Zero-Field Cooled Specific Heat of Stage 5 $FeCl_3$ Intercalated Graphite

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Abstract

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 magnetic 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.

Key words: specific heat; anomaly; zero-field-cooled;

1. Introduction

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 interlayer 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. However, the previous measurements were limited to a base temperature of 1.2 K. 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.

2. Experimental Details

Along with other samples, the stage 5 sample, used here, was prepared in a two-zone oven using 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) diffractograms, before and after measurements. The heat capacity measurements were carried out using ac method [6], which is suitable for slow temperature sweep through phase transitions, and requiring a sample size no bigger that $\sim 0.5 \times 5 \times 7$ 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. The

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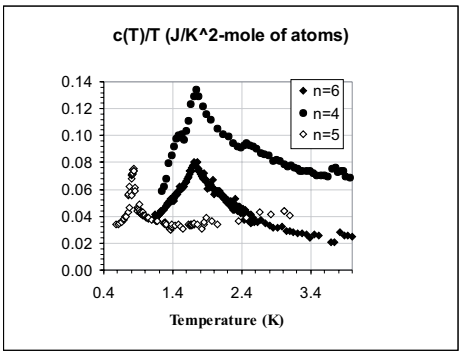

Fig. 1. Specific heat data for $FeCl_3$ intercalated graphite plotted as $c(T)/T$ vs. T, for stages 4 and 6 ($H_a = 0.5$) G stage 5 (zero-field), as indicated.

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.

3. Results and discussion

Figure 1 shows the specific heat (in J/K-mole of atoms) 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 Earths magnetic field ($\sim$ 0.5 G)[3] for comparison of a 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 a factor of 2 lower.

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. Above the transition, for temperature $T > 1.4$ K, where the magnetic contribution is small and goes as $\frac{1}{T^2}$, $c(T)/T$ 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 $c(T)/T$ were least squares fit to the appropriate functional temperature dependence. The result is a value for $\beta = 9.4$ mJ/K^3-mole of atoms, which corresponds to $\theta_D = 160$ 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, with same effects.

The combined observations seem to point to two low temperature ground states that this system has; their accessibility depends on the applied field. This warrants further investigations of these compounds.

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