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LETTER TO THE EDITOR

ELECTRONIC AND MAGNETIC PROPERTIES OF RARE-EARTH IONS IN $REBa_2Cu_3O_{7-x}$ (RE = Dy, Ho, Er) *

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Heat capacity, resistivity, and magnetic susceptibility data have been obtained for the compounds $REBa_2Cu_3O_{7-x}$, where RE = Dy, Ho or Er. Neutron diffraction data on the Ho compound show a structure identical to that of $YBa_2Cu_3O_{7-x}$. Magnetic transitions are observed at $T_m = 0.95$, 0.17 and 0.59 K for Dy, Ho and Er compounds, respectively. It is argued that these are due predominantly to dipolar interactions. Resistivity data show that the magnetic state is coexistent with superconductivity in all cases. From the heat capacity data, the degeneracies of the crystal field ground states are determined, and estimates are given for the magnetic moment in the ground state and the energy separation to the first excited crystal field state.

Following the observation [1] of superconducting transition temperatures, T_c, in excess of 90 K in $YBa_2Cu_3O_{7-x}$, a great deal of interest has developed in determining the nature of the superconductivity and the effect of substituents at various sites in the compound. A number of laboratories have noted that the Y ion can be fully substituted by several rare-earth (RE) ions, with T_c being virtually unchanged [2–12]. At first sight, this is a surprising result since the RE ions are strongly paramagnetic, and our normal experience has been that paramagnetic ions have a strongly negative influence on superconductivity. In order to clarify this situation, we have investigated the magnetic and electronic properties of $REBa_2Cu_3O_{7-x}$ (RE = Dy, Ho and Er). In the following we present resistivity, magnetic susceptibility and low temperature heat capacity results. These data will be used to obtain information about the magnetic moments on the RE ions, the values of magnetic transition temperatures (T_m) and the nature of the crystalline electric field (CEF) interactions on the RE ions. Using this information, the influence of magnetism on the superconducting properties will be assessed.

The samples were prepared from intimate mixtures of the RE-sesquioxides, $BaCO_3$, and CuO, with the metals in a 1:2:3 mole ratio. These powders were heated to 975 °C and then cooled at 100 °/h in flowing oxygen. Resistance data for the three compounds are shown in fig. 1. In all cases, these data give superconducting transition temperatures of $T_c = 92$–93 K. Resistivity data also show that the materials remain superconducting down to $T \approx 0.6$ K for all three cases.

Room temperature powder neutron diffraction data were collected on a sample of $HoBa_2Cu_3O_{7-x}$ using the special-environment powder diffractometer (SEPD) at the Intense Pulse Neutron Source (IPNS) located at Argonne National Laboratory. These data were analysed with the Rietveld struc-

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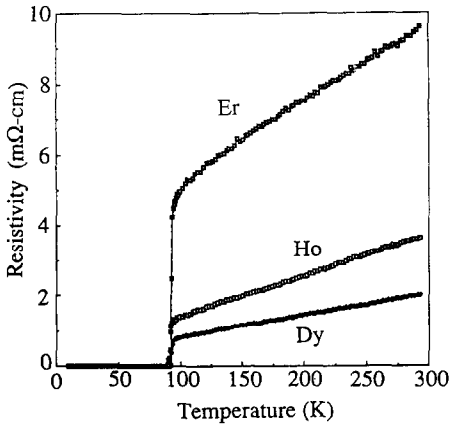

Fig. 1. Resistance vs. temperature for $REBa_2Cu_3O_{7-x}$ compounds.

Table 1
Positional and thermal parameters for $HoBa_2Cu_3O_{6.8}$, space group Pmmm, $a = 3.8239(1)$ Å, $b = 3.8861(1)$ Å, $c = 11.6843(4)$ Å

Atom	x	y	z	B_{iso} (Å^2)	Occupancy
Ho	1/2	1/2	1/2	0.35(2)	1.00
Ba	1/2	1/2	0.1844(3)	0.48(6)	2.00
Cu1	0	0	0	0.46(6)	1.00
Cu2	0	0	0.3559(2)	0.22(4)	2.00
O1	0	1/2	0	0.80(15)	0.90(2)
O2	1/2	0	0.3779(3)	0.29(9)	1.90(2)
O3	0	1/2	0.3788(4)	0.36(7)	2.00
O4	0	0	0.1588(3)	0.61(9) *	2.00

* The form of the anisotropic temperature factor used for O4 is: $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33})$ with $\beta_{11} = 0.020(2)$, $\beta_{22} = 0.007(2)$, and $\beta_{33} = 0.004(2)$.

ture-refinement technique [13], and the sample was found to have a structure identical to that previously determined [14] for $YBa_2Cu_3O_{6.8}$. $HoBa_2Cu_3O_{7-x}$ is orthorhombic, crystallizing in the space group Pmmm, with lattice constants $a = 3.8239(1)$ Å, $b = 3.8861(1)$ Å and $c = 11.6843(4)$ Å. These lattice constants are essentially the same as those found [14] for $YBa_2Cu_3O_{6.8}$, reflecting the similarity in ionic radii of Y^{3+} and Ho^{3+}. The refined atomic positional parameters are given in table 1, with the atom numbering scheme as presented in fig. 2. The structure is composed of O1–Cu1–O1 linear chains along the b-direction, and non-planar Cu2–O2, O3 sheets perpendicular to the c-axis at $z = 0.36$ and $z = 0.64$. The coordination sphere of Ho^{3+} contains 8 nearest neighbour oxygen atoms at distances of 2.410(2) Å for Ho–O2 and 2.379(2) Å for Ho–O3. From the occupation numbers given in table 1, we find the actual composition to be $HoBa_2Cu_3O_{6.8}$. On the basis of X-ray data for all three compounds, and the identical structures for $HoBa_2Cu_3O_{6.8}$ and $YBa_2Cu_3O_{6.8}$, we assume that the Er and Dy compounds are also identical.

Inverse susceptibility data for $DyBa_2Cu_3O_{7-x}$, $HoBa_2Cu_3O_{7-x}$ and $ErBa_2Cu_3O_{7-x}$ are dis-

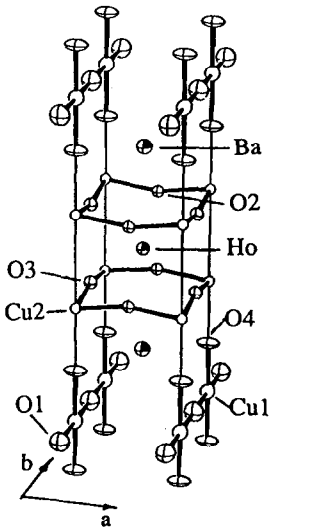

Fig. 2. Structure of $HoBa_2Cu_3O_{6.8}$ as determined from neutron diffraction data.

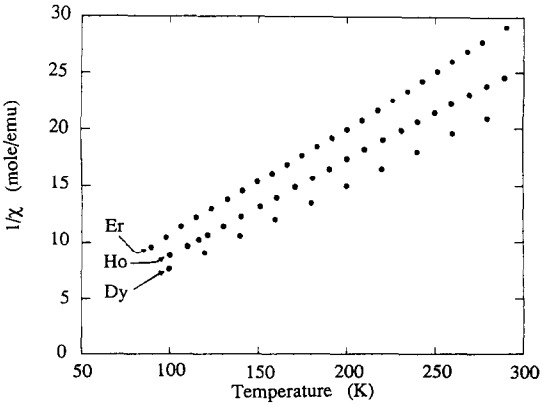

Fig. 3. Susceptibility vs. temperature for $REBa_2Cu_3O_{7-x}$ compounds.

played in fig. 3. In all cases, the inverse susceptibility is approximately linear in T from room temperature down to T_c. From the slope of $1/\chi$ vs. T, we obtain the effective moments listed in table 2 which are in close agreement with, but slightly smaller than the free-ion effective moments of the RE^{3+} ions.

Heat capacity data for $DyBa_2Cu_3O_{7-x}$ are shown in fig. 4. In order to correct for the lattice heat capacity contribution, we have made use of the available data [15] for $YBa_2Cu_3O_{6.8}$. That material has the same T_c as the current compounds and has an identical Cu–O sublattice, but does not contain paramagnetic ions. We therefore assume that we may use the measured heat capacity of $YBa_2Cu_3O_{7-x}$ to obtain all contributions that are not specifically related to the paramagnetic ions. The solid line in fig. 4a shows the results of subtracting the heat capacity of $YBa_2Cu_3O_{7-x}$ from that of $DyBa_2Cu_3O_{7-x}$. A very strong peak observed at low temperatures indicates a magnetic transition, shown in more detail in fig. 4b, which gives a magnetic transition temperature $T_m = (0.95 \pm 0.02)$ K. By integrating C/T vs. T, we can obtain the temperature dependence of the magnetic entropy, which should have the value $R \ln(w)$, where w is the number of non-degenerate energy levels occupied at the temperature T. For this compound, the entropy contained under the peak for $T = 0.1$–4 K is 5 J/mol K. As this is 0.87 R ln 2, we can conclude that the magnetic ordering occurs within a crystal-field doublet groundstate. The heat capacity at higher temperatures is in very good agreement with a Schottky peak due to a second doublet lying at 40 K above the groundstate.

At the lowest temperatures, a small upturn is seen in the heat capacity which is presumably the onset of the Schottky anomaly due to nuclear hyperfine splitting. However, the magnitude of this effect is smaller than is seen, for example, in Dy metal where the maximum hyperfine field for a Dy^{3+} ions is observed [16]. From the sparse data available in this temperature range, we estimate a hyperfine field of ≈ 3.5 MOe, compared to the free-ion value of 6.2 MOe. Since the nuclear magnetic hyperfine field is closely proportional to the electronic magnetic moment for rare-earth ions, this suggests that the magnetic moment in the

Table 2
Properties of $REBa_2Cu_3Co_{6.8}$

RE	T_c (K) [a]	μ_{eff} (μ_B) [b]	T_m (K) [b]	Energy (K)	Moment (μ_B)	Multiplicity
Dy	93.5(1.4)	10.4(2)	0.95(2)	0	≈ 6	2
				40		2
Ho	92.0(2.4)	10.2(3)	0.17(3)	0	≈ 0	
				8		1
Er	91.8(1.8)	9.1(1)	0.59(2)	0	≈ 4.5	2
				90		2

[a] Values given are for the midpoint of the 10–90% resistive transition, and the values in parentheses give the 10–90% width.

[b] Values in parentheses give estimated errors in the last significant figure.

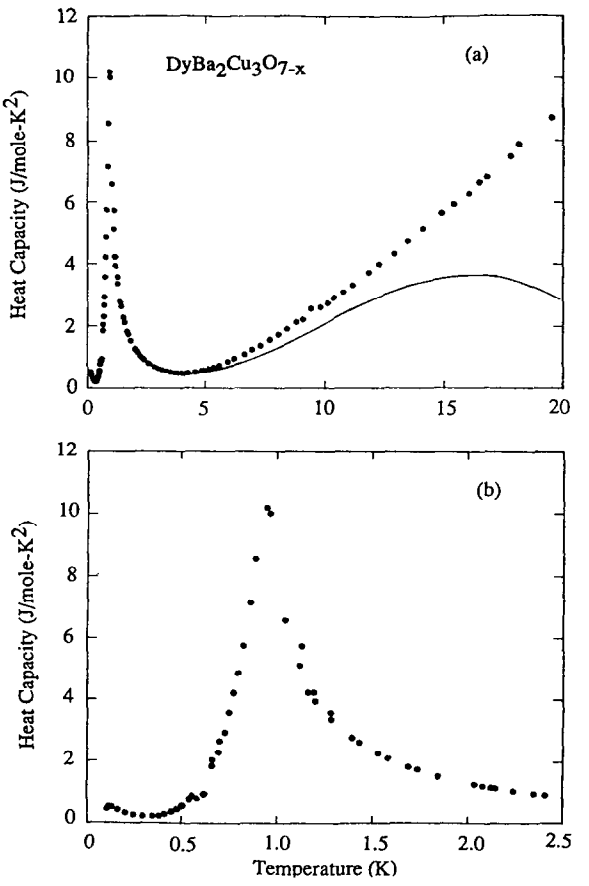

Fig. 4. Heat capacity vs. temperature for $DyBa_2Cu_3O_{7-x}$. The solid line shows the result of subtracting the heat capacity of $YBa_2Cu_3O_{7-x}$.

crystal field ground state is $\approx 6\mu_B$ compared to the free-ion value of $10\mu_B$.

The heat capacity of $HoBa_2Cu_3O_{6.8}$ is shown in fig. 5, and the solid line in fig. 5a shows the result of subtracting the heat capacity of $YBa_2Cu_3O_{6.8}$. Again magnetic ordering is seen at low temperatures (fig. 5b). Although the peak in the heat capacity is rather broad, we estimate the transition temperature as $T_m \approx 0.17$ K. It should be noted that the nuclear hyperfine energy of ^{165}Ho (the only isotope present in unenriched materials) has a value comparable to the magnetic transition energy, i.e. $AIJ = 0.33$ K, where A is the hyperfine coupling parameter, and I and J are the nuclear and electronic angular momenta. We furthermore note that the magnetic entropy associated with the magnetic peak integrated up to 0.6 K is 2.45 J/mol K^2. Since this is only about 50% of R ln 2, and some of that entropy is likely associated with nuclear hyperfine splitting, we assume that the ordering occurs out of a singlet groundstate. This is a frequently discussed set of circumstances in which one anticipates a combined nuclear–electronic ordering [17]. This arises because the nuclear hyperfine interaction induces a small moment in the electronic singlet ground state, and these moments are then coupled site-to-site. Although the magnetic transition temperature here is somewhat larger than is usually observed, it is plausible to assume that such an effect is operating here.

At higher temperatures, the electronic heat capacity rises to a peak at ≈ 5 K and then falls

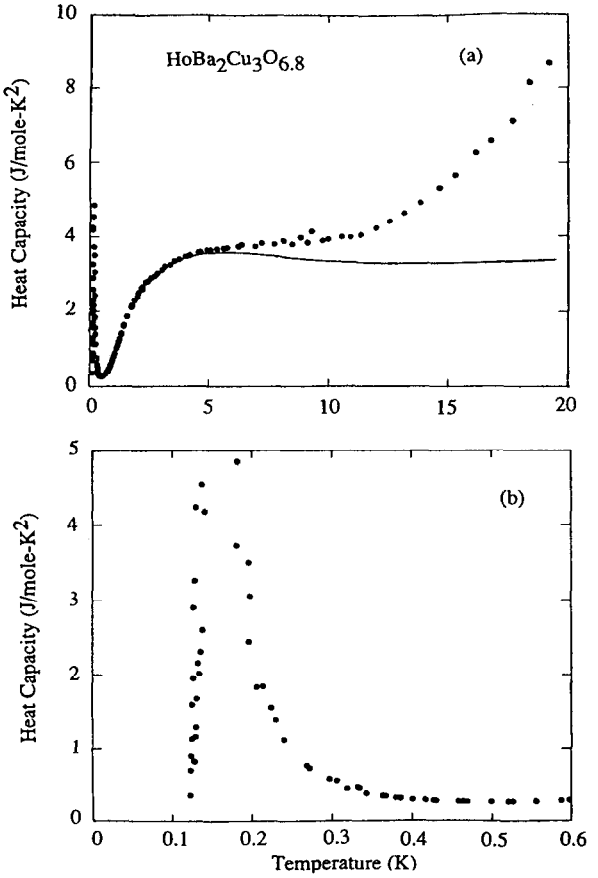

Fig. 5. Heat capacity vs. temperature for $HoBa_2Cu_3O_{7-x}$. The solid line shows the result of subtracting the heat capacity of $YBa_2Cu_3O_{7-x}$.

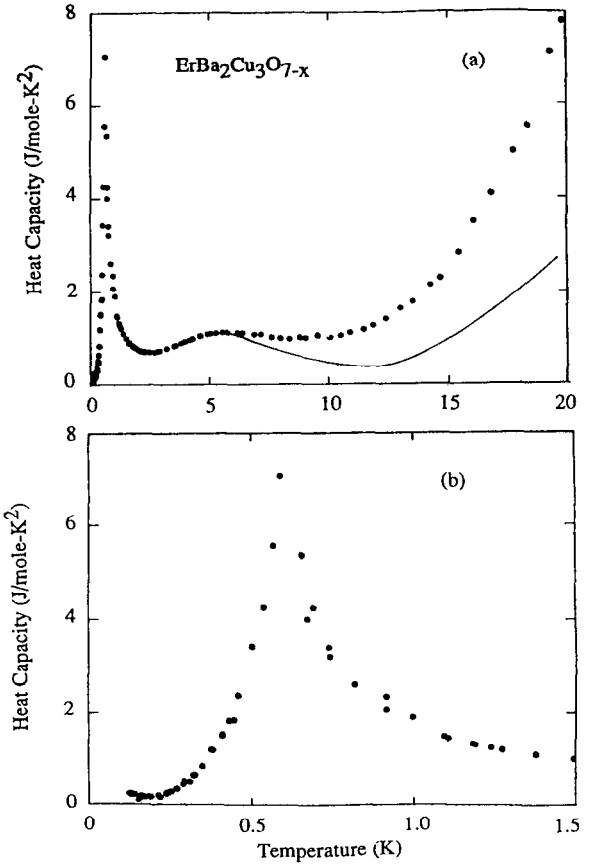

Fig. 6. Heat capacity vs. temperature for $ErBa_2Cu_3O_{7-x}$. The solid line shows the result of subtracting the heat capacity of $YBa_2Cu_3O_{7-x}$.

extremely slowly. This indicates that a number of crystal field levels lie within ≈ 50 K of one another. From the initial rise and the magnitude of the heat capacity at the peak, we estimate that a second singlet state lies approximately 8 K above the ground state.

Heat capacity data for $ErBa_2Cu_3O_{7-x}$ are shown in fig. 6, along with the results of subtracting the heat capacity of $YBa_2Cu_3O_{6.8}$. A magnetic transition is observed at a temperature $T_m = (0.59 \pm 0.02)$ K. Again, a very small upturn is seen at low temperatures, from which we can estimate that the ground state magnetic moment is no more than 50% of the free-ion moment, i.e. $\mu \approx 4.5\mu_B$. The entropy associated with the magnetic peak, integrated to 2.5 K, is 4.6 J/mol K^2, which is $\approx 0.8\ R \ln 2$ and indicates ordering out of a doublet ground state. Above the transition, a weak peak is seen around 5 K whose interpretation is not straightforward. Since the total entropy associated with this feature is no more than 1 J/mol K^2, it can not be associated with a crystal field splitting for which the minimum entropy must be $R \ln 2 = 5.76$ J/mol K^2. In the absence of other information, we associate this with an impurity phase in the material. It also may be noted that the entropy contained in the heat capacity data up to 8 K is exactly $R \ln 2$. This offers the possibility that the 5 K peak represents a broad, incommensurate magnetic transition, followed by an order–order transition at 0.6 K. At higher temperatures, the heat capacity again rises, with a temperature dependence and magnitude that indicates the presence of a second Kramers doublet located at ≈ 90 K above the ground state.

The results described above are collected in table 2. In addition, $GdBa_2Cu_3O_{7-x}$ has been previously reported [3] to become antiferromagnetic at $T_m = 2.24$ K. From the structural data, one sees that the shortest Ho–Ho contacts, 3.82 Å along the *a*-direction and 3.89 Å along the *b*-direction, are considerably longer than the distance found in the metal, indicating that there should be no direct exchange between the Ho atoms. Furthermore, there are no oxygen atoms located in the $x, y, 1/2$ plane, therefore there is no superexchange pathway available for magnetic interactions. In general, the magnetic transition temperatures indicate that exchange interactions mediated through conduction electrons (RKKY interactions) do not provide a good description of the systematics of magnetic interactions. In the $RERh_4B_4$ compounds, where the separation between RE ions is very similar to the present case, the magnetic transition temperatures are roughly an order of magnitude larger [18]. Furthermore, the nature of the crystal field states shows that strong magnetic anisotropy should be present. In the $RERh_4B_4$ compounds this anisotropy resulted, for RKKY interactions, in T_m values which were maxima for Dy rather than for Gd. This variation was shown to have a very general origin [19,20], and so should also be seen in the present case if RKKY interactions were present. For the present compounds, the magnitudes of the T_m values are quite compatible with dipolar interactions. For example, if we take a moment of $\mu = 6\mu_B$ and a rare-earth separation of $r = 3.8$ Å, appropriate to $DyBa_2Cu_3O_{7-x}$, then the dipolar energy is estimated to be $\mu^2/r^3 \approx 0.7$ K. It therefore seems likely that the magnetic interactions in these compounds are completely dominated by dipolar interactions, while RKKY interactions are of much less importance.

Recent experimental data using the ^{155}Gd Mössbauer resonance in $GdBa_2Cu_3O_{7-x}$ have shown that the Gd ion is essentially in an ionic Gd^{3+} state, and hence only very weakly interacting with other electrons in the system [21], implying very weak RKKY interactions. A similar conclusion can be drawn from band-structure calculations [22]. In addition, it is known from other work on magnetic superconductors that superconductivity will depress the RKKY interaction, and will tend to derive the system toward antiferromagnetism [23,24]. Those effects should be very strong here where the superconducting energy gap is large compared to the magnetic interaction energy.

In the present case, it is not known whether the magnetic state is ferromagnetic or antiferromagnetic. The importance of dipolar interactions would generally argue for antiferromagnetism. The absence of reentrant superconductivity, as evidenced by the low temperature resistance data, might also be interpreted in favor of antiferromag-

netism. However, it is conceivable in these materials that ferromagnetism could coexist with superconductivity, either because the magnetic ions are so weakly coupled to the rest of the system, or because the energy gained by forming a magnetic state is small compared to the energy lost in destroying the superconducting state. Neutron diffraction experiments are underway to clarify this question.

In agreement with previous work [2–12], we find that the presence of strongly magnetic ions has virtually no effect on the superconducting transition temperatures. This is again in keeping with weak magnetic interactions, which implies that normal pair-breaking mechanisms will also be very weak. Furthermore, it has been pointed out [25] that dipolar fields on the Cu ions, presumed to be responsible for the superconductivity, will be much smaller than the critical fields of these materials, and so will also have a weak effect on the superconductivity. In general, these materials operate in a far different regime from previous magnetic superconductors. In binary intermetallics, one generally has magnetic interactions which are strong compared to superconducting interactions, and so magnetic effects strongly inhibit superconductivity. Magnetic interactions are comparable to superconducting interactions in most ternary superconductors, such as the $RERh_4B_4$ compounds or the Chevrel phase superconductors, leading to complex behavior where the two types of ordering compete with one another [26]. In the present case, superconductivity dominates the magnetic interactions, so the predominant effects should be those in which magnetism is strongly affected by the superconductivity.

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