SPECIFIC HEAT AND ANISOTROPIC MAGNETIC SUSCEPTIBILITY OF Pr$_2$CuO$_4$, Nd$_2$CuO$_4$ AND Sm$_2$CuO$_4$ CRYSTALS

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Specific heat and magnetic susceptibility measurements on single crystals of RE$_2$CuO$_4$ (RE = Pr, Nd, and Sm) indicate antiferromagnetic order at $T_N < 1.5$ K and 5.95 K for RE = Nd and Sm, respectively. The susceptibility of all RE$_2$CuO$_4$ compounds is highly anisotropic and suggests the presence of crystal field effects.

The CuO$_2$-layered compound La$_2$CuO$_{4+\delta}$ has been a focus of investigation since the discovery that hole-doping by substituting divalent atoms for La [1] or by adding superstoichiometric amounts of oxygen ($\delta > 0$) [2] induces superconductivity with $T_c \sim 40$ K. A structurally similar set of compounds RE$_2$CuO$_4$ also exists for RE = Pr, Nd, Sm, Eu and Gd [3]. A significant structural difference between La$_2$CuO$_4$ and the RE$_2$CuO$_4$ compounds is that Cu atoms are octahedrally coordinated by oxygens in La$_2$CuO$_4$, but in the RE$_2$CuO$_4$ materials, the coordination is square planar [4]. Electronically these two classes of CuO$_2$-layer compounds also differ; Hall coefficient and thermoelectric power measurements on La$_2$CuO$_{4+\delta}$ suggest conduction by hole-like carriers, whereas, in RE$_2$CuO$_4$ the sign difference and magnitude of these effects imply a very small number of electron-like carriers [5]. Recently, Tokura et al. [6] have found that substituting Ce into RE$_{2-x}$Ce$_x$CuO$_4$, where RE = Pr, Nd and Sm, induces electron superconductivity with $T_c \sim 20$ K in these compounds which retain the I4/mmm structure of RE$_2$CuO$_4$ [7]. Therefore, as in the case of La$_2$CuO$_{4+\delta}$, it appears prudent to establish a basic knowledge of the pristine RE$_2$CuO$_4$ materials out of which superconductivity appears upon electron doping.

Some work on the RE$_2$CuO$_4$ compounds has been reported, although most of it has been on sintered compacts [8] from which it is not possible to determine the extent of anisotropic behaviour expected on the basis of strongly two-dimensional nature of the crystal structure. Notable exceptions are studies on single crystal of Eu$_2$CuO$_4$ [9] and Gd$_2$CuO$_4$ [10], which indeed show highly anisotropic magnetic behaviour. Here we report the low-temperature specific heat and anisotropic magnetic susceptibility of Pr$_2$CuO$_4$, Nd$_2$CuO$_4$ and Sm$_2$CuO$_4$ single crystals.

RE$_2$CuO$_4$ crystals were grown from PbO- and CuO-based fluxes. X-ray analysis at room temperature found the I4/mmm crystal structure and that the tetragonal c-axis was perpendicular to the faces of these plate-like crystals. The lead content, if any, was less than 1% of the copper content, as determined by electron microprobe. Specific heat $C$ was measured from 1.6 to $\sim 30$ K in a small-mass calorimeter described in detail elsewhere [11]. These experiments were performed on either a single crystal or at most two crystals, having a total mass of between 10 and 40 mg. Magnetic susceptibility $\chi$ was measured with a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer, with the applied magnetic field parallel $\chi_l$ and perpendicular $\chi_\perp$ to the CuO$_2$ layers.

Figure 1 shows the magnetic susceptibility of Pr$_2$CuO$_4$ determined for orthogonal directions of ap-
plied field. No evidence for magnetic order of either Pr or Cu moments could be detected in these data. A plot of $1/\chi_\parallel$ versus temperature gives Curie-Weiss behaviour above $\sim 100$ K, from which we estimate an effective moment $\mu_{\text{eff}} = (3.68 \pm 0.05)\mu_B/\text{Pr}$ and a paramagnetic Curie temperature $\theta_{\text{p}} = -61 \pm 1$ K. This value of $\mu_{\text{eff}}$ is slightly larger than the Hund's rule value $3.58\mu_B/\text{Pr}^3$ and could indicate some contribution from Cu$^{2+}$. Below 100 K, however, $\chi_\parallel$ has a much weaker temperature dependence than Curie-Weiss, suggesting the possibility of a singlet ground state. This, together with the distinctly non-Curie-Weiss temperature dependence of $\chi_\perp$ (except at the lowest temperatures), may be taken as evidence for the importance of crystalline electric fields in this material. Preliminary inelastic neutron scattering experiments on powder samples [12] support this suggestion. Parenthetically, we note that susceptibility measurements on crystals of Pr$_{1.5}$Ce$_{0.5}$CuO$_4$ (nominal composition) show virtually identical temperature dependences and anisotropies as Pr$_2$CuO$_4$ and an effective moment $\mu_{\text{eff}} = (3.73 \pm 0.05)\mu_B/\text{Pr}$, indicating that Ce enters the structure as Ce$^{3+}$ where $\nu \leq 4$.

The low-temperature specific heat of Pr$_2$CuO$_4$ is displayed in fig. 2 as a plot of $C/T$ vs $T^2$. Above 4.5 K, the data follow $C = \gamma T + \beta T^3$, with $\gamma = 1.3 \pm 0.1$ mJ/mol-Pr K$^2$ and $\beta = 0.29 \pm 0.01$ mJ/mol-Pr K$^4$. From the $T^3$ coefficient, we calculate a Debye temperature $\theta_D = 361 \pm 5$ K. Below 4.5 K, $C/T$ gradually increases but shows no peak above 1.6 K. The low-temperature rise can be fit by a Schottky contribution of the form $\alpha/T^2$, with $\alpha = 21$ mJK/mol. Including this term results in a reduction by $\sim 50\%$ of the estimate for $\gamma$. The value for $\alpha$ is in excellent agreement with that found in elemental Pr [13] in which the Schottky term arises from nuclear hyperfine splitting.

Relative to Pr$_2$CuO$_4$, the susceptibility of Nd$_2$CuO$_4$ is isotropic, at least above $\sim 120$ K (fig. 3). Below this temperature $\chi_\parallel$ and $\chi_\perp$ show different temperature dependencies, with $\chi_\parallel$ increasing more rapidly than $\chi_\perp$ for decreasing temperature. The behaviour shown in fig. 3 implicates crystal field effects as found in Pr$_2$CuO$_4$. Plots of $1/\chi_\perp$ and $1/\chi_\parallel$ versus temperature give $\mu_{\text{eff}} = \mu_{\text{eff}} = (3.56 \pm 0.05)\mu_B/\text{Nd}$ and
θ_p = -62 ± 1 K. Within experimental error, these values of μ_eff correspond to Hund's rules for a 4f^3 configuration. Therefore, the crystal field splitting is expected to be small.

Although there is no clear evidence for magnetic order in susceptibility above 2 K, an antiferromagnetic transition near 1 K might be expected in analogy to NdBa_2Cu_3O_x which orders at 0.52 K [14]. Indirect support comes from specific heat measurements above 1.6 K shown in fig. 4. For T ≥ 16 K, C/T is linear in T^2 and we deduce γ = 0 ± 10 mJ/mol·K and β = 0.42 ± 0.02 mJ/mol·K^4 (θ_D = 319 ± 5 K). However, at lower temperatures C/T increases markedly with a temperature dependence that cannot be fit to an α/T^2 Schottky form, suggesting an imminent magnetic transition. If we assume that T_N is just below 1.6 K, an estimate of the magnetic entropy gives ~0.8R ln 2. This highly suggestive result allows us to constrain T_N to be greater than 1 K but less than 1.6 K, assuming a crystal field doublet ground state. The heat capacity of oxygen deficient Nd_2CuO_4 powder does exhibit a peak near 1.56 K [15].

Unequivocal evidence for antiferromagnetic order at T_N = 5.95 K is found in susceptibility (fig. 5) and specific heat measurements (fig. 6) on Sm_2CuO_4. The sharp drop in χ and weak temperature dependence of χ⊥ below T_N suggest a mean-field-like ordering of Sm moments parallel to the c-axis. The entropy associated with the magnetic transition is 0.97 R ln 2; consistent with a doublet ground state. In the range 15 K ≤ T ≤ 25 K, C = γT + βT^3, giving γ ≈ 82 mJ/mol·Sm·K and β = 353 ± 5 K. This value of γ is much larger than found in other RE_2CuO_4's [10] (γ of Eu_2CuO_4 is 0 ± 1 mJ/mol·K^2) except for Gd_2CuO_4. In Gd_2CuO_4, magnetic correlations appear to exist well above T_N = 6.5 K, thereby making an estimate of γ uncertain. Possibly, similar effects could be present in Sm_2CuO_4, although we point out that the magnetic transition in Sm_2CuO_4 is very sharp.
Fig. 3. Magnetic susceptibility $\chi$ versus temperature for $\text{Nd}_2\text{CuO}_4$ crystals with an applied field of 0.5 T directed parallel ($\chi_\parallel$) and perpendicular ($\chi_\perp$) to the tetragonal $a$-$b$ plane. The inset shows $1/\chi_\parallel$ and $1/\chi_\perp$ as a function of $T$.

Fig. 4. Specific heat divided by temperature versus $T^2$ for a $\text{Nd}_2\text{CuO}_4$ crystal. The low temperature rise in $C/T$ shown in the inset (note vertical scale change) suggests the approach to a magnetic transition.
and that nearly $R \ln 2$ is recovered by 6 K. In this regard, an extrapolation of the low-temperature ($T<4$ K) $C/T$ data to $T=0$ gives $\gamma=0 \pm 10$ mJ/mol Sm K$^2$. Finally, we note a broad minimum in $\chi_\perp$ near 200 K that is expected as low lying $J$ multiplets become thermally populated, which is seen frequently in Sm compounds [16].

Table I compares Néel temperatures of RE$_2$CuO$_4$ with those of REBa$_2$Cu$_3$O$_7$ [14,17,18]. In all cases analysis of the entropy associated with magnetic order indicate that the ground state degeneracy is the same in these two classes of compounds. In spite of the relatively simple ordered magnetic structures found in REBa$_2$Cu$_3$O$_7$ compounds [19,20], the coupling mechanism responsible for $T_N$ is debated. Dunlap et al. [21] have argued, at least for the heavy rare earths (Dy, Ho and Er) in 1-2-3-7 materials, that neither RKKY nor superexchange can account for their observations but that the low Néel temperatures in these systems are due to dipolar interactions. On the other hand, Ramirez et al. [17] found that $T_N$ in REBa$_2$Cu$_3$O$_7$ materials scales approximately linearly with the (Hund's rule) de Gennes factor $(g_J-1)^2J(J+1)$, implying that the dominant interaction is spin–spin exchange. If the latter suggestions were valid for the RE$_2$CuO$_4$'s, we would expect the ratio $T_{N1237}/T_{N14}$ to be constant, which is approximately true for Nd and Gd (table I). If dipole interactions were most important, this same ratio should scale as $[r_{14}/r_{1237}]^3$, where $r$ is the nearest RE–RE distance, but it does not. Further, the Néel temperature of Sm$_2$CuO$_4$ and Gd$_2$CuO$_4$ are much too high to be due to dipolar interactions. The crystal structure of the RE$_2$CuO$_4$ compounds lends itself to the distinct possibility of superexchange, which we suggest may produce antiferromagnetic order in these samples. However, if this be the case, it is curious why Gd moments in Gd$_2$CuO$_4$ order in the $a$–$b$ plane [10]; but in Sm$_2$CuO$_4$, Sm moments order parallel to the $c$-axis. A possible explanation is that Cu moment ordering and a weak crystallographic distortion found in Gd$_2$CuO$_4$ [10] modifies the spin orientation preferred by superexchange. Further, single site anisotropy may plan an important role in
specific heat and susceptibility of RE$_2$CuO$_4$ crystals

Fig. 6. Specific heat divided by temperature versus $T^2$ for Sm$_2$CuO$_4$. Note the vertical scale change on the inset which shows a specific heat anomaly at $T_N = 5.95$ K due to antiferromagnetic order of Sm.

determining the RE-ordering vector. In this regard, knowledge of the ordering direction of Nd, with almost no quadrupole moment, in Nd$_2$CuO$_4$ would be useful.

Finally, it is interesting that, unlike REBa$_2$Cu$_3$O$_7$ materials in which hole doping to produce superconductivity has no effect on the RE magnetism, it appears that electron doping Nd$_{2-x}$Ce$_x$CuO$_4$ weakly depresses the Néel temperature [15]. These differing behaviors most likely are related to the facts that hole doping 1-2-3 compounds is accomplished by filling vacant oxygen sites, whereas electron doping 2-1-4 material is achieved at the expense of periodicity in the RE sublattice. If it were not for disorder on the RE sites, there probably would be no effect on $T_N$, though certainly the possibility of an interaction between RE magnetism and electron superconductivity in RE$_{2-x}$Ce$_x$CuO$_4$ needs to be investigated.

Table I
Néel temperatures of RE$_2$CuO$_4$ and REBa$_2$Cu$_3$O$_7$

<table>
<thead>
<tr>
<th>RE</th>
<th>RE$_2$CuO$_4$</th>
<th>REBa$_2$Cu$_3$O$_7$</th>
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</thead>
<tbody>
<tr>
<td>Pr</td>
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<td>-</td>
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<tr>
<td>Nd</td>
<td>$1 &lt; T_N &lt; 1.6$ K</td>
<td>0.52 K (c)</td>
</tr>
<tr>
<td>Sm</td>
<td>5.95 K</td>
<td>0.6 K (d)</td>
</tr>
<tr>
<td>Eu</td>
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<td>$J=0$ (e)</td>
</tr>
<tr>
<td>Gd</td>
<td>6.5 K (b)</td>
<td>2.24 K (e)</td>
</tr>
</tbody>
</table>

(a) Ref. [9]; (b) Ref. [10]; (c) Ref. [17]; (d) Ref. [14]; (e) Ref. [18].

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References


