Low-dimensional magnetism in the high-T_c superconductor $L\mathrm{Ba_2Cu_3O_{7-y}}$ (L = Gd, Ho, Er): Heat-capacity study

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Heat capacities have been measured for the high-T_c superconductors $L\mathrm{Ba_2Cu_3O_{7-y}}$ (L = Gd, Ho, Er, Y) between 0.15 and 100 K. While the superconducting phase-transition temperatures of these compounds are nearly the same at $T_c = 92$ K, the heat-capacity data indicate magnetic ordering in the system of rare earths at $T_m = 2.21$ K for $\mathrm{GdBa_2Cu_3O_{7-y}}$ and at $T_m = 0.60$ K for $\mathrm{ErBa_2Cu_3O_{7-y}}$. In both cases, the cooperative heat-capacity peak resembles that of the two-dimensional (2D) Ising model. In addition, broad heat-capacity anomalies, which cannot be attributed to crystalline field splittings, are found. A semiquantitative fit can be obtained by assuming that two-thirds of the rare earths constitute a 2D Ising system and the rest of them form a 1D Ising-like system. The heat capacity of the $\mathrm{HoBa_2Cu_3O_{7-y}}$ shows a very flat maximum at ~5 K. The separation of the two lowest-lying singlet levels of Ho^{3+} ions is estimated to be ~7 K.

One of the striking features of the 90-K superconductor $\mathrm{YBa_2Cu_3O_{7-y}}$ is the insensitivity of T_c to the replacement of Y by most of the rare earths.[1-7] Superconductivity has been observed in $L\mathrm{Ba_2Cu_3O_{7-y}}$ with all of the common rare-earth elements (L), except for Ce, Pr, and Tb. The superconducting transition temperatures for these compounds reported by many different research groups fall within the range 92 ± 5 K. Even this small divergence appears to be caused, for the most part, by different sample preparation methods, ambiguity of the critical temperature T_c due to the often rounded nature of the phase transition and, possibly, uncertainty in thermometer calibrations. Our own results for the Y, Ho, and Er compounds show that the dispersion in their T_c's is less than 0.5 K.[7]

This is in marked contrast with the strong suppression of superconductivity in elemental superconductors caused by the formation of a dilute alloy with various magnetic atoms. The situation is somewhat similar to that in the rare-earth ternary compounds such as $\mathrm{GdMo_6S_8}$, $\mathrm{ErMo_6Se_8}$, and $\mathrm{NdRh_4B_4}$, in which coexistence of superconductivity and antiferromagnetism has been found.[8] In some other ternary systems, the magnetic interactions are ferromagnetic and curious effects of the interplay of magnetism and superconductivity have been noted.[9] In these cases, however, T_c varies widely from one kind of rare-earth compound to another.

The susceptibility data on $L\mathrm{Ba_2Cu_3O_{7-y}}$ above T_c show that these systems have essentially the paramagnetism of the given trivalent rare-earth ion, L^{3+}. For L = Ho and Er, we found that the susceptibility follows a Curie-Weiss law with Weiss constants of -46 and -24 K for the Ho and Er compounds, respectively.[7] These fairly large Weiss constants of antiferromagnetic sign suggest the onset of antiferromagnetic ordering of L^{3+} moments at temperatures which, while rather high, are well below the superconducting transition. Tarascon *et al.*[6] indeed found a susceptibility maximum around 2 K for $\mathrm{GdBa_2Cu_3O_{7-y}}$ measured in a field of 10 kOe, which was large enough to suppress the superconducting state. Other rare-earth compounds, however, were found by these authors to remain paramagnetic in such a field down to 1.6 K, the lowest temperature achieved in their measurements. To study the magnetic ordering in zero external field and also to obtain information about the crystalline-field splittings, we have initiated low-temperature heat-capacity measurements on several members of the series of $L\mathrm{Ba_2Cu_3O_{7-y}}$ superconductors. In this paper we will report results for the Gd, Ho, Er, and Y compounds. After completion of most of this work, we learned of other heat-capacity studies with similar objectives carried out by other groups.[10,11] The parallels, and some discrepancies, with the present results will be discussed.

The samples were prepared from intimate mixtures of L_2O_3, $BaCO_3$, and CuO, with the metals in 1:2:3 mole ratio. The powders were heated in air at 900 °C overnight and were slowly cooled to room temperature in the furnace. One (or more) regrinding and reheating of the product was usually necessary before the x-ray powder diffraction pattern indicated the orthorhombic single-phase $L\mathrm{Ba_2Cu_3O_{7-y}}$ compound.

Heat capacities have been measured between 0.5 and 100 K in a He^3-cooled cryostat by an adiabatic, discontinuous heating method. The heat capacity of the copper capsule which held the specimen and the petroleum ether used to ensure heat transfer between the powder sample and capsule had been determined in a separate run. Typical sample weight amounted to ~70 g, corresponding to about 0.1 mole of rare-earth atoms. For $\mathrm{HoBa_2Cu_3O_{7-y}}$, the measurement was extended to 0.15 K using a He^3-He^4 dilution refrigerator.

The overall results for four compounds are summarized in Fig. 1 in a double-logarithmic plot. No appreciable

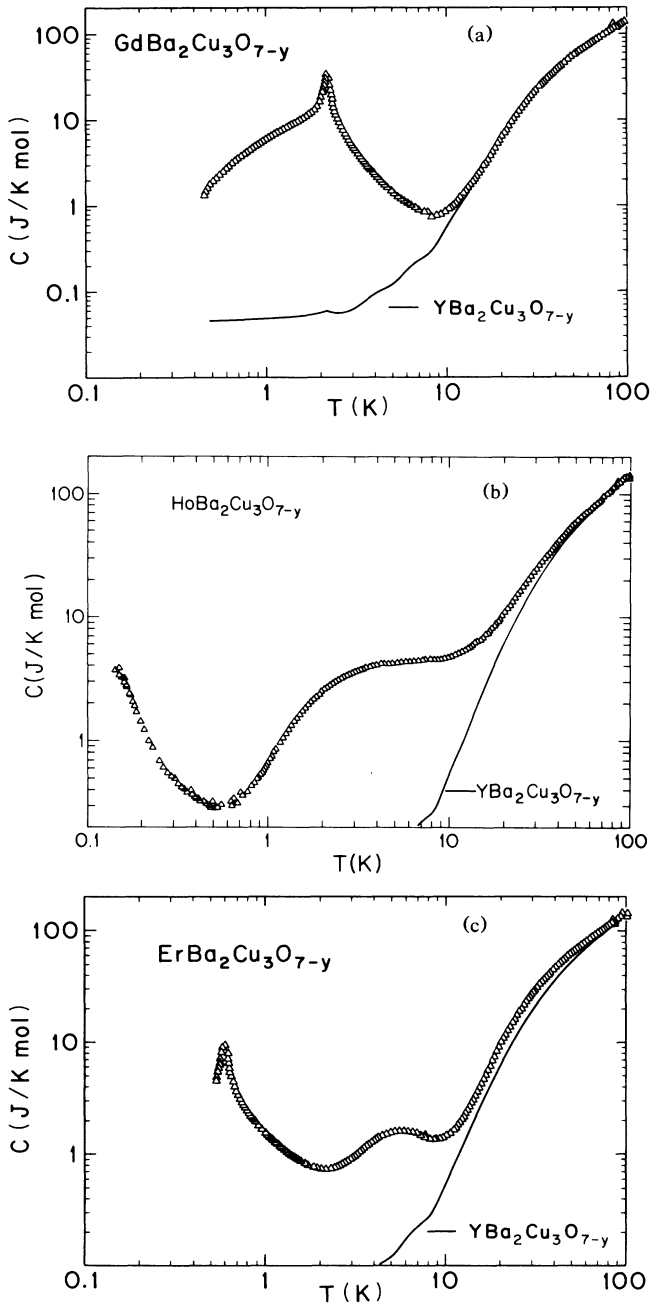

FIG. 1. Heat capacities of four high-T_c superconductors as functions of temperature in a double logarithmic plot; (a) $GdBa_2Cu_3O_{7-y}$, (b) $HoBa_2Cu_3O_{7-y}$, (c) $ErBa_2Cu_3O_{7-y}$. The results for $YBa_2Cu_3O_{7-y}$, which are used to extract the magnetic contribution to the heat capacity, are shown by solid lines in each figure.

anomaly can be seen at the superconducting transition temperature, ~92 K. This, however, is consistent with the findings of Kitazawa *et al.*[12] who reported that the heat-capacity jump at T_c in $YBa_2Cu_3O_{7-y}$ amounts to only 2 J/K mol. Nevitt and Klippert report a larger value, 5.5 J/K mol.[13] The anomaly at T_c will be studied separately under high resolution in a more appropriate apparatus.

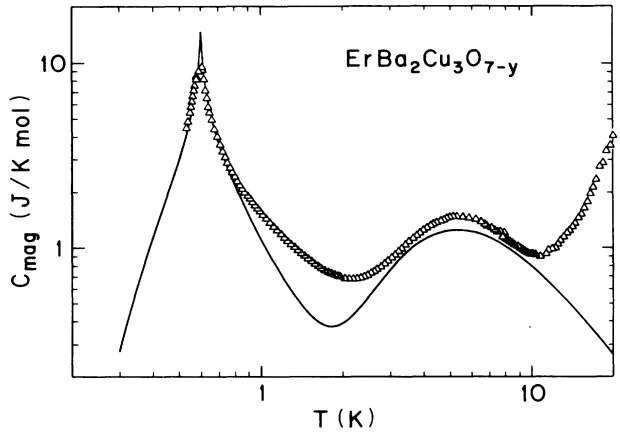

FIG. 2. Magnetic contribution to the heat capacity of $ErBa_2Cu_3O_{7-y}$ below 20 K. Combined heat-capacity curve of the 2D Ising model with $|J_{2D}/k_B| = 0.53$ K and 1D Ising model with $|J_{1D}/k_B| = 13$ K is shown by a solid line. (See text.)

In extracting the magnetic contribution to the heat capacity, one first notes that the heat capacities of the Gd and nonmagnetic Y compounds are practically identical above ~15 K [Fig. 1(a)]. This indicates that the crystalline-field splitting of the ground multiplet ^8S of the Gd^{3+} ion is small, as expected. The heat capacity of $GdBa_2Cu_3O_{7-y}$ can be well fitted with a formula $33/T^2+5.9\times10^{-4}T^3$ (J/K mol Gd) for 5 K $< T <$ 20 K. The coefficient of the T^3 term obtained here agrees fairly well with the value 7.1×10^{-4} reported by Willis *et al.*[10] and approximates the lattice heat capacity for $0 < T < 20$ K. Since the heat capacity of $YBa_2Cu_3O_{7-y}$ appears to represent the lattice contribution of $GdBa_2Cu_3O_{7-y}$, we use the data for the Y compound in estimating magnetic contributions in the other compounds as well.

The heat capacity of $YBa_2Cu_3O_{7-y}$ shows a curious deviation from the T^3 law below ~7 K and decreases much more slowly than expected as the temperature is lowered. It is almost temperature-independent below 2 K. Part of this anomaly must be due to a magnetic impurity effect as evidenced by a tiny peak at 2.2 K, which coincides with the magnetic ordering temperature T_m of $GdBa_2Cu_3O_{7-y}$. It is unclear whether the major share is due to conduction electrons or to other degrees of freedom. Since this excess amounts to no more than 5% of the magnetic contributions in the magnetic compounds we have studied, the discussion of the heat-capacity anomalies in those materials will not be affected in any substantial way by its presence.

A very sharp heat-capacity peak, which clearly indicates magnetic ordering, is found at 0.60 K for $ErBa_2Cu_3O_{7-y}$ (Fig. 2). An additional broad heat-capacity maximum is also seen at ~5 K. This is not a contribution from the excited doublet states of the Er^{3+} ion. An estimate of the entropy at 10 K yields only $R\ln2$, i.e., the amount contributed by the ground doublet. Dunlap *et al.* also found a similar subsidiary maximum in the C_p of $ErBa_2Cu_3O_{7-y}$ and attribute it either to an impurity phase or an incommensurate magnetic transition.[11] We

feel it rather unlikely that independently prepared samples of a given material would show very similar heat-capacity anomalies due to an impurity phase. One is tempted to attribute the rounded maximum to short-range ordering and the sharp peak to long-range ordering within a single spin system. However, the relative sizes and the large separation of these two anomalies defy explanation in this way. A natural explanation of these facts is possible if L atoms on $L\mathrm{Ba_2Cu_3O_{7-y}}$ occupy two different kinds of lattice sites and behave approximately as two distinct magnetic systems. The available x-ray and neutron diffraction results appear to exclude this possibility.[14,15] However, there is some recent evidence that the actual structure of the $L\mathrm{Ba_2Cu_3O_{7-y}}$ compounds may be more disordered than the regular structure previously deduced. For example, Ourmazd *et al.*[16] propose a structure for $\mathrm{YBa_2Cu_3O_{7-y}}$ with two different rare-earth sites to explain the planar defects which they have found by electron microscopy. In this structure the rare-earth ions are found between planes of linearly linked copper and oxygen atoms as well as in the normal position between the two-dimensional networks of copper and oxygen. However, the fraction of the L atoms in the defect position is very small in this model. Very recently, it has been reported that a considerable fraction (20%–30%) of copper atoms have been found by x-ray absorption techniques to exchange their positions with rare earths.[17]

The shape of the cooperative peak bears a strong resemblance to that of a two-dimensional Ising system as shown in Fig. 2. Considering the nearly tetragonal symmetry and large separation of Er^{3+} sheets in the c axis direction, it is not surprising that the system of Er^{3+} ions, each with a ground doublet, belongs to the same universality class as does the 2D Ising system. One can get a proper amplitude by simply multiplying the theroetical heat-capacity values for the 2D Ising system by two-thirds. It is interesting to note that one-third of the heat-capacity values of a 1D Ising model reproduces the anomaly at ~ 5 K rather well. The combined heat-capacity curve of the 2D Ising with $|J_{2D}|/k_B = 0.53$ K and 1D Ising model for $|J_{1D}|/k_B = 13$ K is shown in Fig. 2.

A cooperative heat-capacity peak is found at 2.21 K for $\mathrm{GdBa_2Cu_3O_{7-y}}$. This is in good agreement with the results by Willis *et al.* who found $T_m = 2.24$ K.[10] The shape of the anomaly again shows a similarity with that of a 2D Ising model. Furthermore, if the theoretical results for the $S = \frac{1}{2}$ 2D Ising model with $|J_{2D}|/k_B = 1.95$ K are multiplied by $\ln 8/\ln 2 = 3$ to get proper scaling to a $S = \frac{7}{2}$ system, and then multiplied by a factor of $\frac{2}{3}$, as in the case of $\mathrm{ErBa_2Cu_3O_{7-y}}$, we find a surprisingly good fit to the experimental data. It is very tempting to attribute the broad shoulder below T_m to the second (possibly one-dimensional) magnetic system which constitutes $\frac{1}{3}$ of the total. Such a theoretical curve for a 1D Ising system with $|J_{1D}|/k_B = 2.3$ K is given in Fig. 3. A 2D Ising-like heat-capacity peak is also found for $\mathrm{DyBa_2Cu_3O_{7-y}}$ in which $T_m = 0.95$ K.[11] Although no obvious second maximum is found in this case, the experimental data can be reproduced very well by a combined theroetical curve for the 2D Ising system with $|J_{2D}|/k_B = 0.85$ K and the 1D Ising system with $|J_{1D}|/k_B = 2.5$ K.

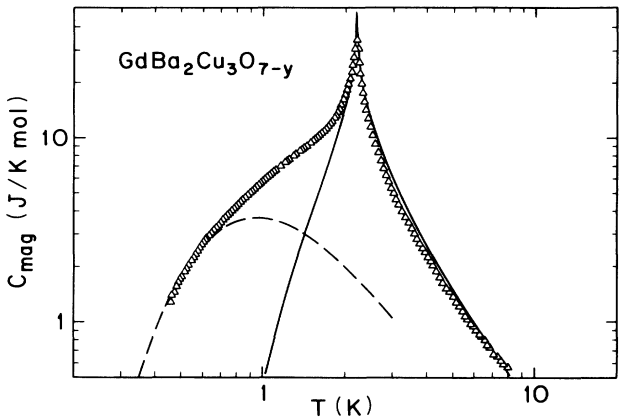

FIG. 3. Magnetic contribution to the heat capacity of $\mathrm{GdBa_2Cu_3O_{7-y}}$ for $T < 8$ K. The solid line indicates the properly scaled theoretical value for the 2D Ising model with $|J_{2D}/k_B| = 1.95$ K. The dashed line shows the similarly scaled values for the 1D Ising system with $|J_{1D}/k_B| = 2.3$ K. (See text).

Down to 0.5 K, the heat capacity of the non-Kramers compound $\mathrm{HoBa_2Cu_3O_{7-y}}$ is dominated by a Schottky-like anomaly due to crystalline-field splitting. It begins to rise below 0.5 K, probably reflecting on increased degree of ordering in the strongly coupled nucleus-electron spin system. However, no clear sign of long-range ordering is found down to 0.15 K. The heat-capacity anomaly at ~ 6 K is extremely flat and the entropy difference between 0.6 and 15 K amounts to 9.3 J/K mol which exceeds $R\ln 3$. The crystalline-field splitting appears to be rather complicated. We infer that the first two singlets are separated by ~ 7 K. Dunlap *et al.*[11] have obtained heat-capacity data on the Ho compound which extend down to ~ 0.1 K and found a rather atypical heat-capacity peak at ~ 0.17 K. They interpret the results as indicative of the ordering of hyperfine-induced electronic moments in the singlet ionic ground states. While this is certainly a possible explanation, it makes the rapid drop in the heat capacity reported below T_m rather puzzling. In this picture the 0.17 K peak should primarily show changes in the nuclear entropy. However, it appears to be too small to account for all of the large entropy of the Ho nuclei ($R\ln 8$). Thus one would expect C_p still to be large at 0.1 K and probably increasing with falling temperature.[18] In our measurements, an apparent tendency for C_p to decline at the lowest temperatures was found to be a spurious effect due to the rapidly increasing thermal relaxation time.

The origin of the magnetic interactions which cause the ordering in $L\mathrm{Ba_2Cu_3O_{7-y}}$ compounds is not clear. The large distance between the magnetic ions, nearly 4 Å, appears to exclude a direct exchange mechanism. With dipolar interaction, summation over the orthorhombic lattice favors an antiferromagnetic ordering with an energy gain of ~ 0.6 K for the Gd compound. This is significantly smaller than the observed $T_m = 2.21$ K. In addition, the apparent 2D Ising behavior is incompatible with long-range dipolar interactions. It is interesting to note, as shown in Table I, that T_m appears to scale as

$S(S+1)$, where S is the total spin angular momentum of the rare-earth ion. This seems to suggest that some kind of exchange mechanism couples the magnetic ions. The systematic variation of T_m with $S(S+1)$ or equivalently the "de Gennes factor," $(g_J-1)^2J(J+1)$, where J is the total angular momentum, is found for a number of series of rare-earth intermetallic compounds. In these systems exchange interactions mediated by conduction electrons [Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism] are found to be dominant.[19]

In summary, our heat-capacity data at low temperatures have led us to suggest that the high T_c superconductors $L\mathrm{Ba_2Cu_3O_{7-y}}$ with L=Gd and Er appear to contain two nearly independent magnetic systems, namely, a 2D Ising system which constitutes as much as perhaps $\frac{2}{3}$ of the rare-earth atoms and a 1D Ising system which is made up of the rest. The relation of oxygen vacancies to this feature of the magnetism of the $L\mathrm{Ba_2Cu_3O_{7-y}}$ superconductor is under study.

Note added in proof. Recent heat-capacity data reveal long-range ordering in $\mathrm{SmBa_2Cu_3O_{7-y}}$ at T_m=0.585 K, while $\mathrm{NdBa_2Cu_3O_{7-y}}$ shows only short-range order down to 0.4 K with a rounded maximum at 0.9 K (Ref. 20).

TABLE I. Comparison of T_m for the $L\mathrm{Ba_2Cu_3O_{7-y}}$ compounds.

L	T_m (K)	$\mu_{\mathrm{free}}/\mu_B$	$T_m/S(S+1)$	$T_m/(g_J-1)^2J(J+1)$
Gd[a]	2.21	7.94	0.14	0.14
Dy[b]	0.95	10.65	0.11	0.13
Er[a]	0.60	9.58	0.16	0.24

[a]This work. [b]Reference 11.

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