

Structural implications of oxygen stoichiometry in $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{6-\delta}$

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Abstract

The local coordination of copper and europium in the compound of composition $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{6-\delta}$ has been examined by extended X-ray absorption fine structure. The results are consistent with a model in which ordered anionic vacancies create a unique one-dimensional tunnelled oxygen sublattice built from vertex linked CuO_5 square pyramids and with the partial occupation by strontium of some of the lanthanide sites.

1. Introduction

The structural chemistry of mixed-valence copper oxides has received much attention since the discovery of high temperature superconductivity [1-3]. In these compounds, the partial oxidation of copper beyond its divalent state is achieved either by varying the cation ratios or by annealing. Non-superconducting complex copper oxide phases have also been described in terms of mixed-valence copper species [4-8]. These include phases reported by Nguyen *et al.* [4] which are based on the semimetallic-semiconducting $\text{Ln}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6-\delta}$ ($\text{Ln} = \text{La, Eu, Sm, Gd}$) solid solution series.

The structure of $\text{La}_2\text{SrCu}_2\text{O}_6$ (Fig. 1) is derived from $\text{Sr}_3\text{Ti}_2\text{O}_7$ and can be regarded as a layered intergrowth containing features of both La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$. The central block containing the double CuO_2 layers is similar to that observed in $\text{YBa}_2\text{Cu}_3\text{O}_7$ where the eight-coordinate cation is Y. The structural properties of compounds of the type $\text{Ln}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6-\delta}$ have been described in terms of two different oxygen ordering models. Nguyen *et al.* [4] by refinement of X-ray powder diffraction data recorded from $\text{Ln}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6-\delta}$ ($\text{Ln} = \text{Nd, Eu, Sm}$) described the materials in terms of a tripled $\text{La}_2\text{SrCu}_2\text{O}_{6-\delta}$ unit cell containing ordered anionic vacancies which create alternating corner-linked octahedral and square pyramidal copper oxygen coordination (Fig. 2). The 4i site was described as being statistically occupied by both lanthanum and strontium ions. Subsequently Grasmeyer and Weller [9] used the results of Nguyen to analyse the neutron diffraction data recorded from $\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_{6-\delta}$ and described the material in terms of a tripled $\text{La}_2\text{SrCu}_2\text{O}_{6-\delta}$ unit cell containing ordered anionic vacancies which create

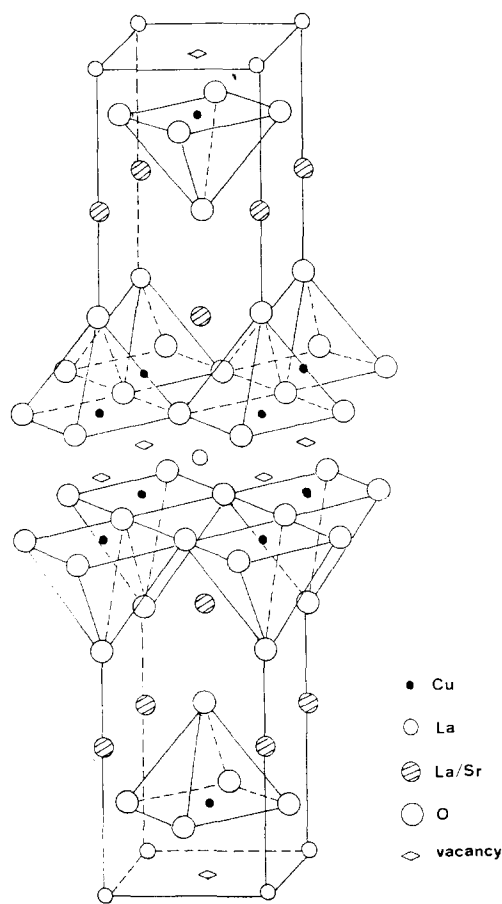
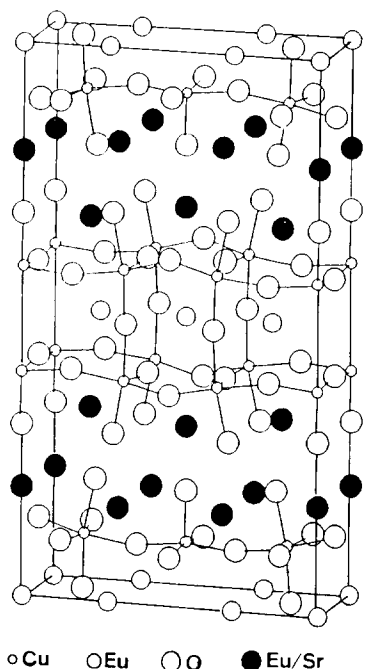


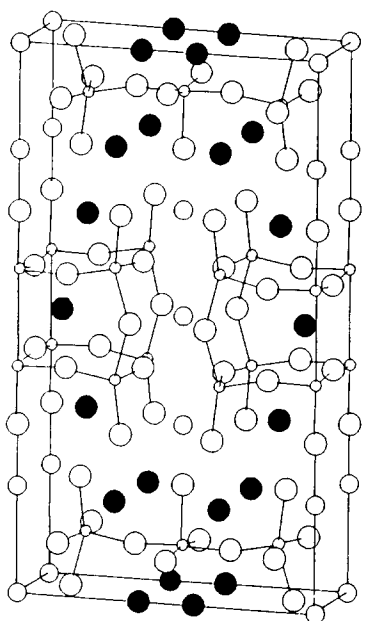
Fig. 1. Structure of $\text{La}_2\text{SrCu}_2\text{O}_6$.

a unique one-dimensional tunnelled oxygen sublattice built from vertex-linked CuO_5 square pyramids (Fig. 3). The 4g site was described as being statistically



○ Cu ○ Eu ○ O ● Eu/Sr

Fig. 2. Structure of $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ according to Nguyen *et al.* [4].



○ Cu ○ Eu ○ O ● Eu/Sr

Fig. 3. Structure of $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ according to Grasmeyer and Weller [9].

occupied by both strontium and neodymium ions. Hence, although the main structural features of the lanthanide double-layer materials are common to both models, the oxygen ordering patterns as well as the distribution of strontium atoms on the cation sublattices are distinctly different.

In order to achieve a better understanding of the structural chemistry of these complex copper oxides we have conducted some further investigations and we report here on our studies of the compound $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{6-\delta}$ by extended X-ray absorption fine structure (EXAFS).

2. Experimental details

The compound of composition $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{6-\delta}$ was prepared from appropriate proportions of europium (III) oxide, strontium carbonate and copper oxide. The powdered mixture was heated in air in an alumina crucible at 1050 °C for 48 h. The absence of peaks in the X-ray powder diffraction patterns which could be attributed to unreacted starting materials was taken as the criterion of purity.

X-ray powder diffraction data were recorded with a Philips PW 1050/70 diffractometer using Cu $K\alpha$ radiation. Thermogravimetric analysis was performed with a Stanton Redcroft STA-780 thermal balance by heating the samples in a flowing 10% hydrogen–90% nitrogen gas mixture at temperatures between 25 °C and 940 °C.

EXAFS measurements were performed in transmission mode [10] at the Synchrotron Radiation Source at the SERC Daresbury laboratory at station 7.1 (europium L_{III} -edge 6.985 KeV and copper K-edge 8.982 KeV) under operating conditions of 2 GeV and maximum beam currents of 280 mA. A Si(111) or Si(220) double crystal order sorting monochromator was used to minimise the harmonic content of the monochromatic beam [11]. All data were recorded at room temperature and pressure. After calibration of the monochromator angle to energy the EXAFS was normalised to a unit metal atom and extracted from the background absorption by a method previously described [12]. The EXAFS data were converted into k space using $k[2m_e(E - E_0)/h^2]^{1/2}$, where E and E_0 are the energy of the incident beam and of the absorption edge of the metal atom, respectively, and k is the photoelectron wavevector. The EXAFS data were analysed using the non-linear least squares minimisation program EXCURV88 [13], which calculates the theoretical EXAFS function using the fast curved wave theory [14]. Curve fitting was carried out on data smoothed by Fourier filtering in the range 0–13 \AA^{-1} and weighted by k^3 in order to compensate for the diminishing amplitude of the EXAFS at high k . Phase shifts were calculated by *ab initio* methods as described elsewhere [15].

During the initial analysis of the data the values for coordination numbers were fixed and the occupancies, metal–oxygen distances, and Debye–Waller factors were

allowed to refine. The estimated error for the shell radii is $\pm 0.02 \text{ \AA}$. Curve-fitting errors are considerably smaller. The resolution of separate shells contributing to the EXAFS was estimated from $\Delta R = (\pi/2\Delta k)$ where Δk is the energy interval in k space. In the results presented here $\Delta k \approx 9 \text{ \AA}^{-1}$ which gives a resolution of about 0.17 \AA . The quality of the simulation was assessed by: (i) a goodness of fit parameter (the fit index) defined as $\sum |k^3(X_{\text{th}} - X_{\text{exp}})|^2/n$ where X_{th} and X_{exp} are the theoretical and experimental EXAFS respectively and n is the number of points in the experimental spectrum; and (ii) visual inspection of the fitted data. The enhancement of the copper backscattering amplitudes resulting from alignment of the Cu–O–Cu bonds in the basal layer of the compounds was accounted for by including multiple scattering contributions during iterative refinement cycles of the copper K-edge EXAFS to generate the atomic parameters.

3. Results and discussion

The X-ray powder diffraction data recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{6-\delta}$ were successfully fitted to an orthorhombic unit cell ($Immm$) with parameters $a = 3.7433(2) \text{ \AA}$, $b = 11.3170(5) \text{ \AA}$ and $c = 20.0184(6) \text{ \AA}$ indicating the tripling of the unit cell along the b -direction as previously reported [4, 9]. The value of δ in $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{6-\delta}$ was estimated as 0.35 by thermogravimetric analysis and thereby indicated the presence of Cu^{1+} in an oxygen deficient material of nominal stoichiometry $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$. The material gave a ^{151}Eu Mössbauer spectrum confirming the presence of Eu^{3+} .

Bond distances in $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ were calculated using atomic parameters derived from the International Crystal Structures Database and the CRAD computer program of the Chemical Database Service at SERC Daresbury Laboratory. Thus, for copper in the central position, individual bond distances were derived for both the 4i and 81 sites. These distances were grouped according to value, atom type, and vacancy formation. Average copper site coordination spheres were finally calculated by weighting the bond distances arising from the 81 site twice as high as those arising from the 4i site.

A similar procedure was used when considering the europium coordination spheres. The calculations were complicated by the presence of three metal ion sites (2a, 4g and 4i), the partial occupancy of some of these sites by strontium ions, and vacancy formation. For simplicity, the partial occupancy of strontium on these sites was fixed at 50%. In the Nguyen model [4] strontium ions were considered as occupying the 4i site whereas Grasmeyer and Weller [9] restricted strontium occupancy to the 4g site. Importantly the multiplicity of

bonds arising from the 4i site in the Nguyen model [4] and from the 4g site in the Grasmeyer and Weller model [9] are effectively halved in relation to the 50% occupation by europium of these sites. Therefore bond distances from the Nguyen data were weighted 1:2:1 for the 2a, 4g and 4i sites which alter significantly to a ratio of 1:1:2 for the Grasmeyer model.

The best-fit parameters to the copper K-edge EXAFS recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ refined according to the Nguyen model are collected in Table 1 whilst those refined according to the Grasmeyer model are contained in Table 2. The simulations of the copper K-edge EXAFS and their Fourier transforms when fitted according to the two models are shown in Figs. 4 and 5. The most satisfactory fit to the data was provided by the model of Grasmeyer (fit index 1.48), indeed visual inspection of the fit according to the Nguyen model is clearly not suitable. The unacceptable fitting of a near shell coordination about copper according to Nguyen's description of the structure which involved two oxygen atoms at 1.91 \AA was further indicated by the large Debye–Waller factor of 0.063 \AA^2 . Furthermore, the large Debye–Waller factors of 0.129 \AA^2 for the europium shell at 3.324 \AA and of 0.046 \AA^2 for the copper shell at 3.959 \AA are indicative of the difficulty in fitting the data to the more distant shells required

TABLE 1. Best fit parameters to copper K-edge EXAFS recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ and fitted according to the model of Nguyen et al. [4]

Atom	type	R (\AA)	$2\sigma^2$ (\AA^2)
1.17	0	1.889	0.003
2	0	1.910	0.063
2	0	2.000	0.005
2.67	Sr	3.162	0.024
4	Eu	3.197	0.020
1.33	Eu	3.324	0.129
2.67	Cu	3.959	0.046
1.67	Cu	3.808	0.013

Fit index = 4.573

TABLE 2. Best fit parameters to copper K-edge EXAFS recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ and fitted according to the Grasmeyer and Weller model [9]

Atom	type	R (\AA)	$2\sigma^2$ (\AA^2)
1	0	1.819	0.003
2	0	1.919	0.004
1.33	0	2.011	0.004
1	0	2.160	0.002
2.67	Sr	3.145	0.025
1.33	Eu	3.179	0.035
4	Eu	3.192	0.023
2.33	Sr	3.801	0.015

Fit index = 1.479

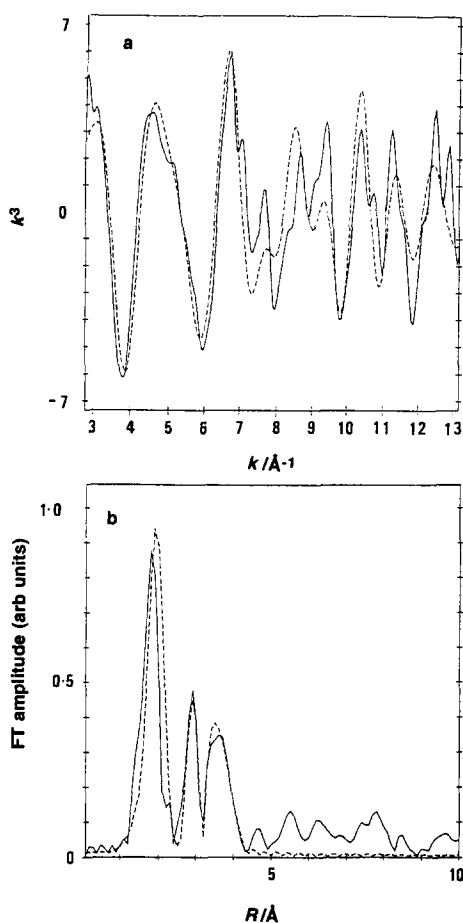


Fig. 4. (a) k^3 -Weighted simulation of the copper K-edge EXAFS; (b) Fourier transform recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ and fitted according to the model of Nguyen *et al.* [4].

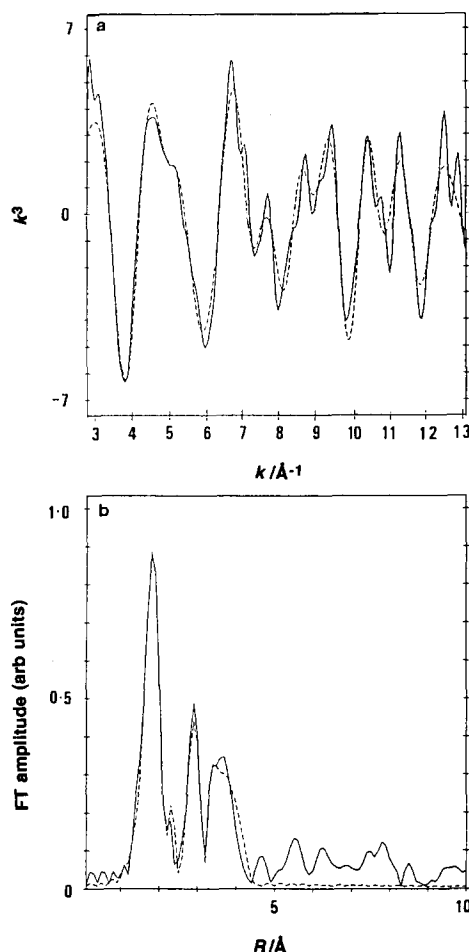


Fig. 5. (a) k^3 -Weighted simulation of the copper K-edge EXAFS; (b) Fourier transform recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ and fitted according to the model of Grasmeyer and Weller [9].

by the Nguyen model. In contrast the Debye–Waller factors for the fit of the data according to the structural description of Grasmeyer and Weller are all better with highly acceptable Debye–Waller factors (less than 0.005 \AA^2) for the near shell oxygen coordination.

The best fit parameters to the europium L_3 -edge EXAFS recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ refined according to the models of Nguyen *et al.* and Grasmeyer and Weller are collected in Tables 3 and 4 respectively whilst the simulations of the EXAFS and their Fourier transforms are collected in Figs. 6 and 7. A superior fit of the europium L_3 -edge EXAFS data was achieved using the Grasmeyer and Weller model (fit index 1.3). Indeed, the Fourier transforms clearly demonstrate that fitting the first and second shell data to the Nguyen model is unsatisfactory. The large Debye–Waller factors for the oxygen shell at 2.914 \AA and for copper at 3.581 \AA are a further indication of the poor fit to the data when Nguyen's description of the structure is used. In contrast the fitting of the data according to the Grasmeyer and Weller model is more acceptable and gives coordination numbers with acceptable Debye–Waller

TABLE 3. Best-fit parameters to the europium L_3 -edge EXAFS recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ and fitted according to the Nguyen *et al.* model [4]

Atom	type	R (\AA)	$2\sigma^2$ (\AA^2)
$\frac{1}{2}$	0	2.265	0.067
1	0	2.376	0.001
2	0	2.476	0.016
4	0	2.557	0.030
1	0	2.786	0.012
2	0	2.914	0.114
1	0	2.096	0.041
2	Cu	3.133	0.006
3	Cu	3.264	0.014
1	Eu	3.299	0.023
1	Sr	3.451	0.060
2	Cu	3.581	0.122
2	Eu	3.774	0.020
$1\frac{1}{2}$	Sr	3.773	0.047
1	Eu	3.949	0.023

Fit index = 2.218

TABLE 4. Best fit parameters to the europium L_3 -edge EXAFS recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ and fitted according to the Grasmeyer and Weller model [9].

Atom	type	R (\AA)	$2\sigma^2$ (\AA^2)
$\frac{1}{2}$	0	2.229	0.066
2	0	2.361	0.001
1	0	2.455	0.002
4	0	2.550	0.011
1	0	2.696	0.040
1	0	2.790	0.011
1	0	3.096	0.004
2	Cu	3.133	0.005
4	Cu	3.285	0.12
$\frac{3}{2}$	Eu	3.484	0.013
$\frac{1}{2}$	Sr	3.540	0.014
$2\frac{1}{2}$	Sr	3.735	0.009
2	Eu	3.744	0.007
1	Eu	3.905	0.013

Fit index = 1.301

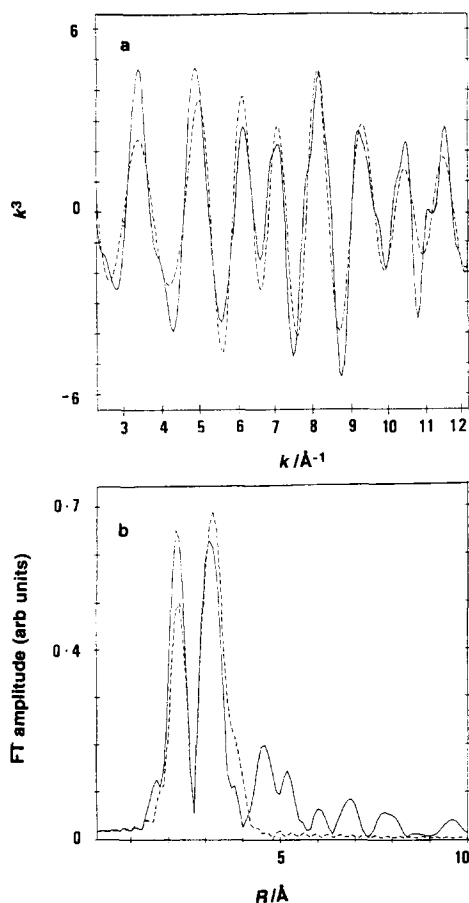


Fig. 6. (a) k^3 -Weighted simulation of the europium L_3 -edge EXAFS; (b) Fourier transform recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ and fitted according to the model of Nguyen *et al.* [4].

factors. A better lanthanide to strontium distribution on the metal ion sites was also achieved by fitting the europium L_3 -edge EXAFS data to Grasmeyer's de-

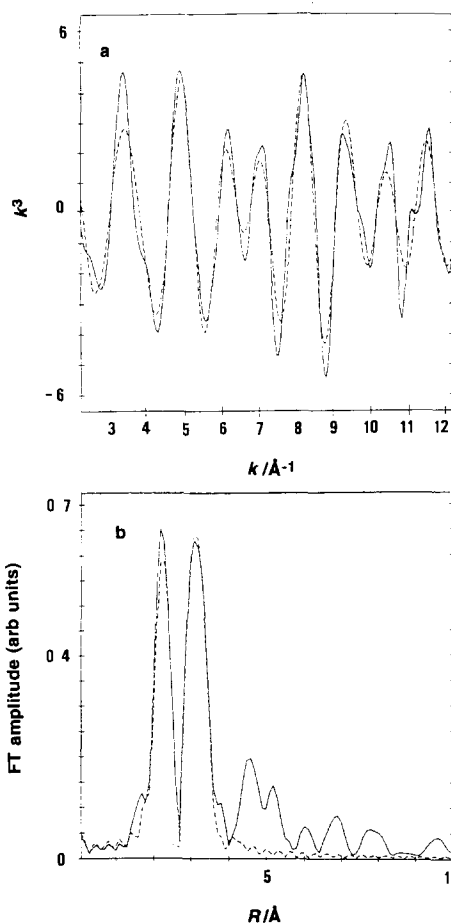


Fig. 7. (a) k^3 -Weighted simulation of the europium L_3 -edge EXAFS; (b) Fourier transform recorded from $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ and fitted according to the model of Grasmeyer and Weller [9].

scription of the compound. Hence superior fits to both the copper K-edge EXAFS and the europium L_3 -edge EXAFS were achieved using the structural description of Grasmeyer and Weller. The superiority of the Grasmeyer and Weller model is indicative of a similarity in the oxygen ordering in $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{6-\delta}$ and in $\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_{6-\delta}$ which create a one dimensional tunnelled oxygen sublattice built from vertex linked CuO_5 square pyramids and in which some of the lanthanide sites are partially occupied by strontium.

Finally, we would mention that the annealing of $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ at 350 °C for 48 h under 240 bar oxygen pressure gave a material which was shown by thermogravimetric analysis to be of composition $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.72}$. The results demonstrate the amenability of the relatively open $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ structure to oxygen incorporation. Low temperature magnetic susceptibility measurements failed to find any evidence for superconductivity in either $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ or $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.72}$.

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