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Superconductivity at 28 K in a cuprate with a niobium oxide intermediary layer

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A new copper oxide based superconductor is reported based on the ordered interleaving of NbO₆ or TaO₆ octahedra between the apices of copper oxide pyramids. Good bulk superconductivity is observed for only a narrow range of temperatures, annealing times and cooling rates. The relatively low T_c of the prototype compound Sr₂Nd_{1.5}Ce_{0.5}NbCu₂O_{10-δ} may be due to the presence of the insulating NbO₆ layers or the wide (Nd, Ce)₂O₂ layers which separate the CuO₂ planes.

The family of copper oxide superconductors is broadly based on the structural interleaving of CuO₂ planes with a variety of metal–oxygen layers. These layers act as separators, in effect defining the CuO₂ planes, and also often as charge reservoirs to control the hole or electron concentration. In the past two years the discovery of new cuprate superconductors has become more difficult, as simple combinations of elements and standard processing techniques have become exhausted in the search. Complex chemistry, high oxygen pressures or high hydrostatic pressures have been employed recently to discover new materials [1–7]. Here we report the discovery of bulk superconductivity at 28 K in Sr₂Nd_{1.5}Ce_{0.5}NbCu₂O_{10-δ} (and the Ta analog), a previously reported compound [8,9] with a single Nb(Ta)O₆ octahedral layer between the apices of pyramidal (CuO₅)_∞ planes. The bases of the pyramids are separated by a fluorite layer (fig. 1). The Nb(Ta)O₆ octahedral layer is a new kind of intermediary layer for high- T_c copper oxides, and the Nb and Ta charges of +5 are the highest yet on cations to be accommodated in such a layer. The (Nb, Ta–O) octahedral layers join (Tl–O) and (Pb, Cu–O) octahedral layers, (PbO–Cu–PbO) and (Bi–O) distorted pyramids, Cu–O sticks and chains, and possibly GaO₄ tetrahedra [6,7], as building blocks for new materials. The octahedra in the new layer share corners, not edges as

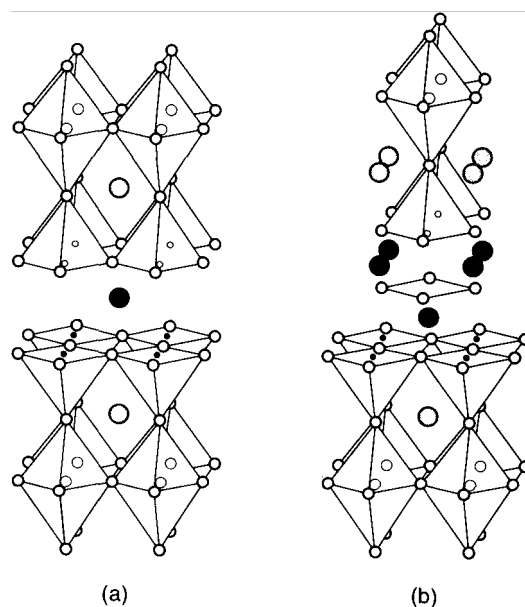


Fig. 1. The relationship between the crystal structures of (a) nonsuperconducting Ba₂LaNbCu₂O₈ [10–12] and (b) superconducting Sr₂Nd_{1.5}Ce_{0.5}NbCu₂O₁₀. (a) is derived from Ba₂YCu₃O₇ by the replacement of the CuO₄ chains with NbO₆ octahedra. (b) is derived from (a) by the addition of an MO₂ fluorite layer between the bases of the pyramids. CuO₅ pyramids and Nb(Ta)O₆ octahedra are emphasised in both figures. Large shaded circles: Ba, Sr, and rare earths; oxygen, intermediate open circles; copper and niobium, smaller and larger circles within the coordination polyhedra.

in (Ti–O) and (Pb, Cu–O) octahedral intermediary layers. The compound is a good bulk superconductor only for a narrow range of compositions and conditions of oxygen pressure, temperature, reaction time and cooling rate, striking a delicate balance among solid solubility, cation ordering, and oxygen content in the determination of its properties.

Efforts to determine the composition and optimal processing conditions for the superconducting phase were concentrated in the Nb based material. Starting materials were SrCO₃, freshly dried Nd₂O₃, Ce₂(C₂O₄)₃·9H₂O, Nb₂O₅(Ta₂O₅) and CuO, mixed to yield Sr₂Nd_{2–x}Ce_xNbCu₂O₁₀ for 0.4 ≤ x ≤ 0.7, Δx=0.05, based on the earlier reported composition of the phase [8,9] and the expected optimal concentration for superconductivity, x=0.6 (which corresponds to a nominal hole concentration of 0.2/Cu). The phase had been reported to be semiconducting in this composition range, although some resistive Ta based samples showed a peak in ρ(T) near 60 K

which was attributed either to a magnetic transition or filamentary superconductivity [8,9]. Our initial mixtures were heated at 200°/min to 1000°C in flowing O₂ and then heated at that temperature in O₂ for 70–90 h with 2 intermediate mechanical grindings. Powders were then pressed into pellets and subjected to a variety of treatments (table 1). The processing procedures were designed in the attempt to separate the effects of phase purity, cation order/disorder, and oxygen stoichiometry in the attainment of superconducting material. Although small amounts of superconductivity were observed for many processing procedures, only under a narrow set of conditions was bulk superconductivity obtained in essentially single phase material, allowing identification of the Sr₂Nd_{2–x}Ce_xNbCu₂O₁₀ type phase as a bulk superconductor. Optimal Ce concentrations were found to be between x=0.5 and 0.6. The best processing involved long treatment times (60 h or more) at temperatures of 1100–1125°C in an oxygen or 25

Table 1
Synthetic conditions^{a)} and magnetic characterization^{b)} of the superconductivity for Sr₂Nd_{2–x}Ce_xNbCu₂O_{10–δ}

#	Temp (°C)	Atm	Time(h)	Pretreatment #	Cooling ^c	x			
						0.4	0.5	0.6	0.7
1	1000	O ₂	16		Q	P	VW	VW	P
2	1000	O ₂	16		FC	P	VW	VW	P
3	1025	O ₂	12		FC	P	W	VW	P
4	950	30 atm O ₂	48	3	SC1	P	W	VW	P
5	900	O ₂	60	3	FC	P	W	W	P
6	900	2% O ₂	60	3	FC	P	P	P	P
7	1075	O ₂	16		FC	P	M	M	VW
8	1100	O ₂	60		FC	VW	S	VS	M
9	1100	O ₂	60		FC, Q FROM 800	VW	VW	VW	VW
10	1100	Air	60		FC	VW	W	W	W
11	1100	O ₂	0.5	8	1° /min to 400	W	S	S	M
12	1100	O ₂	85		100° /hr to 500	W	VS	S	M
13	1100	25 atm O ₂	90		SC2	W	M	W	W
14	1125	O ₂	12		FC	VW	S	VW	VW
15	1125	O ₂	85		100° /hr to 500	M	VS	VS	S
16	1125	25 atm O ₂	60		FC	VW	VS	VW	VW
17	1125	25 atm O ₂	80		100° /hr to 500	M	M	M	VW
18	600	N ₂	4	16	Q	P	P	P	P
19	1150	O ₂	12		FC	W	VW	VW	VW

^{a)} Initial treatments: 70–90 h 1000°C, O₂.

^{b)} AC shielding signals at 4.2 K; p=paramagnetic; VW, W, M, S, VS: a linear scale of increasing diamagnetism with VS=half (or greater) of the shielding signal from an equivalent volume Pb standard.

^{c)} Q=quenched, FC = cooled in furnace, SC1=step cool: soaked at T=–100°C increments for 5 h to 550°C then out; SC2=step cool: same as SC1 except 1 h soaks to 500°C.

atmosphere oxygen ambient [3] with cooling in the furnace to 500°C before removal. The 25° temperature window between 1100 and 1125°C, long treatment times, and cooling rate are all critical to the attainment of good quality material.

Although the phase assemblages are different in detail at the different processing temperatures, the $\text{Sr}_2\text{Nd}_{1-x}\text{Ce}_x\text{NbCu}_2\text{O}_{10}$ type phase is present at the 90% or greater level for $0.5 \leq x \leq 0.7$ in all cases. This suggests that the long time/high temperature treatment is necessary either to promote cation ordering, (for instance among Nb and Cu; or Sr, Ce and Nd) or that the superconductivity occurs in bulk material only in the narrow composition range near $\text{Ce}=0.5$ –0.6 and that nearly perfect single phase material is necessary to observe it. The best phase purity was observed in the 1100 and 1125 treatments at 25 atm O_2 pressure. At 1125°C and 25 atm for instance, there was less than 5% impurity phase in the composition range $0.5 \leq x \leq 0.7$. It would be very unusual for small differences in phase purity or Ce content to have such a profound effect on the occurrence of superconductivity in this kind of system suggesting that the processing procedure is very critical. Cation ordering, probably between Nb and Cu, is likely to be the key result of the long anneals.

Samples which were quenched from 800°C or higher were not bulk superconductors suggesting that oxygen uptake below 800°C on cooling could be crit-

ical to the occurrence of superconductivity but not excluding the possibility of order/disorder effects. The disappearance of superconductivity in all good materials, however, was always accompanied by a small weight loss. Treatment of good superconducting $\text{Sr}_2\text{Nd}_{1.5}\text{Ce}_{0.5}\text{NbCu}_2\text{O}_{10-\delta}$ (prepared at 1125°C, 25 atm O_2) for 4 h at 600°C in N_2 resulted in a weight loss of 0.25% (and single phase material) corresponding to an oxygen loss of approximately 0.13 per formula unit, or 0.13 holes per copper, and the loss of superconductivity. This indicated, along with the introduction of superconductivity in poor samples by re-treatment in O_2 , that the oxygen content of the phase is a critical parameter. Determination of the absolute oxygen content of the material is difficult because Nb_2O_5 and CeO_2 are only partially reducible (not to stoichiometric oxides) on heating in the TGA to 1000° in H_2 , our standard method for oxygen content determination. Finely powdered material can, however, be reduced in a 5% H_2 –95% N_2 mixture at 500°C, a temperature where CeO_2 and

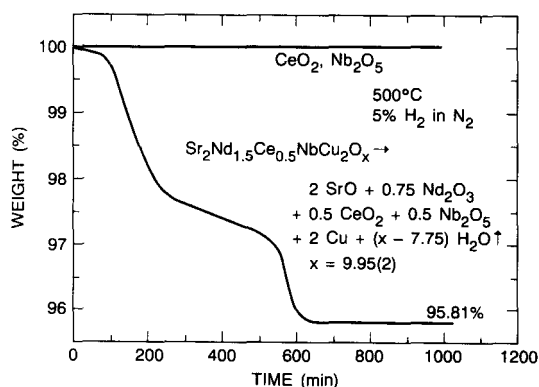


Fig. 2. Weight loss data used to determine the oxygen content $\delta=0.05(2)$ in $\text{Sr}_2\text{Nd}_{1.5}\text{Ce}_{0.5}\text{NbCu}_2\text{O}_{10-\delta}$ prepared at 1125°C, 25 atm O_2 . Powdered sample heated quickly in a 5% H_2 –95% N_2 mixture to 500°C and maintained for several hours. Also shown are the data that show that fact that finely powdered Nb_2O_5 and CeO_2 do not lose weight under the same conditions.

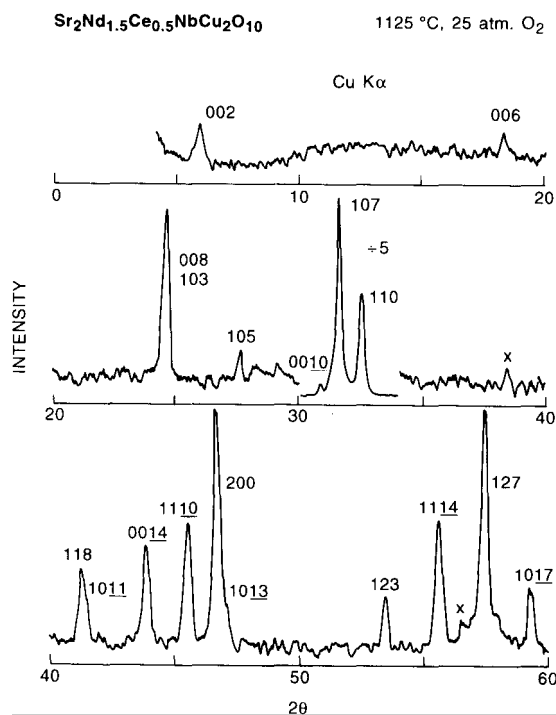


Fig. 3. Powder X-ray diffraction pattern for the $\text{Sr}_2\text{Nd}_{1.5}\text{Ce}_{0.5}\text{NbCu}_2\text{O}_{10-\delta}$ sample prepared at 1125°C and 25 atm. The impurity peaks, which are approximately 3% of the maximum peak intensity, are marked with an X.

Nb_2O_5 will not lose any oxygen on heating. Reduction of $\text{Sr}_2\text{Nd}_{1.5}\text{Ce}_{0.5}\text{NbCu}_2\text{O}_{10-\delta}$ prepared at 1125°C and 25 atm O_2 pressure indicated that $\delta=0.05$ (2), yielding an approximate doping of 0.2 holes/copper; near the optimal expected value. The weight loss data are shown in fig. 2. Note that samples annealed at 25 atm O_2 pressure and cooled by turning off the furnace are better superconductors than those cooled more slowly (entries 16 and 17 in table 1), suggesting that over-oxygenation may be possible for $\text{Ce}_{0.5}$.

High Resolution Electron Microscopy (HREM) was performed with a Philips CM30ST electron microscope operating at 300 kV, equipped with a side entry $25^\circ/25^\circ$ tilt specimen holder. Samples were

prepared by grinding and mounting on a carbon coated holey film supported by a Cu grid. Electron diffraction patterns of the sample prepared for 60 h at 1125°C in 25 atm O_2 showed a tetragonal-unit cell with a very weak superlattice in the a - b plane indicating a supercell of $a=b=\sqrt{2}\times 3.88 \text{ \AA}$ and $c=28.9 \text{ \AA}$. Systematic absences on this cell were hhl , $h=2n+1$. Superlattice reflections were strongly streaked along c^* , indicating that the supercell ordering along c is poor. The powder X-ray pattern for the same sample (fig. 3) was greater than 97% pure, with refined (18 reflections) subcell parameters $a=b=3.885(1)$, $c=28.864(9)$. The weak, diffuse, superlattice reflections are not seen in the powder X-

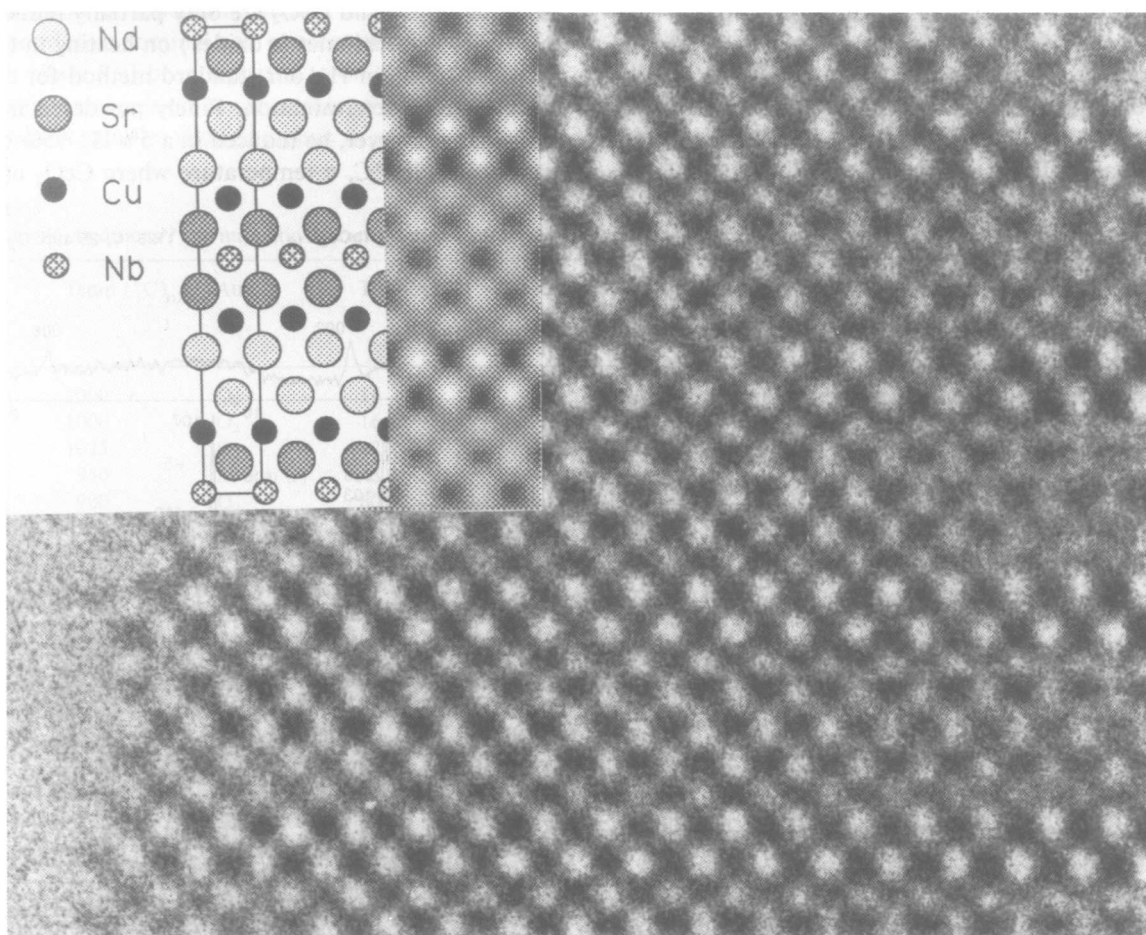


Fig. 4. HREM structure image of $\text{Sr}_2\text{Nd}_{1.5}\text{Ce}_{0.5}\text{NbCu}_2\text{O}_{10}$ viewed along $[110]$. The position of the cations are indicated schematically in the top left part of the image. Next to this is an image calculated from proposed atom positions [8,9] using the parameters: $C_s=1.2 \text{ nm}$, $\Delta f=8 \text{ nm}$, defocus = -50 nm , beam convergence = 0.9 mrad , and objective aperture = 6.5 nm^{-1} .

ray pattern, which is well accounted for by the $3.88 \times 28.86 \text{ \AA}^2$ angstrom body centered subcell. There were no peaks present from T^* -type $(\text{Nd,Sr,Ce})_2\text{CuO}_4$ to the detectability limit of approximately 2%. Figure 4 shows the HREM image in the 110 plane. The image confirms the proposed structure of this phase [8,9], as is shown schematically in fig. 1(b).

Figure 5 presents the magnetic susceptibility data for various samples cooled in a field of 4.1 Oe in a SQUID magnetometer. The data show that although the best sample was $\text{Sr}_2\text{Nd}_{1.5}\text{Ce}_{0.5}\text{NbCu}_2\text{O}_{10}$ annealed for 60 h at 1125°C in 25 atm O_2 pressure, the sample of $\text{Sr}_2\text{Nd}_{1.4}\text{Ce}_{0.6}\text{NbCu}_2\text{O}_{10-\delta}$ annealed at 1125°C for 85 h at 1 atm O_2 pressure is not significantly worse. Because the magnitude of the superconducting signal and T_c are very sensitive to cooling rate as well as temperature and O_2 pressure, it is probable that a set of processing conditions at 1 atm O_2 could yield a sample equivalent in quality to those made at 25 atm. For these two samples the flux expulsion is between 20 and 30% that of an ideal diamagnet, indicating the presence of good, bulk superconductivity for both 1 atm and 25 atm synthetic conditions. Shown also in the figure is the field cooled susceptibility for $\text{Sr}_2\text{Nd}_{1.5}\text{Ce}_{0.5}\text{TaCu}_2\text{O}_{10}$ treated at 1125°C in O_2 for 85 h. Although the volume fraction of superconductivity is lower, bulk superconductivity also clearly is observed in the Ta analog of this

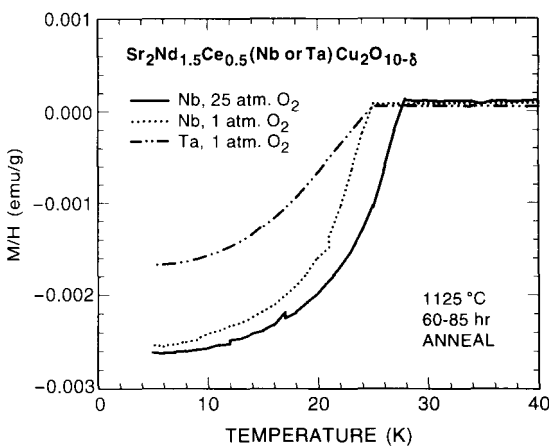


Fig. 5. Magnetic superconducting transitions for $\text{Sr}_2\text{Nd}_{1.5}\text{Ce}_{0.5}\text{NbCu}_2\text{O}_{10}$ prepared at 25 and 1 atm oxygen pressure, and $\text{Sr}_2\text{Nd}_{1.5}\text{Ce}_{0.5}\text{TaCu}_2\text{O}_{10}$ prepared at 1 atm O_2 . DC magnetization data, cooled in a field of 4.1 Oe.

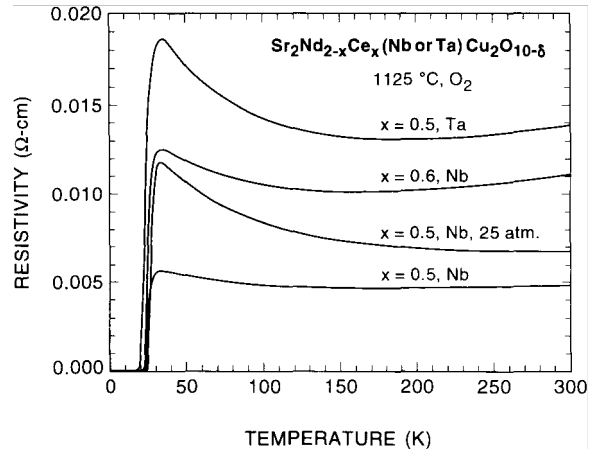


Fig. 6. Temperature dependent resistivities of superconducting samples.

phase. For all samples the screening (zero field cooled) diamagnetic signals are only 10–20% larger than the field cooled signals.

Figure 6 shows the temperature dependent resistivities for samples of $\text{Sr}_2\text{Nd}_{2-x}\text{Ce}_x(\text{Nb or Ta})\text{Cu}_2\text{O}_{10-\delta}$ prepared at 25 atm and 1 atm O_2 pressure. The fact that the resistivities are high and generally show weakly semiconducting behavior at low temperatures, in spite of the high fraction of field cooled diamagnetism, indicates that the connectivity between the superconducting crystallites is poor, consistent with the near equivalence of screening and field cooled magnetization. Investigation of the grain boundary regions of these samples by TEM did not reveal any outstanding differences, but given the delicate balance of conditions necessary to make good quality samples, the difference could be quite subtle.

In conclusion, we have found superconductivity at 28 K in a copper oxide superconductor with a new kind of intermediary layer based on Nb or Ta oxide octahedra. TEM investigations have revealed the existence of related phases occurring in defective regions of these samples, suggesting that more members of this family might be isolated. We expect that the relatively low T_c of this material with respect to other double pyramidal layer copper oxide superconductors is due either to the fact that the intermediary Nb(Ta) O_6 layer is insulating, or that the CuO_2 planes are separated (and shifted) by a relatively wide insulating fluorite block.

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