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Stoichiometric CeCuOS − A Well-Behaved Ce(III) Layered Oxysulfide

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The reported anomalously small cell volume and magnetic moment of the layered oxysulfide CeCuOS are apparently the results of copper deficiency arising from exposure to ambient moist air; the stoichiometric compound does exist and is a well-behaved Ce^{III} compound.

Layered oxychalcogenides and oxypnictides are receiving increasing attention. *Ln*CuOS (*Ln* = lanthanide) have received particular attention in the development of new wide band gap semiconductors for possible application as photovoltaic materials or as *p*-type transparent conductors.[1] The discovery of high temperature superconductivity in electron-doped derivatives of *Ln*FeOAs[2] has initiated intense research on arsenides. Both *Ln*CuOS and *Ln*FeOAs adopt the versatile ZrCuSiAs structure type[3] in which lanthanide oxide PbO-type layers separate copper sulfide or iron arsenide anti-PbO-type layers (Figure 1). The properties (e.g., bandgaps in *Ln*CuOS and related compounds[4] and superconducting transition temperatures in *Ln*FeOAs derivatives) may be tuned by varying the lanthanide radius which decreases significantly and almost monotonically across the lanthanide series.

Cerium-containing compounds can prove anomalous because of the ready oxidation of Ce^{3+}. Analysis of single crystal samples by Chan et al.[5] showed that $CeCu_{1-x}OS$ readily accepts a copper deficiency (e.g., $x = 0.25$) supporting the original conclusions of Charkin et al.[6] that the smaller than expected lattice parameters exhibited by “CeCuOS” samples were a consequence of variable copper deficiency. Ueda et al.[7] reported however a sample of apparently stoichiometric CeCuOS which appeared single phase by laboratory powder X-ray diffraction (PXRD) and which also had lattice parameters which were highly contracted relative to the trend exhibited by the other *Ln*CuOS members. On the basis of this result it was proposed that CeCuOS had an exotic electronic ground state with Ce in an intermediate valence state. Here we demonstrate how the apparent conflicts between these reports arise and describe the synthesis, structure, and magnetic properties of the first sample of almost stoichiometric CeCuOS and its oxidation product.

CeCuOS was prepared as a 6 g powder sample using a stoichiometric mixture of $CeCuS_2$, CeO_2, and Cu (1:1:1) with 0.5 mol equiv of dried KCl added as a flux. The mixture was loaded into an alumina crucible, sealed in an evacuated silica tube, and then heated to 900 °C for 10 days. The KCl flux was removed by washing with methanol under a nitrogen atmosphere using standard Schlenk techniques. This sample (Sample 1) was dark olive green in color and highly air sensitive. Half of this sample (~3 g) was exposed for 16 h to a flow of O_2 bubbled through H_2O at ambient temperature. This treatment with “moist air” resulted in a jet black powder (Sample 2) which was significantly more absorbing than Sample 1 in the visible and near-IR (Figure S4) in line with the results presented by Ueda et al. in ref 8. PXRD analysis showed that the samples were apparently phase pure. Analysis of the PXRD patterns calibrated using a silicon standard showed two things: first, the olive green phase had lattice parameters much larger than those reported previously for any $CeCu_{1-x}OS$ phases,[5−7] and second, exposure of the sample to a moist oxygen flow resulted in a 2.6% decrease in cell volume producing lattice parameters approximately equal to the smallest values claimed for phases of nominal composition CeCuOS.[7] The olive green phase and its larger lattice parameters can be regenerated by heating the black oxidized sample to 400 °C in a flow of H_2/N_2 gas.

Rietveld refinement (Figure 2) against powder neutron diffraction (PND) data obtained on the POLARIS diffractometer at the ISIS facility, UK revealed that the CeCuOS phase in the olive green sample (Sample 1) is very close to stoichiometric. The data were collected in the *d*-spacing range

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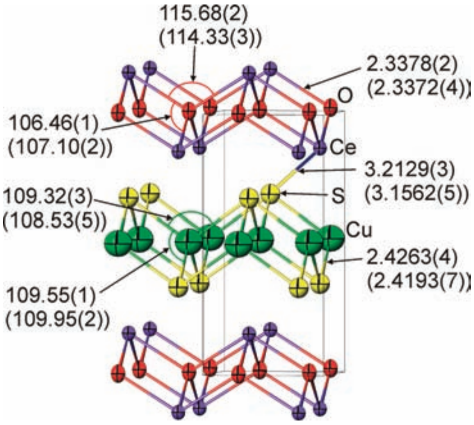

Figure 1. Crystal structure of $CeCu_{0.987(2)}OS$ (Sample 1) refined against powder neutron diffraction data (99% displacement ellipsoids). Bond distances are given in Å, and angles in degrees; values in brackets refer to the structure of $CeCu_{0.862(3)}OS$ (Sample 2) obtained by oxidation of Sample 1. See also Table S1 and Figure S3.

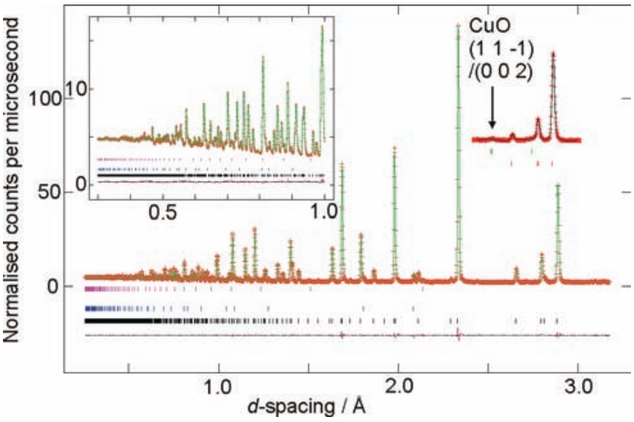

Figure 2. Rietveld refinement against PND data collected on $CeCu_{0.987(2)}OS$ (Sample 1). Low *d*-spacing region inset. The data (red points), fit (green line), and difference (lower line) are shown. Tick marks indicate reflection positions for (from bottom) the main oxysulfide phase, elemental Cu, and the vanadium sample container. The detail at top right shows part of the fit to the data on the $CeCu_{0.862(2)}OS$ sample (Sample 2) obtained by oxidation of Sample 1; the peak broadening, lattice parameter contraction, and broad reflections arising from CuO are evident.

Table 1. Room Temperature Structural Parameters

Sample	Sample 1	Sample 2	% change[b]	$CeCu_{0.76}OS$[5]
Cu occ.	0.987(2)	0.862(2)		0.762
a/Å	3.95828(2)	3.92759(9)	−0.78	3.9072(3)
c/Å	8.45071(5)	8.3596(2)	−1.08	8.2834(10)
V/Å^3	132.405(1)	128.955(5)	−2.61	126.46(2)
c/*a*	2.135	2.128	−0.33	2.120
Cu−S [4][a]/Å	2.4263(4)	2.4193(7)	−0.29	2.4064(9)
Ce−S [4]/Å	3.2129(3)	3.1562(5)	−1.76	3.1245(8)
Ce−O [4]/Å	2.3378(2)	2.3372(4)	−0.03	2.3342(2)
S−Cu−S [2]/deg	109.32(3)	108.53(5)	−0.72	108.55(6)
S−Cu−S [4]/deg	109.55(1)	109.95(2)	+0.37	109.93(3)

[a] Numbers in square brackets indicate the multiplicity of the angles or bond lengths. [b] Percentage change on oxidation of Sample 1 to Sample 2.

from 0.3 Å to 8 Å. Such data enable precise and accurate independent refinement of fractional site occupancies and atomic displacement parameters. The refined composition of Sample 1 was $CeCu_{0.987(2)}OS$. In contrast, refinement of the composition of the CeCuOS phase in the black sample obtained by oxidation (Sample 2) revealed a composition of $CeCu_{0.862(2)}OS$ showing that exposure of the stoichiometric sample to moist oxygen results in a significant copper deficiency. Both samples contained approximately 3.5 mol % elemental Cu suggesting that the refinements may systematically overestimate the Cu content by 2% or so. Close inspection of the PND patterns of $CeCu_{0.868(3)}OS$ (Sample 2) also revealed several very broad peaks of low intensity that are consistent with the presence of CuO of very low crystallinity. To investigate this further we synthesized a sample of composition $CeCu_{0.85}OS$. Reaction of this sample with a flow of H_2/N_2 at 400 °C for 8 h resulted in changes of lattice parameters of less than 0.02%. However the addition of 0.15 mol equiv of CuO to a portion of this sample followed by the same reduction treatment was accompanied by a 3% increase in lattice parameters of the oxysulfide phase and resulted in the formation of an olive-green sample (Sample 3) which was single phase according to PXRD (i.e., the added crystalline CuO had been consumed) with a unit cell volume exceeding by 0.4% that of the almost stoichiometric material (Sample 1) investigated using PND. This suggests that this two-stage synthetic method may be optimal for synthesizing truly stoichiometric samples. Sample 3 was significantly less strongly absorbing in the near-IR region than Sample 1 (Figure S4) showing the high sensitivity of the optical properties to the copper content. Figure 1 shows the refined crystal structure of Sample 1 ($CeCu_{0.987(2)}OS$) analyzed by PND. Bond lengths and angles for this phase and for the Cu-deficient material (Sample 2) derived from it by oxidation are indicated and are listed in Table 1.

Magnetometry measurements on the two samples investigated by PND measurements revealed that both display Curie−Weiss paramagnetism above 150 K (Figure 3). Below this temperature there is some deviation from the Curie−Weiss Law, which has previously been ascribed to crystal field splitting in the $J = 5/2$ ground state of Ce^{3+}.[5] The measured values of the Curie constants obtained from fits in the Curie−Weiss region from 150 to 300 K produced effective magnetic moments per formula unit (μ_{eff}) of 2.53(2) μ_B for Sample 1 ($CeCu_{0.987(2)}OS$) and 2.38(4) μ_B for Sample 2 ($CeCu_{0.862(2)}OS$) after correction for core electron diamagnetism and taking into account the mass and paramagnetism of CuO in Sample 2. Sample 3 with the largest cell volume, obtained by the reduction of a mixture of $CeCu_{0.85}OS$ and 0.15CuO, had a μ_{eff} of 2.55(2) μ_B. The values of μ_{eff} for the compounds that are close to stoichiometric (Samples 1 and 3) are equal within experimental uncertainty to the theoretical free-ion value of 2.54 μ_B for Ce^{3+}, confirming that the stoichiometric material is a bona fide Ce^{3+} ($4f^1$) compound. The observed μ_{eff} of 2.38(4) μ_B for $CeCu_{0.862(2)}OS$ (Sample 2) is similar to the expected value of 2.36 μ_B calculated for a mixed-valence system $[Ce^{4+}{}_{0.14}Ce^{3+}{}_{0.86}]Cu_{0.86}OS$.

On oxidation (Sample 1 converting to Sample 2) the unit cell volume contracts by 2.6%. The basal lattice parameter *a* contracts by 0.8% while *c* contracts by 1.1%. The Cu−S distance decreases by only 0.29% so the contraction in the basal direction means that the almost perfectly regular tetrahedra in the almost stoichiometric phase in Sample 1 become slightly elongated along *c*. The OCe_4 tetrahedra undergo a similar deformation on oxidation because the Ce−O distance remains almost invariant (0.03% decrease on oxidation). The 0.3% decrease in the *c*/*a* ratio results from

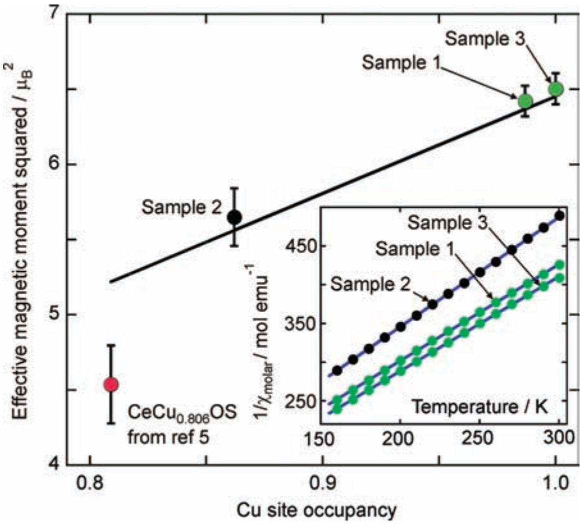

Figure 3. Correlation between the square of the effective moment per formula unit (i.e., proportional to the Curie constant) with Cu site occupancy (inferred from cell volume for Sample 3, otherwise measured directly by diffraction methods). The line shows the expectation for one Ce^{3+} ion per Cu^+ ion in the formula $CeCu_{1-x}OS$ with no moment reduction. Values have been corrected for the effect of core electron diamagnetism.

the 1.8% decrease in the Ce−S bond length (Figure 1, Table 1) which is the only nearest-neighbor interaction that changes significantly. Presumably the loss of Cu^+ ions and consequent underbonding of sulfide is compensated by a decrease in the Ce−S bond length and the increase in the Ce oxidation state. The changes in structural parameters on oxidation are summarized in Table 1. The trends continue with increasing copper deficiency according to the results of Chan et al. on $CeCu_{0.76}OS$.[5]

The conclusions are that stoichiometric or very close to stoichiometric CeCuOS may be synthesized and, in contrast to previous reports,[6−9] it is a well-behaved Ce^{3+} compound with lattice parameters which conform to the expectations of the lanthanide contraction (Figure 4). However, as was originally reported by Charkin et al.[6] and confirmed quantitatively by the studies of Chan et al.,[5] the compound readily accepts a copper deficiency. This could lead to oxidation of Ce^{3+} or to oxidation of the antibonding states at the top of the Cu-3*d*/S-3*p* band (which forms the readily depleted valence band in LaCuOS).[1] The calculations of Chan et al.[5] show that the Ce-4*f* states lie very close to the Fermi level and above the Cu-3*d*/S-3*p* states, implying that copper deficiency should result in mixed-valent Ce. This is in line with our results and theirs[5] and with the photoemission results of Sato et al.[10] which probed this directly on a sample which we presume was highly copper deficient.

We have shown in this work that the copper deficiency can arise from oxidation of stoichiometric CeCuOS in moist air or moist oxygen. Our evidence implies that the sample described as stoichiometric CeCuOS by Ueda et al.[7] and with a small cell volume is in fact copper deficient by approximately 15%, a suggestion made earlier by Chan et al. on the basis of bond valence calculations and comparison of the lattice parameters and magnetic moments with that of their well-characterized $CeCu_{0.76}OS$ and $CeCu_{0.81}OS$ samples.[5] The linear correlation between accurately obtained copper site occupancy and unit cell volume (Figure 4) suggests that the samples reported by Charkin et al. are all significantly more copper deficient (by ∼10%) than was indicated in their paper.[6]

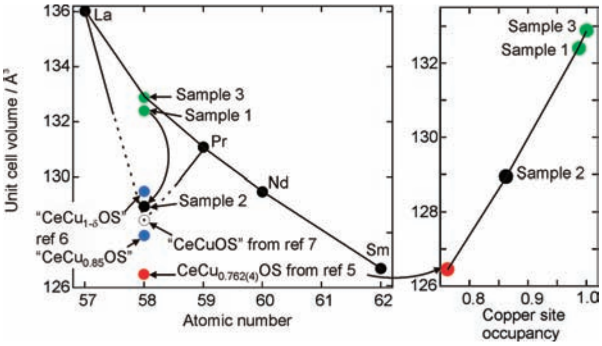

Figure 4. Plots of unit cell volumes for *Ln*CuOS phases[6] including several $CeCu_{1-x}OS$ phases.[5−7] Sample 1 ($CeCu_{0.987(2)}OS$) and sample 3 have cell volumes which lie close to the expectations of the lanthanide contraction (left). The linear correlation of unit cell volumes with reliably determined copper site occupancies (from high-*Q* single crystal X-ray[5] or powder neutron diffraction data) (right) suggests that all previously reported samples of stoichiometric CeCuOS[6,7] have been at least 10% deficient on the Cu site. Lines are guides to the eye.

This clarification of the behavior of CeCuOS further demonstrates that copper may readily be extracted from and inserted into anti-PbO-type copper sulfide layers under mild conditions[11,12] and suggests that other compounds containing similar copper chalcogenide layers and oxidizable metal cations[4] may be susceptible to controlled oxidation. Further investigations of the $CeCu_{1-x}OS$ phases are required to clarify the extent to which Ce^{4+} ions may coexist with sulfide and to investigate the possibility of Ce deficiency.[9]

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Supporting Information Available: Further synthetic and experimental detail, comparative diffractograms for Samples 1 and 2, Rietveld refinement[13] results and lists of refined structural parameters and bond lengths for Samples 1 and 2, diffuse reflectance data for Samples 1, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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