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Specific heat near T_N in (Pr, Nd, Sm, Gd, and Dy)$Ba_2Cu_3O_7$: Evidence for spin-exchange-driven ordering

A. P. Ramirez, L. F. Schneemeyer, and J. V. Waszczak
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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Magnetic ordering at 2.2 K has been reported for $GdBa_2Cu_3O_7$. In order to characterize the relevant magnetic interaction we have synthesized and measured the specific heat of polycrystalline $RBa_2Cu_3O_7$, where R = Pr, Nd, Sm, Gd, and Dy. The ordering temperatures are found to vary systematically with the de Gennes factor, suggesting the dominance of spin-spin exchange over dipolar energies for these compounds. The field dependence of the specific-heat peak for $DyBa_2Cu_3O_7$ implies the order is of antiferromagnetic nature.

One of the interesting aspects of the high-T_c superconducting compound $GdBa_2Cu_3O_7$ is that magnetic ordering occurs around 2 K, and is seemingly independent of the superconducting electrons, as first demonstrated by Willis *et al.*[1] The coexistence of superconductivity and magnetic order in this compound is intriguing because of the special conditions usually required to support both types of order. In addition, there is also the possibility that this compound, and the other rare-earth analogues, will provide, due to their extreme crystalline anisotropy, a new set of model systems in which to study two-dimensional magnetism. It is essential, therefore, to understand the nature of the interaction responsible for the ordering, as well as the spin configuration of the ordered state.

We have synthesized the compounds $RBa_2Cu_3O_7$, where R = Pr, Nd, Sm, Gd, and Dy, and measured their specific heat in order to establish a systematic trend between the ordering temperature and the magnitude of the local R^{3+} moments involved. Similar to the Gd compound, the Sm and Dy compounds order at 0.60 and 0.92 K, respectively, but with the entropy expected for a Kramers doublet. The Nd compound exhibits ordering-precursor behavior down to 0.5 K, and exhibits a broad crystal-field anomaly in the neighborhood of 1 K. No evidence for electronic order is found for the Pr compound. Above 0.6 K, T_N in these compounds scales linearly with the de Gennes factor $(g_j-1)^2J(J+1)$, where g_J and J are the Landé g factor and total moment, respectively. This implies that the ordering in this temperature range is dominated by a spin-spin exchange interaction. The ordering peak in $DyBa_2Cu_3O_7$ decreases with increasing field, the behavior expected for an antiferromagnet.

Specific-heat measurements were performed in a top-loading ^{3}He cryostat, using the semiadiabatic heat-pulse method. The calorimeter consisted of a 0.254×6.35 ×6.35 mm sapphire plate, onto which a small piece of the interior of a Speer resistor, along with a 350 Ω strain gauge were epoxied, for use as a thermometer and heater, respectively. The samples, which were typically ~20 mg, were affixed along a smooth, flat surface with < 1 mg of silicone vacuum grease. The addendum contribution to the heat capacity was measured separately and is negligible (< 1%) in the region of interest.

The samples used in the present study were prepared by standard ceramics procedures as described in Ref. 2. Powder x-ray diffraction revealed no crystalline impurity traces > 5%. The samples (with the exception of $PrBa_2Cu_3O_7$) were further characterized by ac susceptibility and resistance measurements and exhibited superconducting transitions less than 2 K wide. Room-temperature resistivities were in the range $\rho < 10$ mΩ cm.

In Fig. 1 we show the specific heat for four of the compounds. The ordering temperatures for the Sm, Dy, and Gd compounds are 0.60, 0.92, and 2.2 K, respectively. Although $NdBa_2Cu_3O_7$ does not exhibit ordering in the present temperature range ($T > 0.5$ K), the upswing in C below 0.7 K is possibly an indication of a lower-temperature phase transition. The broad hump in the Nd curve has an integrated entropy of nearly $R\ln2$ and corresponds to a crystal-field doublet centered at around 4 K. Such a level most likely results from splitting of the Γ_8 quartet[3] of $J=\frac{7}{2}$ due to the monoclinic distortion of the ligand field at the rare-earth site. Data on the Pr compound lie off the scale of Fig. 1 and they form a relatively featureless line yielding a low temperature $\gamma \sim 200$ mJ/mol K^2. A small upturn observed below 0.8 K might be interpreted as the onset of electronic magnetic order-

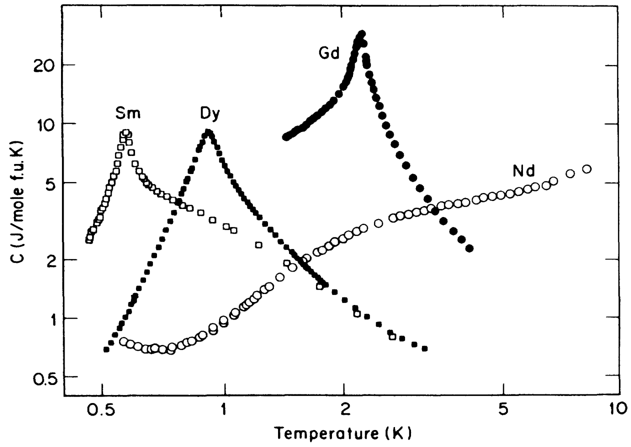

FIG. 1. Specific heat of $RBa_2Cu_3O_7$, for R = Nd, Sm, Dy, and Gd.

ing, but is more likely the result of nuclear ordering.

In Fig. 2 we show the specific heat of $SmBa_2Cu_3O_7$ from 0.5 to 3 K on a smaller scale than that of Fig. 1. The sharp peak at 0.60 K is interpreted as the development of (two-dimensional) long-range magnetic order among the Sm^{3+} ions since the entropy, shown in the inset, is tending towards the value $R\ln 2$ expected for degeneracy lifting in a system of Kramers doublets. In Fig. 3 we show the $DyBa_2Cu_3O_7$ data, which display qualitatively similar ordering at 0.92 K. The behavior for these two ions is in contrast to the Gd compound which develops an entropy of $R\ln 8$ corresponding to the full spin degeneracy, $2S+1=8$, of trivalent Gd.

In Fig. 4 we show the effect of applied magnetic fields greater than H_{c1} on the ordering behavior of $DyBa_2Cu_3O_7$. The ordering peak moves to lower temperatures as the field is increased, the usual behavior of antiferromagnets. The broadening of the peak is interpreted as resulting from the random orientation of the individual crystallites. The data in Fig. 3 were obtained after cooling the sample from $T_c \sim 90$ K in zero applied field, and in order of increasing field. In fact, upon lowering the applied field, hysteretic behavior corresponding to flux trapping was observed. Therefore, the phase diagram shown in the inset of Fig. 3 is a function of the penetration depth of the crystallites as well as the interactions between the magnetic moments.

The two types of interaction usually responsible for local moment ordering at low temperatures are the dipole-dipole interaction and the spin exchange mechanism. One can estimate the relative strength of the former interaction by comparing the ordering temperature to the binding energy of a moment interacting with its nearest neighbors via its dipole field. Although these two energy scales are approximately equal for each of the Gd and Dy compounds, for the Sm compound one calculates a dipole energy $4(g_J\mu_B J)^2/a^3 \sim 0.023$ K, much smaller than the ordering temperature of 0.6 K. This result illustrates the need to consider an exchange mechanism. Further evidence for the dominance of a spin exchange energy comes from the linear dependence of T_N on the de Gennes factor $(g_{J-1})^2 J(J+1)$ as shown in Fig. 5. This is the expected behavior of T_N for a system whose Hamiltonian consists only of an $S\cdot S$ exchange term, assuming the coupling parameter remains constant as J is varied, and that $S \propto (g_J-1)J$. In the present study, however, we consider ordering of the effective spins $S_{\rm eff}$ corresponding to a crystal-field multiplet. While it is not obvious that $S_{\rm eff} \propto (g_J-1)J$, the observed correlation can be interpreted as empirical evidence for the validity of this relation. For the sake of comparison we also plot the variation of T_N with $(g_J J)^2$, the scaling form for dipole-dipole energies (assuming equivalent moment configurations). This illustrates the lack of systematic behavior for a coupling of this form.

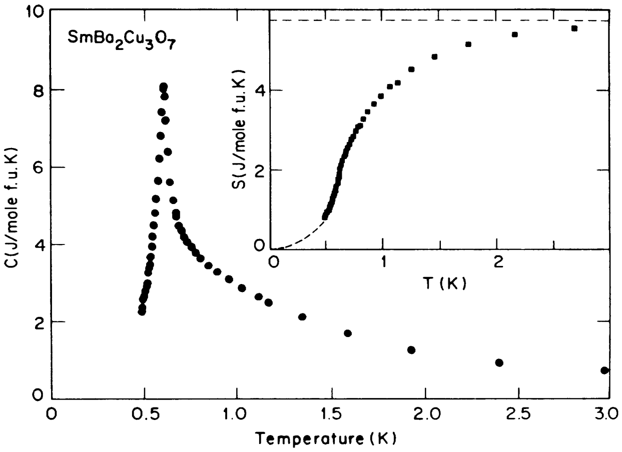

FIG. 2. Specific heat of $SmBa_2Cu_3O_7$. C is extrapolated to $T=0$ using a T^3 law appropriate for antiferromagnetic magnons. The entropy is shown in the inset, where the horizontal dashed line corresponds to $R\ln 2$.

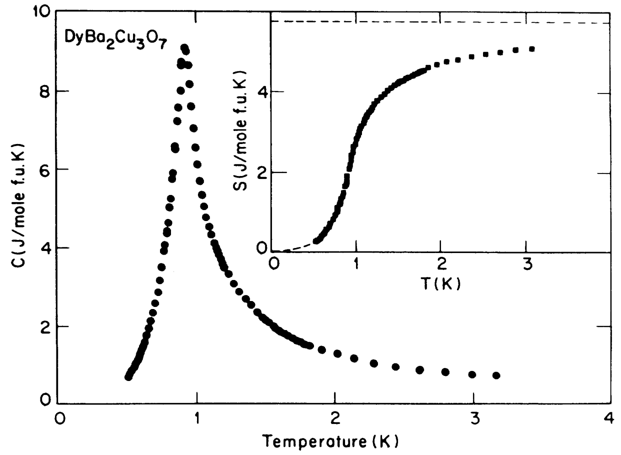

FIG. 3. Specific heat of $DyBa_2Cu_3O_7$. C is extrapolated to $T=0$ using a T^3 law appropriate for antiferromagnetic magnons. The entropy is shown in the inset, where the horizontal dashed line corresponds to $R\ln 2$.

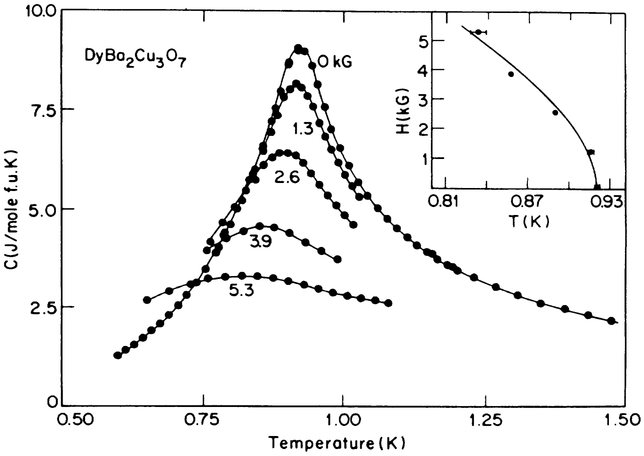

FIG. 4. Specific heat in a field for $DyBa_2Cu_3O_7$. The inset shows the peak temperatures as a function of field.

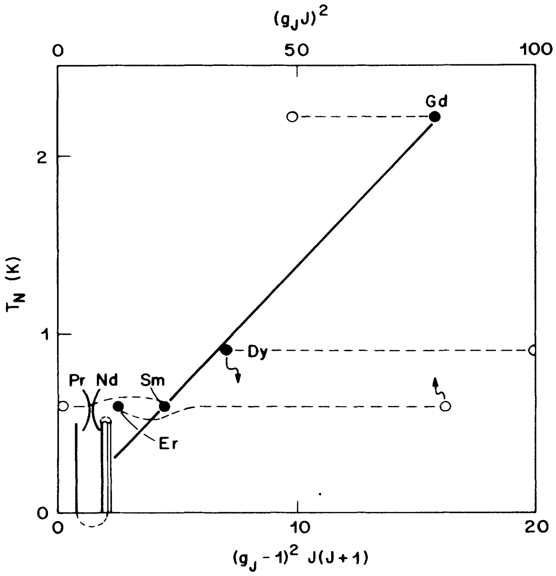

FIG. 5. Ordering temperatures for the compounds described in the text. Solid circles or bars refer to lower horizontal scale, and open circles or bars refer to the upper scale. Open and closed icons for the same compound are connected by dashed lines. Data for the Er compound is from Ref. 7.

Various alloys of rare earth and yttrium also obey the scaling of Curie temperature with $(g_J - 1)^2 J(J+1)$.[4,5] For these, and other rare-earth metals, the exchange interaction is believed to be of the indirect, Ruderman-Kittel-Kasuya-Yosida (RKKY) type.[6] Although the monotonic behavior shown in Fig. 5 seems to indicate that such an exchange mechanism is operative, it is not possible, on the basis of the present data, to rule out a constrained-orbital superexchange interaction. If, however, an itinerant mechanism is the correct interpretation for the present compounds, then it offers an explanation for a second ordering anomaly seen both in specific-heat measurements on $GdBa_2Cu_3O_7$ (Ref. 7) and in ultrasonic sound velocity[8] and thermal relaxation measurements[9] on the Sm compound. For RKKY systems, multiple transitions frequently occur due to a reorientation of the spins into a helical state resulting from the long-range oscillatory nature of the interaction.[10] On the other hand, the development of three-dimensional correlations cannot be ruled out for explaining these phenomena.

Finally we comment on the behavior of the other members of the substitution series. To our knowledge, the specific heat has been measured elsewhere only for Ho (Ref. 11) and Er (Refs. 7,11), as well as the Gd (Ref. 1) and Dy (Refs. 7,11) compounds studied in the present work. For the non-Kramers Ho a nuclear ordering peak is observed at 0.17 K, and for the Kramers ion Er an ordering peak at 0.59 K with $R \ln 2$ entropy is found. The absence of purely electronic ordering in Ho can be taken as an indication of a ground-state singlet. The transition temperature for Er places it above the line drawn in Fig. 5. However, differences in lattice parameters (interaction strengths) and especially the influence of the dipole-dipole energy for the large-$(g_J J)$ Er ion might explain the discrepancy. Thus with the exception of the Tb compound, which we have not been able to isolate in single-phase form, and Pm, which is intensely radioactive, the rare earths $4f^n$ for $n = 2$ through 11 have been scanned (Eu^{3+} has no moment). The observation that the low-lying magnetic states in all of these materials are either Kramers doublets or crystal-field singlets leads to the question of whether or not this is a general result of the monoclinic symmetry of the crystal field. More work is needed to determine the effective g factors, the range of the interactions both within and between planes, and the spin configurations in the ordered state.

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