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Physica C 282–287 (1997) 1403–1404

PHYSICA C

Magnetic Field Dependence of Low Temperature Heat Capacities of $GdBa_2Cu_4O_8$

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Calorimetric measurements were made on a coprecipitation-synthesized $GdBa_2Cu_4O_8$ at temperatures between 0.5 and 13 K and in magnetic fields up to 7 T. The heat capacity data in zero field show an antiferromagnetic transition with $T_N \cong 2.2$ K followed by a broad shoulder below, which is identified from entropy consideration to be also associated with the Gd^{3+}-ordering. Similar observations were made in a magnetic field of 2 T, except that T_N was lowered to 1.6 K. At a higher field of 4 T the calorimetric signature of a long range ordering disappeared, leaving behind a Schottky-type anomaly with a peak near 1 K. This peak moved to 2.5 K at 7 T.

INTRODUCTION -- For the $RBa_2Cu_3O_7$ series (R = rare earth) with the same orthorhombic structure of the parent compound $YBa_2Cu_3O_7$, only $PrBa_2Cu_3O_7$ is nonsuperconducting and exhibits an anomalous magnetic ordering near 17 K. Otherwise, the highest Néel temperature $T_N \cong 2.2$ K occurs when R = Gd [1]. Fairly close T_N values for antiferromagnetic Gd^{3+} ordering prevail in nonsuperconducting $GdBa_2Cu_3O_{6+\delta}$ [2] and many other related cuprate compounds such as $TlBa_2GdCu_2O_7$ [3], $TlSr_2GdC_2uO_7$ [4], $(Pb_{.5}Cu_{.5})Sr_2GdCu_2O_7$ [4], and $Pb_2Sr_2GdCu_3O_8$. [4], while $Bi_2Sr_2GdCu_2O_8$ [5] exhibits a slightly lower value of 1.6 K. This report describes a calorimetric study on $GdBa_2Cu_4O_8$, which differs from $GdBa_2Cu_3O_7$ by having one additional Cu-O chain layer in the unit cell. Using Mössbauer spectroscopy Bornemann et al [6] have found antiferromagnetic order of Gd moments at low temperatures. Of more interest is the fact that there appears to be invariably a broad shoulder below T_N in the zero-field heat capacity data for the previously studied Gd-containing compounds. This work examines the magnetic field effect on such an anomaly.

EXPERIMENTAL -- Like $YBa_2Cu_4O_8$, $GdBa_2Cu_4O_8$ was first synthesized by solid state reaction under high pressure of oxygen. In contrast, the sample used in this work was prepared by a coprecipitation technique. A mixture of Gd_2O_3, $BaCO_3$ and CuO with stoichiometric ratios was first dissolved and thoroughly stirred at 80°C in an appropriate amount of concentrate nitric acid. After the clear solution was diluted with water, oxalic acid and diethylamine were added to adjust its pH value to above 10. Fine grains of precipitation formed immediately. They were filtered out and dried overnight in the incubator at 110°C, followed by pyrolysis at 600°C to form powder precursor. The latter was calcined in flowing oxygen at 800°C and 1 atm pressure, and then sintered at 815°C for 10 days under the same oxygen flow. The product is single phase $GdBa_2Cu_4O_8$ as confirmed by x-ray powder diffraction. Resistance as well as SQUID data in Fig. 1 yield $T_c = 74$ K. Calorimetric measurements using a thermal relaxation technique [3] were made between 0.5 K and 14 K in a ^{3}He cryostat equipped with a 7-T superconducting magnet.

RESULTS AND DISCUSSION -- Fig. 2 shows the heat capacity data as a function of temperature. Gd^{3+} ordering clearly occurs just above 2.2 K in zero field. T_N decreases not surprisingly with increasing field, reaching 1.6 K at 2 T. The long range order eventually disappears at 4 T, reverting to a Schottky-type behavior. By assuming a Debye temperature of 350 K and the corresponding lattice heat capacity based on most other high T_c materials, Fig. 3 presents the temperature dependence of C_m/T, where the magnetic heat capacity $C_m = C - 0.00070T^3$. The anticipated shoulder in heat capacity below T_N

PII S0921-4534(97)00797-1

becomes more apparent. Again, it shifts toward lower temperatures with increasing field before the long range order is quenched. Fig. 3 provides the convenient format to derive the magnetic entropy $S_m = \int(C_m/T)dT$. With a linear extrapolation to absolute zero below 0.5 K, a simple integration for zero field yields S_m above T_N only a few percent higher than $R\ln(2J+1) = 17.3$ J/mol K as expected for Gd^{3+} with $J = 7/2$. The small discrepancy could be the consequence of certain minor phases in the sample. Nevertheless, the entropy consideration suggests that the heat capacity shoulder below T_N is associated with the Gd^{3+} ordering process. Its origin is likely due to spin fluctuations in the normally ordered state, and such fluctuations are more pronounced for larger spins [7]. Gd^{3+} has indeed the largest spin of 7/2 among all R^{3+} ions. Same statement can be made for the low field data. At higher fields the Schottky-type C_m extends beyond the range of measurements.

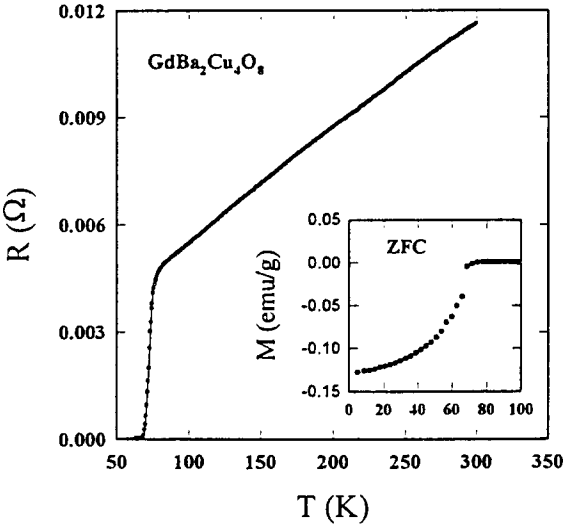

Fig. 1 Resistive and magnetic data showing superconducting transition.

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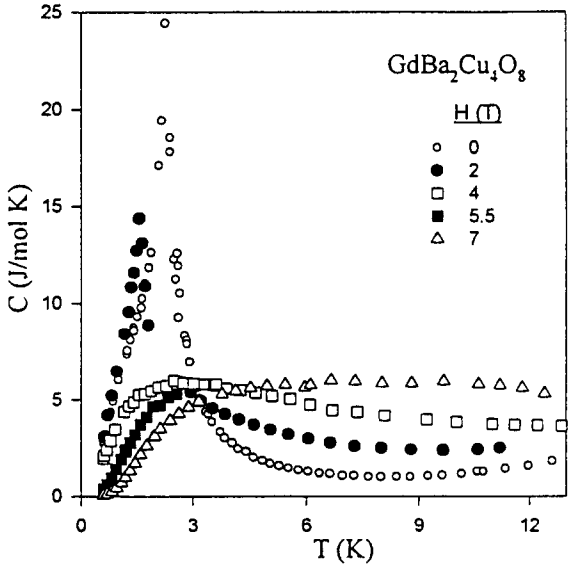

Fig. 2 Temperature dependence of heat capacity in various magnetic fields.

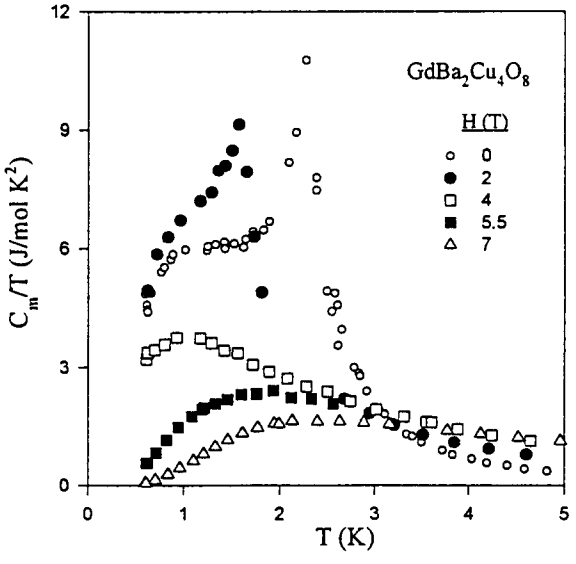

Fig. 3 Temperature dependence of C_m/T, yielding magnetic entropy.