

Zero-Field Cooled Specific Heat of Ferric Chloride Intercalated graphite

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Previous ac and dc magnetic susceptibility and specific heat measurements on ferric chloride intercalated graphite compounds, in the temperature range $1.2 < T < 4.2$ K and a magnetic field $H \sim 0.5$ G, have shown them to undergo a phase transition ~ 1.8 K, for all stages 1 through 6 and 8. Here, specific heat measurements on a stage 5 sample, that was cooled in zero magnetic field as generated by a μ -metal shield, have been carried out down to below 0.5 K. In these measurements the specific heat anomaly is lowered to the temperature $T \sim 0.9$ K. Further, the removal of the magnetic shield does not restore the higher temperature anomaly, even after the sample's temperature was raised above 10 K. The data also show a T^2 behavior above 1.4 K for the lattice component ($\theta_D \sim 160$ K), which is indicative of a 2D phonon spectrum. However, similar measurements on a stage 2 sample just reproduce the phase transition ~ 1.8 K, while extending the temperature range allowing the measurements of the electronic contribution to the specific heat.

Sorting category:

Keywords: superfluidity, rubidium, cuprate

Zero-Field Cooled Specific Heat Of FeCl_3 Intercalated Graphite

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Abstract. Specific heat measurements on a stage 5 sample, that was cooled in zero magnetic field as generated by a μ -metal shield, have been carried out down to below 0.5 K. In these measurements the specific heat anomaly is lowered to the temperature $T \sim 0.8$ K. Further, the removal of the magnetic shield does not restore the higher temperature anomaly, even after the sample's temperature was raised above 10 K. The data also show a T^2 behavior above 1.4 K for the lattice component ($\theta_D \sim 160$ K), which is indicative of a 2D phonon spectrum. However, similar measurements on a stage 2 sample just reproduce the phase transition ~ 1.8 K, while extending the temperature range allowing the measurements of the electronic contribution to the specific heat.

Keywords: specific heat, phase transition, lattice and electronic.

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The layered and highly anisotropic materials, FeCl_3 intercalated graphite compounds, which are characterized by the number of graphite layers (stage n) sandwiched between the magnetic salt layers, are known to undergo a phase transition ~ 1.8 K, which was elusive because of its sensitivity to low magnetic fields. Previously, low temperature magnetic susceptibility^[1,2], specific heat^[3] and magnetization^[4] measurements on these compounds concentrated on the stage dependence of the characteristics of the transition, since the stage index, n , is a direct measure of magnetic inter-layer repeat distance. The magnetic measurements showed the strong stage dependence, studied the applied field effects on the phase change, and pointed out its suppression with as low a field as 20 G. Also, the magnetization, $M(T)$, for stages 1, 2, 3, 4, 5, 6 and 8 showed a sharp increase with cooling through 1.8 K and a subsequent saturation^[4]. The saturation magnetization, $M(1.1 \text{ K})$, for stage 6 exhibits^[4] a linear dependence on the applied magnetic field down to 0.1 G. However, all the previous measurements were limited to a base temperature of 1.2 K, using ^4He as refrigerant. Due to a continuing investigation, here is a report on the results of the specific heat measurements on a stage 5 sample cooled in zero field (using a μ -metal magnetic shield) and an extended temperature range, down to 0.5 K. It is believed that these are the first

measurements on these compounds at this low temperature and field.

Along with other samples, the stage 2 and stage 5 samples, used here, were prepared in a two-zone oven using highly ordered pyrolytic graphite (HOPG) as the host and in-situ synthesized ferric chloride, a standard preparation method^[5]. As usual, it was characterized for stage fidelity and purity using the (00l) x-ray diffractograms, before and after measurements. The heat capacity measurements were carried out using the ac method^[6], which is suitable for slow temperature sweeps through the phase transitions, and requiring a sample size no bigger than $0.5 \times 5 \times 7 \text{ mm}^3$ and mass less than 50 mg. The addenda consists of a gauge 40 constantan wire no longer than 3.5 in. and the thermometer used is a ruthenium oxide thick film bare resistor chip, as well as some diluted GE varnish. In order to extend the temperature range to below 1 K, the measurements were carried out in a ^3He refrigerator. The zero magnetic applied field was provided by a μ -metal shield around the cryostat's tail both during the cool-down process and during the measurements. The magnetic shield was kept on during few thermal cycles in the temperature range of interest, then it was removed and the sample was allowed to warm up to slightly above 10 K. After that the measurements were repeated in the Earth's

magnetic field (0.5 G), and in an applied field, $H_a \sim 1$ kG, for comparison.

Figure 1 shows the specific heat (in J/K-mole of atoms, as per a previously adopted convention^[7]) data as the usual plot of $c(T)/T$ vs. T , in the temperature range 0.5 K to 4 K, for three different successive stages, 4, 5 and 6. The new data for the stage 5 sample, which was cooled in a zero magnetic field is presented with that for stages 4 and 6, which were cooled in the Earth's magnetic field (~ 0.5 G)^[3] for comparison of magnitude and transition temperature. It is seen that while the stages 4 and 6 data exhibit a transition around 1.8 K, the stage 5 data exhibit a sharper anomaly and at a temperature slightly below 0.85 K.

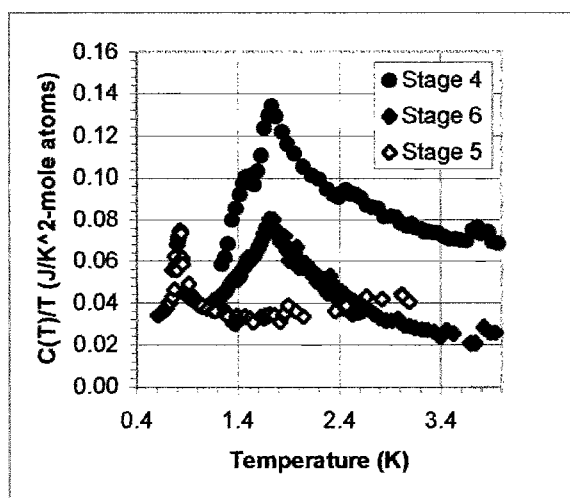


FIGURE 1. Specific heat data for FeCl_3 intercalated graphite plotted as $c(T)/T$ vs. T , for stages 4 and 6 ($H_a = 0.5$ G) stage 5 (zero-field), as indicated.

The total specific heat for this system can be written as: $c(T) = \gamma T + \beta T^2 + c_M(T)$

where the three terms represent the electronic, lattice and magnetic contributions, respectively. For stage 5 above the transition, for temperature $T > 1.4$ K, where the magnetic contribution is small and goes as T^2 , $c(T)/T$ has a definite linear temperature dependence, as can be seen in Figure 1. This is a strong indication for a 2-D phonon spectrum, which is the case for layered materials such as the graphite intercalation compounds.

Within the limited range of temperature, both $c(T)$ and $\int_{0}^T \frac{c(T)}{T} dT$ were least squares fit to the appropriate functional temperature dependence. The result is a value for the lattice contribution to the

specific heat, $\beta = 9.4 \text{ mJ/K}^3$ -mole of atoms, which corresponds to Debye temperature, $\theta_D = 160$ K, a value between that of stages 4 and 6^[3] and same order of magnitude as other acceptor compounds^[7].

One striking observation is that when the magnetic shield was removed and the sample temporarily heated up to above 10 K and then cooled down, the low temperature transition persisted, and there was no indication of any transition around 1.8 K. Further, an application of a field as high as 1 kG did not remove the lower temperature transition, nor did it restore the higher one. Similar measurements on a stage 2 sample just reproduce the phase transition ~ 1.8 K^[8], while extending the temperature range allowing the measurements of the electronic contribution to the specific heat.

The combined observations seem to point to two low temperature ground states that this system can settle in; their accessibility depends on the stage index and the applied field during cooling. An aspect about intercalated graphite compounds based on HOPG as a host material is that the crystallites have a c-axis size of the order of 100 to 500 Å, which makes them a collection of nano particles. This warrants further investigations of these compounds, and the purpose of this communications is a report of first time experimental observation as a result of on going investigation on these compounds.

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