cooled showed the diffraction from the
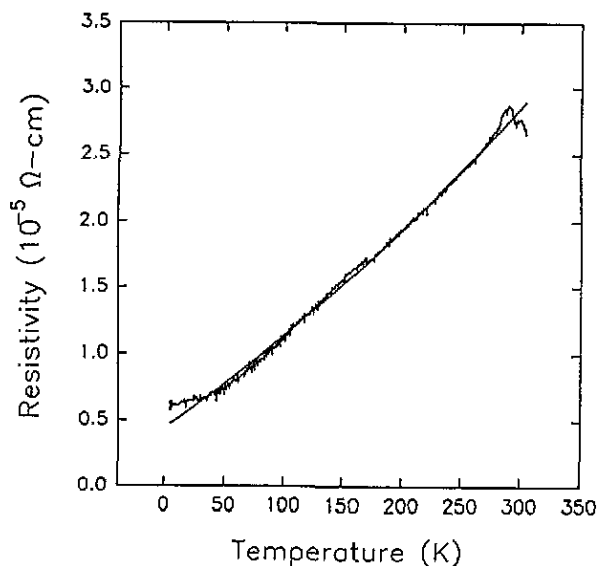
Figure 3. Resistivity versus temperature of the stage 2 $InCl_3$ GIC after the first cooling–warming cycle. The solid curve is a fit of $\rho = a + bT + cT^2$.
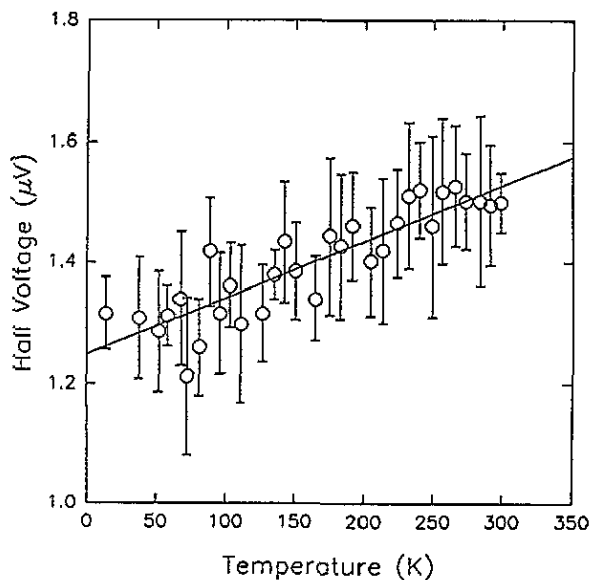

Figure 4. The Hall voltage versus temperature of the stage 2 $InCl_3$ GIC. The line is a linear fit of the data.

graphite lattice and no evidence of the intercalant superlattice. Finally, the diffraction of an intercalated single crystal which had been cooled to 4.2 K with the procedure used for the resistivity measurements was studied. A reproduction of the $(hk0)$ diffractogram taken with Cu radiation is shown in figure 6. Diffraction with smaller but weaker diffraction spots from Cu Kα radiation was used for precise measurements. There are three rings of
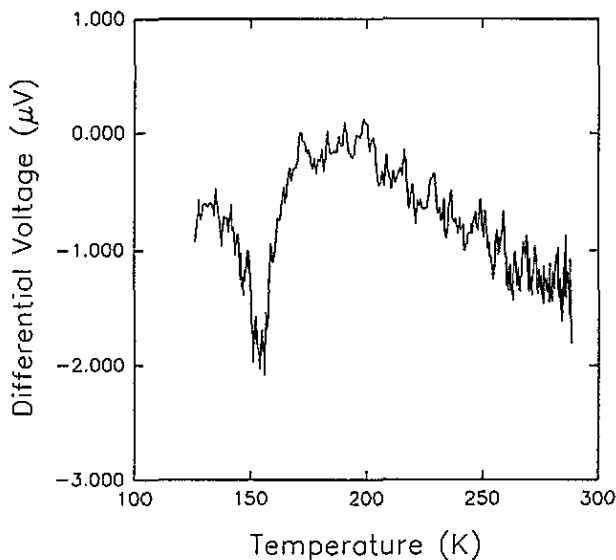
Figure 5. The DTA voltage during warming with a sample of stage 2 InCl₃ GIC and a reference of Cu powder.
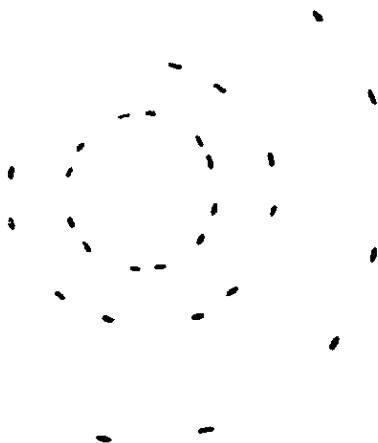

Figure 6. A reproduction of the $(hk0)$ diffraction taken at room temperature with a precession camera of a stage 2 InCl₃ GIC single crystal after it was cooled to 4.2 K.

diffraction spots from the third, fifth and ninth orders. X-ray diffraction experiments could not be carried out below room temperature to determine the change in the intensity of the Bragg peaks at the transition.

4. Discussion

The sharp decrease in the resistivity during the first cooling of a sample indicates a decrease in the electron scattering. There is no change in carrier density because there is no corresponding change in the Hall voltage. The decrease in scattering is attributed to a change of the intercalant layer from a disordered to an ordered structure. This transition is

not reversible because there is no sharp increase during warming. Thus, there is intercalant ordering at room temperature after a sample has been cooled below 155 K. This is confirmed by the $(hk0)$ diffraction studies which showed intercalant order at room temperature in a sample which had been cooled.

However, the transition detected by DTA is reversible during cooling and warming through 155 K. This change is attributed to reversible short-range ordering which does not affect the resistivity and the order detected by x-ray diffraction. These measurements are sensitive to long-range order which is frozen in during the first cooling of a sample. The long-range order is described by the $4\sqrt{3} \times 4\sqrt{3}$ unit cell which is measured by x-ray diffraction. The short-range order could be an orientation ordering of the molecules that is not detected in the resistivity and x-ray measurements.

The in-plane diffraction pattern of the sample cooled to 4.2 K shows three orders of diffraction spots (see figure 6). In each of these orders the spots are grouped in pairs with each pair rotated $60°$ from the centre of the neighbouring pairs. In the lowest observable diffraction order six pairs of spots are visible completing a circle around the centre of the pattern. The diffraction of the two spots that make up any pair in this order is separated by $20°$. The next diffraction order out from the centre has five pairs of diffraction visible with one pair missing. In this order the diffraction in each pair is separated by $24°$. The third ring farthest out only has three pairs that are weakly visible. The distances from the centre of the diffraction pattern to each observable order of spots are proportional to 3:5:9. This indicates that the lowest observable order of spots is not a first-order diffraction but is instead a third-order diffraction pattern. This is supported by the spacing between the diffraction that makes up each pair in the two orders closest to the centre. The measured angles of $20°$ and $24°$ are consistent with the diffraction spacing of a lattice with hexagonal symmetry in third- and fifth-order diffraction patterns, respectively. From these angles and the ratio of distances to the orders we can confirm that we are observing third-, fifth- and ninth-order diffraction patterns.

The intercalant lattice spacing is determined by measuring the distance from the centre of the pattern to each order. The pattern gives a spacing of 16.81 Å between the lattice points of a hexagonal lattice with an angle of $60°$ between the lattice vectors (see figure 7). The ordering of the x-ray diffraction pattern dictates that the intercalant lattice is commensurate with the hexagonal lattice of graphite producing a superlattice. By dividing the magnitude of the intercalant lattice vector by the magnitude of the lattice vector for graphite (2.46 Å) we obtain the intercalant lattice spacing with respect to the graphite lattice parameters. The ratio of intercalant lattice spacing to graphite lattice spacing in this case is 6.83:1. The three commensurate lattices providing ratios in this range are $(\sqrt{43} \times \sqrt{43})R7.59°$, $(\sqrt{48} \times \sqrt{48})R30°$ and $(7 \times 7)R0°$ with ratios 6.55:1, 6.93:1 and 7:1, respectively. The $(\sqrt{48} \times \sqrt{48})R30°$ lattice is the closest of these available commensurate structures to the calculated lattice spacing. The 6.83:1 ratio corresponds to within 1.5% to a commensurate superlattice with lattice vectors $4\sqrt{3}$ times the length of that of graphite and rotated by $30°$ from the direction of the graphite lattice vectors as shown in figure 7. As a result we can say that the InCl$_3$ molecules form a $(4\sqrt{3} \times 4\sqrt{3})R30°$ hexagonal superlattice with respect to the hexagonal graphite lattice after cooling below 155 K.

A $(\sqrt{3} \times \sqrt{3})R30°$ in-plane ordering has been observed in several other GICs. The unit cell of stage 1 LiC$_6$ is hexagonal in the $P6/mmm$ space group [9]. The unit cell is $(\sqrt{3} \times \sqrt{3})R30°$ with respect to the hexagonal lattice. The rare earth metal GICs, YbC$_6$ and EuC$_6$, also exhibit an intercalant $(\sqrt{3} \times \sqrt{3})R30°$ superlattice [10]. Thus, the superlattice reported for the InCl$_3$ GIC is reasonable.

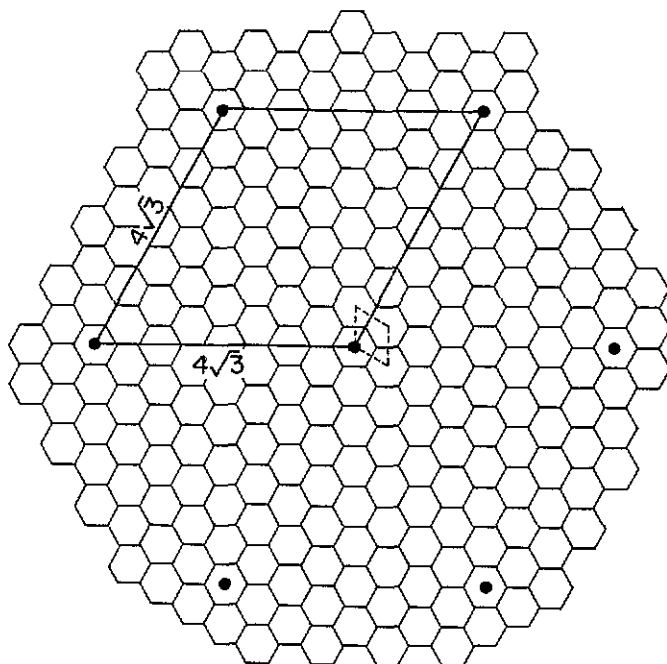The ordering transition in the stage 2 SbCl$_5$ GIC also reduces the resistivity by a factor of

Figure 7. The $4\sqrt{3} \times 4\sqrt{3}$ unit cell indicated by heavy solid lines and the graphite unit cell indicated by dashed lines on a hexagonal lattice.

two [5]. Usually the transition does not affect the resistivity during warming and subsequent warming–cooling cycles. Studies of the superlattice in the stage 2 InCl$_3$ GIC by electron diffraction are warranted as was done with the SbCl$_5$ GIC [2–4].

5. Conclusions

The stage 2 GIC with InCl$_3$ can be prepared at a temperature of 480 °C with HOPG graphite and 500 °C with single-crystal graphite. The c axis repeat distance I_c is 12.8 Å. There is an ordering transition at 155 K indicated by the resistivity during the first cooling of a sample. This ordering as indicated by the resistivity is not reversible and is not in subsequent cooling–warming cycles. There is a reversible short-range ordering at 155 K as indicated by differential thermal analysis. The x-ray diffraction of intercalated single crystals at room temperature shows no ordering in a sample that has not been cooled and a superlattice after it has been cooled to 4.2 K. There is a $(4\sqrt{3} \times 4\sqrt{3})$R30° unit cell of the superlattice with respect to the hexagonal graphite lattice.

Acknowledgments

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