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SPECIFIC HEAT AND ANISOTROPIC MAGNETIC SUSCEPTIBILITY OF Pr_2CuO_4, Nd_2CuO_4 AND Sm_2CuO_4 CRYSTALS

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Specific heat and magnetic susceptibility measurements on single crystals of RE_2CuO_4 (RE=Pr, Nd, and Sm) indicate antiferromagnetic order at $T_N \lesssim 1.5$ K and 5.95 K for RE=Nd and Sm, respectively. The susceptibility of all RE_2CuO_4 compounds is highly anisotropic and suggests the presence of crystal field effects.

The CuO_2-layered compound $La_2CuO_{4+\delta}$ 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_2CUO_4 also exists for RE=Pr, Nd, Sm, Eu and Gd [3]. A significant structural difference between La_2CuO_4 and the RE_2CuO_4 compounds is that Cu atoms are octahedrally coordinated by oxygens in La_2CuO_4, but in the RE_2CuO_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 $La_2CuO_{4+\delta}$ suggest conduction by hole-like carriers, whereas, in RE_2CuO_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 $RE_{2-x}Ce_xCuO_4$, 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_2CuO_4 [7]. therefore, as in the case of $La_2CuO_{4+\delta}$, it appears prudent to establish a basic knowledge of the pristine RE_2CuO_4 materials out of which superconductivity appears upon electron doping.

Some work on the RE_2CuO_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_2CuO_4 [9] and Gd_2CuO_4 [10], which indeed show highly anisotropic magnetic behaviour. Here we report the low-temperature specific heat and anisotropic magnetic susceptibility of Pr_2CuO_4, Nd_2CuO_4 and Sm_2CuO_4 single crystals.

RE_2CuO_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 ~ 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 χ was measured with a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer, with the applied magnetic field parallel $\chi_\parallel$ and perpendicular $\chi_\perp$ to the CuO_2 layers.

Figure 1 shows the magnetic susceptibility of Pr_2CuO_4 determined for orthogonal directions of ap-
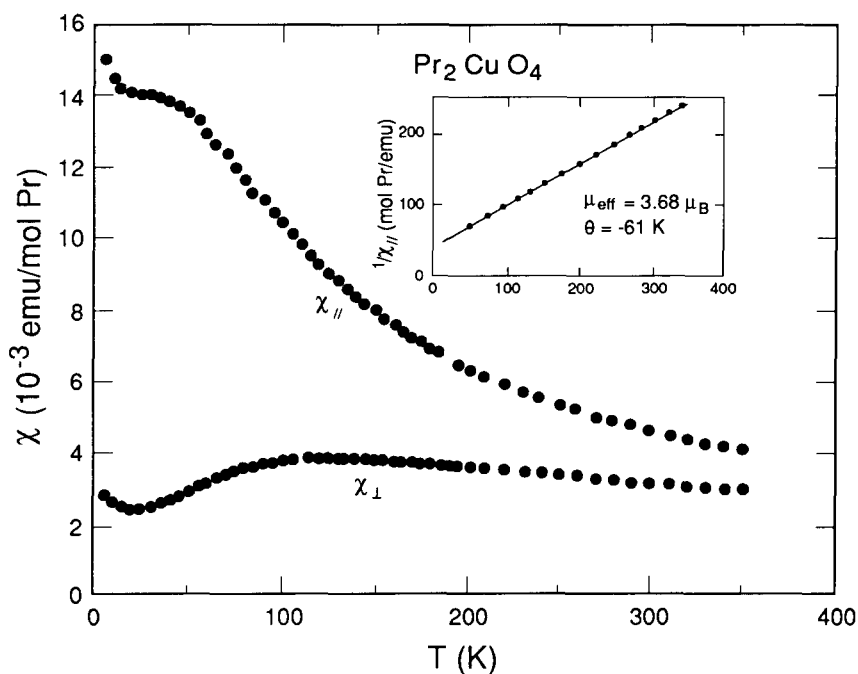
Fig. 1. Magnetic susceptibility χ of Pr$_2$CuO$_4$ as a function of temperature. Measurements were made with a 0.5 T field applied parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to the CuO$_2$ planes. The inset shows $1/\chi_{\parallel}$ vs temperature.

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 ~ 100 K, from which we estimate an effective moment $\mu_{\text{eff}\parallel} = (3.68 \pm 0.05)\mu_{\text{B}}/\text{Pr}$ and a paramagnetic Curie temperature $\theta_{\text{p}\parallel} = -61 \pm 1$ K. This value of $\mu_{\text{eff}\parallel}$ is slightly larger than the Hund's rule value $3.58\mu_{\text{B}}/\text{Pr}^{3+}$ 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$_{1.9}$Ce$_{0.1}$CuO$_4$ (nominal composition) show virtually identical temperature dependences and anisotropies as Pr$_2$CuO$_4$ and an effective moment $\mu_{\text{eff}\parallel} = (3.73 \pm 0.05)\mu_{\text{B}}/\text{Pr}$, indicating that Ce enters

the structure as Ce$^{+\nu}$ where $\nu \lesssim 4$.

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 $\theta_{\text{D}} = 361 \pm 5$ 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 α/T^2, with $\alpha = 21$ mJK/mol. Including this term results in a reduction by $\sim 50\%$ of the estimate for γ. The value for α 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 ~ 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 $\mu_{\text{eff}\parallel} = \mu_{\text{eff}\perp} = (3.56 \pm 0.05)\mu_{\text{B}}/\text{Nd}$ and
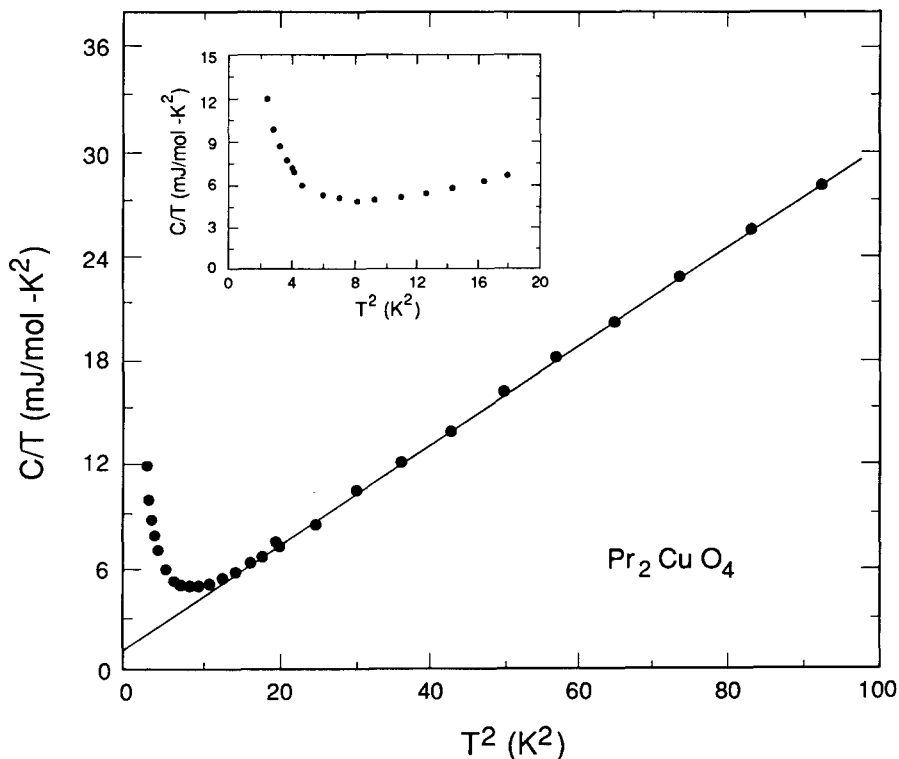
Fig. 2. Specific heat C divided by temperature T versus T^2 for Pr_2CuO_4. The inset shows an expanded view of the low temperature upturn in C/T that has the functional form α/T^2.

$\theta_p = -62 \pm 1$ 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 $T \geqslant 16$ K, C/T is linear in T^2 and we deduce $\gamma = 0 \pm 10$ mJ/mol-Nd K² and $\beta = 0.42 \pm 0.02$ mJ/mol K⁴ ($\theta_D = 319 \pm 5$ 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 $\sim 0.8R \ln 2$. 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].

Unequivical 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 $\chi_\perp$ and weak temperature dependence of $\chi_\parallel$ 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 $\leqslant T \leqslant 25$ K, $C = \gamma T + \beta T^3$, giving $\gamma \simeq 82$ mJ/mol Sm K² and $\theta_D = 353 \pm 5$ 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 K²) 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
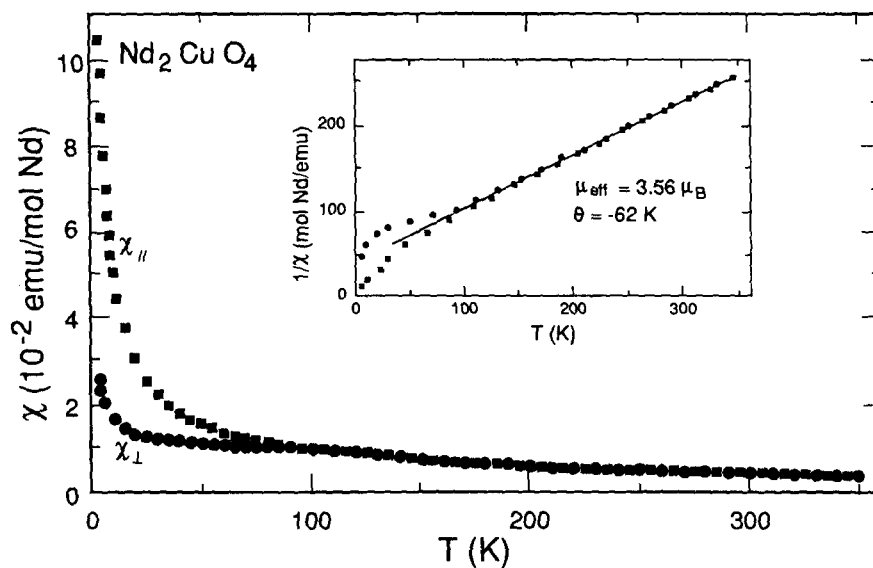
Fig. 3. Magnetic susceptibility χ versus temperature for Nd_2CuO_4 crystals with an applied field of 0.5 T directed parallel ($\chi_\parallel$) and perpendicular ($\chi_\perp$) to the tetragonal a–b plane. The inset shows $1/\chi_\parallel$ and $1/\chi_\perp$ as a function of T.
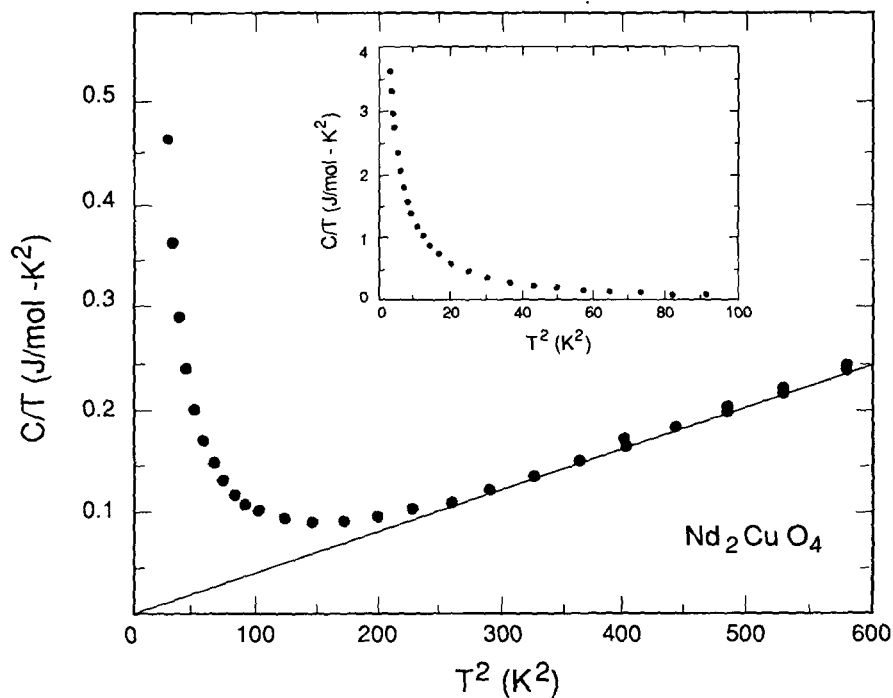

Fig. 4. Specific heat divided by temperature versus T^2 for a Nd_2CuO_4 crystal. The low temperature rise in C/T shown in the inset (note vertical scale change) suggests the approach to a magnetic transition.
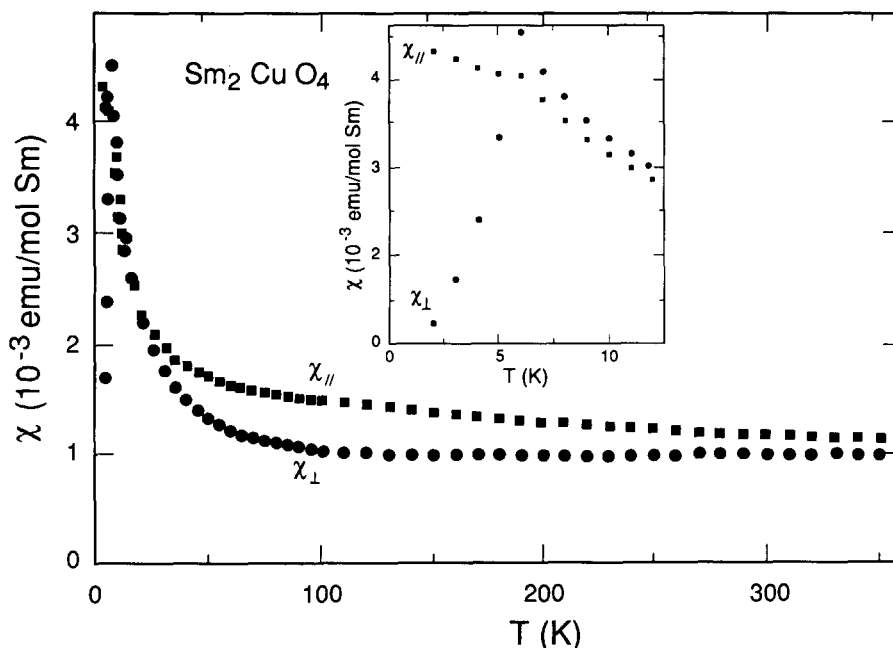
Fig. 5. Susceptibility versus temperature for Sm_2CuO_4 crystals subjected to 0.5 T field applied parallel $(\chi_\parallel)$ and perpendicular $(\chi_\perp)$ to the CuO_2 planes. The inset suggests a mean-field like antiferromagnetic transition near 6 K, with the Sm moments lying along the tetragonal c-axis.

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_2CuO_4 with those of $REBa_2Cu_3O_7$ [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 $REBa_2Cu_3O_7$ 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 $REBa_2Cu_3O_7$ materials scales approximately

linearly with the (Hund's rule) de Gennes factor $(g_J - 1)^2 J(J + 1)$, implying that the dominant interaction is spin–spin exchange. If the latter suggestions were valid for the RE_2CuO_4's, we would expect the ratio T_N^{1237}/T_N^{214} 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 $[r^{214}/r^{1237}]^3$, where r is the nearest RE–RE distance, but it does not. Further, the Néel temperature of Sm_2CuO_4 and Gd_2CuO_4 are much too high to be due to dipolar interactions. The crystal structure of the RE_2CuO_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_2CuO_4 order in the a–b plane [10]; but in Sm_2CuO_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_2CuO_4 [10] modifies the spin orientation preferred by superexchange. Further, single site anisotropy may plan an important role in
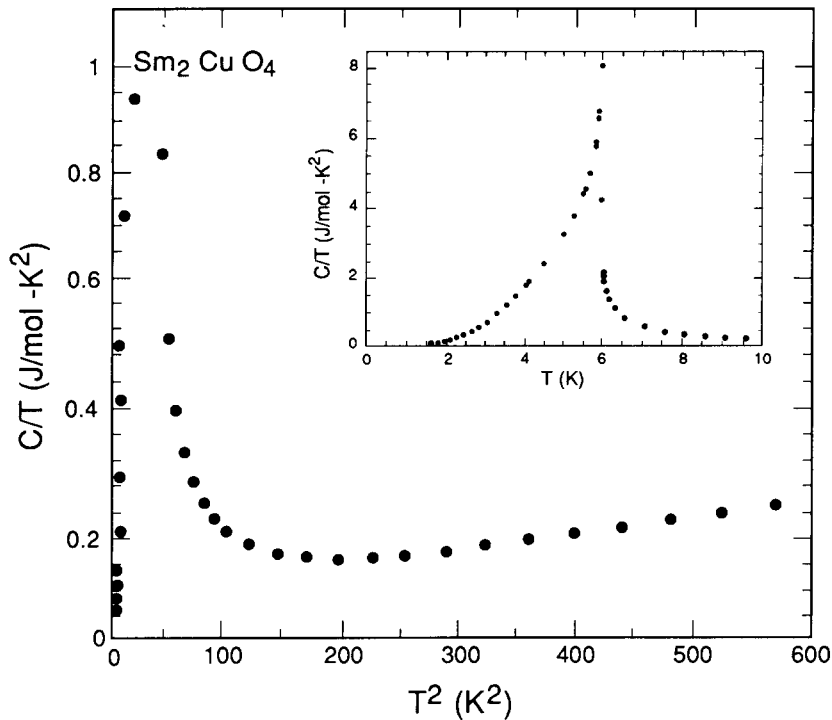
Fig. 6. Specific heat divided by temperature versus T^2 for Sm_2CuO_4. Note the vertical scale change on the inset which shows a specific heat anomaly at $T_N = 5.95$ K due to antiferromagnetic order of Sm.

determining the RE-ordering vector. In this regard, knowledge of the ordering direction of Nd, with almost no quadrupole moment, in Nd_2CuO_4 would be useful.

Finally, it is interesting that, unlike $REBa_2Cu_3O_7$ materials in which hole doping to produce superconductivity has no effect on the RE magnetism, it appears that electron doping $Nd_{2-x}Ce_xCuO_4$ weakly depresses the Néel temperature [15]. These differ-

ing 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 $RE_{2-x}Ce_xCuO_4$ needs to be investigated.

Acknowledgements

Table I
Néel temperatures of RE_2CuO_4 and $REBa_2Cu_3O_7$

RE	RE_2CuO_4	$REBa_2Cu_3O_7$
Pr	–	–
Nd	$1 K < T_N < 1.6$ K	0.52 K (c)
Sm	5.95 K	0.6 K (d)
Eu	$J=0$ (a)	$J=0$ (e)
Gd	6.5 K (b)	2.24 K (e)

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

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