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Synthesis, Structure, and Magnetism of $La_{15.9(2)}Cr_{5.4(2)}S_{32}$: A Cr(III) Sulfide Containing d^3-d^3 $Cr_2S_9^{12-}$ Bioctahedra with Large Antiferromagnetic Coupling

J. Brian Litteer, Scott A. Sirchio,
James C. Fettinger, Vera Smolyaninova,
Bryan W. Eichhorn,* and Richard L. Greene

Departments of Chemistry and Physics, Center for Superconductivity Research, University of Maryland, College Park, Maryland 20742

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There is renewed interest in mixed valent d^3-d^4 metal oxides due to the discovery of novel magnetoresistive (MR) effects in some of these materials (e.g. $La_{1-x}A_xMnO_3$, A = Ca, Sr, Ba).[1] Recent studies have shown that large MR effects can also be found in nonoxide materials such as $Eu_{14}MnPn_{11}$ (where Pn = Sb, Bi)[2,3] and the ACr_2S_4 spinels (A = Fe, Cu).[4] The larger, more polarizable anions in the latter compounds may give rise to enhanced magnetic exchange[5] relative to the oxides and make them ideal candidates for studying the origin of the MR effect in mixed valent systems. In order to systematically vary magnetic and transport properties, tunable mixed valent systems are necessary (such as pseudoternary sulfides) in which the metal oxidation state can be adjusted through A-site substitution. These compounds would be analogous to the manganese oxides in terms of their formal electronic configuration of the ions, but the transport and magnetic properties would be mediated through metal−sulfur interactions.

An ideal compound for studying these issues would be the "La_2CrS_4" phase which has been reported several times in the literature. La_2CrS_4 appears to have the requisite Cr(II) d^4 metal ions that can potentially be oxidized to Cr(III) d^3 by substituting Sr^{2+} for La^{3+} (e.g., $La_{2-x}Sr_xCrS_4$). The first reports of La_2CrS_4 appeared from Patrie et al. in which the compound was characterized by powder XRD as being face-centered monoclinic with a hexagonal substructure.[6,7] A subsequent study by Kurbanov et al.[8] reported an orthorhombic cell. Later, Flahaut[9] characterized La_2CrS_4 to be of the $La_{32.6}M_{11}S_{60}$ type[10] (space group $R3m$)[11] with divalent chromium, but cell parameters or structural details were not given. We report here the synthesis, structure, and magnetic properties of "La_2CrS_4" which has the actual composition $La_{15.9(2)}Cr_{5.4(2)}S_{32}$. The $La_{15.9(2)}Cr_{5.4(2)}S_{32}$ compound has significant structural and compositional differences from the reported[9] $La_{32.6}M_{11}S_{60}$ structure type and does not contain divalent chromium or $R3m$ crystal symmetry.

The title compound was prepared in a sealed silica ampule from La_2S_3, Cr, and S in a 1:1:1 molar ratio in the presence of 20 wt % $LaCl_3$ flux. The mixture was fired at 1050 °C for 48 h and quenched to room temperature. The sample was washed with ethanol to remove the flux, leaving a brown powder with irregularly shaped opaque dark brown single crystals. Black Cr_2S_3 byproduct is formed in the reaction (WDS and XRD analysis) which primarily separates to the walls of the reaction vessels. Powder XRD analysis on the remaining sample showed the compound to be single phase (see supporting material), however, SEM analysis shows small pockets of Cr_2S_3 in the samples that go undetected in the XRD analysis. Repeated attempts to prepare the compound from a stoichiometric ratio of reagents and varying reaction conditions leads to the formation of the known[12−15] misfit layer compound $(LaS)_{1.20}CrS_2$. Refiring single-phase samples also leads to the formation of $(LaS)_{1.20}CrS_2$ and other unidentified phases. Wavelength dispersive microprobe analysis (WDS) of the single crystals gave atomic percentages[16] of La, 29.8(±0.4)% and Cr, 10.2(±0.2)% which is in excellent agreement with the formula determined from the X-ray refinement (La, 30.08%; Cr, 9.92%; S, 60.00%) and magnetic susceptibility studies (see below). The average of the X-ray and WDS compositions gives the formula $La_{15.9(2)}Cr_{5.4(2)}S_{32}$ (La, 29.9(±0.4)%; Cr, 10.1(±0.3)%; S, 60.0%). Repeated microprobe analysis on multiple crystals showed no chloride incorporation into the structure. This finding is consistent with the fact that polycrystalline $La_{15.9(2)}Cr_{5.4(2)}S_{32}$ can be prepared in the absence of flux at 1400 °C whereas other closely related chlorosulfides (e.g., $Nd_{15.2(2)}Cr_{4.6(2)}S_{27.8}Cl_{4.2}$)[17] require chloride in their synthesis mixtures.

$La_{15.9(2)}Cr_{5.4(2)}S_{32}$ is rhombohedral, space group $R\bar{3}m$, with cell dimensions $a = 13.979(1)$ Å and $c = 21.845(1)$ Å.[18] These dimensions are very close to those reported for the $La_{32.66}M_{11}S_{60}$ (M = Mn, Fe) phases[10] transformed to the hexagonal setting of the $R3m$ rhombohedral cell.[11] The original report of La_2CrS_4 by Patrie et al.[7] gave hexagonal sub-cell constants of $a_h = 8.102$ Å, $c_h = 7.25$ Å. These parameters are related to those of the $La_{15.9(2)}Cr_{5.4(2)}S_{32}$ cell by the following: $a = \sqrt{3}a_h$ and $c = 3c_h$,

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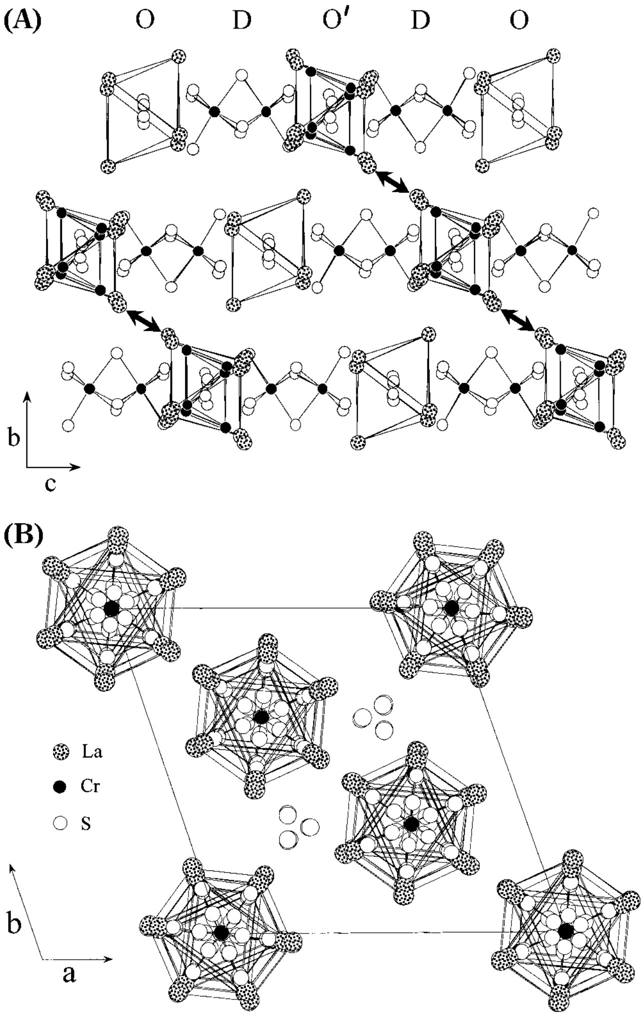

Figure 1. (A) The −O−D−O′−D− chains of $\mathrm{La_{15.9(2)}Cr_{5.4(2)}S_{32}}$ running parallel to the *c*-axis. La−S bonds have been omitted for clarity. The $\mathrm{Cr_2S_9}^{12-}$ dimers (D), $\mathrm{La_6S_{13}}$ edge-bridged octahedral cluster (O), and the $\mathrm{La_{3.6}Cr_{1.4}S_{13}}$ edge-bridged octahedral cluster (O′) are labeled and the short 2.72(1) Å La3B−La3B separation is indicated by the double headed arrow. (B) Projection down the *c*-axis showing the −O−D−O′−D− chains. The edge-bridging sulfides of the O and O′ clusters have been omitted for clarity.

indicating that the compounds are the same. Intensity statistics and examination of the monoclinic solution of the structure clearly indicate that the compound has $\bar{3}m$ crystal symmetry.

The structure contains $\mathrm{Cr_2S_9}^{12-}$ face-shared bioctahedra that reside on the $\bar{3}$ axes of the cell. The $\mathrm{Cr_2S_9}^{12-}$ dimers (D) are alternately linked by two types of $\mathrm{M_6S_{13}}$ edge-bridged octahedral cluster units (O and O′), forming chains running parallel to the *c*-axis (Figure 1). The three subunits will be described individually below. In addition there is a seven-coordinate lanthanum ion, La1, separating the −O−D−O′−D−O− chains.

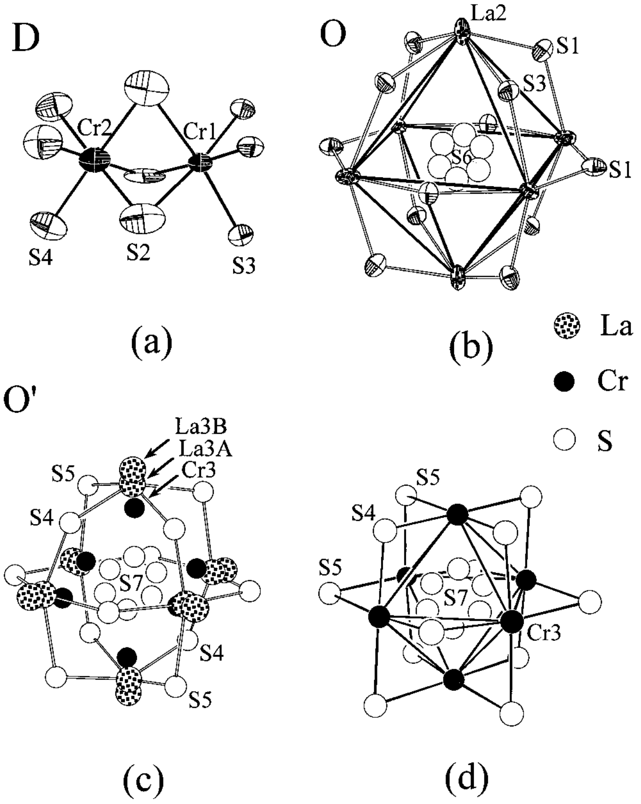

Figure 2. (a) The $\mathrm{Cr_2S_9}^{12-}$ dimer, (b) the $\mathrm{La_6S_{13}}$ edge-bridged octahedral cluster, O, (c) the $\mathrm{La_{3.6}Cr_{1.4}S_{13}}$ edge-bridged octahedral cluster, O′ (only La3A−S bonds shown), and (d) the O′ cluster showing only the Cr3 sites (La3A and La3B omitted). The lines between the metal ions in O and O′ denote the octahedral arrangement of metal atoms and do not signify metal−metal bonding.

The $\mathrm{Cr_2S_9}^{12-}$ dimers are distorted face-shared bioctahedra (FSBO)[19,20] with Cr−Cr distances of 3.014(5) Å (Figure 2a). The terminal Cr−S distances are 2.410(6) and 2.490(5) Å, whereas the bridging Cr−S2 distances are 2.545(6) and 2.626(7) Å. The Cr1−S contacts are uniformly ~0.08 Å shorter than those to Cr2. This asymmetry in the $\mathrm{Cr_2S_9}^{12-}$ unit (and the large thermal motion associated with Cr2, S2, and S4) may be caused by the bridge to the partially occupied $\mathrm{M_6S_{13}}$ unit (O′) adjacent to Cr2. Analysis of the metric parameters in the $\mathrm{Cr_2S_9}^{12-}$ dimer[21] using the structural moduli for d^3-d^3 FSBOs developed by Cotton and Ucko[20] indicates that the metal−metal interactions are intermediate to those of the weakly interacting $\mathrm{Cr_2X_9}^{3-}$ ions (X = Cl, Br, I; $d_{\mathrm{Cr-Cr}} = 3.12-3.32$ Å)[20,22−27] and the M−M bonded $\mathrm{Mo_2X_9}^{3-}$ ions (X = Cl, Br, I; $d_{\mathrm{Mo-Mo}} = 2.38-2.82$ Å).[5,20,28,29] This conclusion is in good agreement with the magnetic exchange constants, *J*, for the same series (see below).

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(18) X-ray data for $\mathrm{La_{15.9(2)}Cr_{5.4(2)}S_{32}}$: rhombohedral, space group $R\bar{3}m$, $a = 13.979(1)$ Å, $c = 21.845(1)$ Å, $V = 3697.17(5)$ Å^3, $Z = 6$, $D_x = 4.756$ g cm^{-3}; $T = 153(2)$ K, $R(F) = 5.51\%$, w$R(F^2) = 10.18\%$ and GOF = 1.11 for all 828 unique data. Data were collected and the structure solved (SHELXTL) in a monoclinic setting and subsequently transformed up to the rhombohedral cell $R(\mathrm{int}) = 5.4\%$. Free refinement of all sites and occupancies gave residuals of $R(F) = 5.8\%$, w$R(F^2) = 10.82\%$ (all data) and a formula of $\mathrm{La_{15.9}Cr_{5.2}S_{32}}$ with an average Cr oxidation state of +3.1. A SUMP instruction was written to fix the Cr oxidation state at +3 in the final refinement which gave the formula $\mathrm{La_{15.9(2)}Cr_{5.4(2)}S_{32}}$.

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Ball-and-stick drawings of the regular La_6S_{13} edge-bridged octahedral cluster (O) and the disordered edge-bridged octahedral cluster (O′) are shown in Figures 2b–d, respectively. The general atom positions of O and O′ are reminiscent of the edge-bridged octahedral M_6X_{12} clusters (X = halide).[30] The metal halide structures are defined by an octahedron of metal atoms in which 12 halide ions bridge each octahedral edge. These units are found in some binary metal halides, such as $PtCl_2$[31] and ZrI_2,[32] but the clusters in $La_{15.9(2)}Cr_{5.4(2)}S_{32}$ differ from the prototypical M_6X_{12} clusters in several important aspects. The differences are best illustrated in cluster O. First, the long La–La separations within the octahedra are all greater than 5 Å in contrast to the relatively short M–M interactions in many of the La_6 subhalide clusters (e.g., LaI, $d_{La-La} = 3.93$).[33] Second, the La2 atoms in the La_6S_{13} clusters (O) sit outside of the S_4 faces of the S_{12} array by ~1.7 Å (see Figure 2b), in contrast to the typical square planar MX_4 coordination in the M_6X_{12} metal halides. Third, there is a 6-fold disordered sulfur atom, S6, on the inside of the octahedral cluster. This site is reminiscent of the disordered cations in the cubic holes between the M_6S_8 clusters of the Chevrel phases,[34,35] such as $InMo_6S_8$ and $Li_xMo_6S_8$.[36,37] These two features allow the La2 ions to increase their coordination numbers from five in an idealized M_6X_{12} system to eight in the present compound. The eight La2–S contacts are in the range 2.903(7)–3.197(24) Å. Finally, there is a slight compression of the La_6 octahedron along the $\bar{3}$ axes.

The second edge-bridged octahedral cluster (O′) is more complicated than O and is plagued by four partially occupied sites (see Figure 2c). The M_6 octahedron in O′ is a composite of Cr3, La3A, and La3B and is only 89% occupied in total. Of the total 5.3 metal atoms per octahedron, 1.4 are Cr and 3.9 are La. As shown in Figure 2c, there are two La sites that are outwardly displaced from Cr3 by 1.12(2) Å (La3A) and 1.67(2) Å (La3B). The Cr3 atoms are centered in the S_4 faces of the S_{12} arrays forming a fairly regular M_6X_{12} unit (see Figure 2d). The La3B sites are reminiscent of the La2 sites in cluster O. There is also a 6-fold disordered sulfur atom, S7, in the center of this cluster but a somewhat smaller compression along the $\bar{3}$ axis relative to cluster O. In contrast to the metal ions and S7, the remaining 12 sulfide sites of O′ are fully occupied and well behaved. Because of the partial occupancy and disorder associated with the M3 and S7 sites, the exact coordination geometries and bond distances are difficult to assess. Cr3 is five-coordinate with bonds to S4 and S5 of 2.53(1) Å and 2.64(1) Å, respectively. The most reasonable Cr3–S7 distance is 2.34(2) Å, but because there are six equivalent S7 sites, each 1/6 occupied, five other contacts are possible which range 1.70(6)–3.42(2) Å. The outward displacements of La3B and La3A allow these ions to achieve higher coordination numbers relative to Cr3. La3B is eight-coordinate with La–S distances in the range 2.708(13)–3.217(7) Å, and La3A is seven-coordinate with La–S distances in the range 2.710(11)–3.225(6) Å.

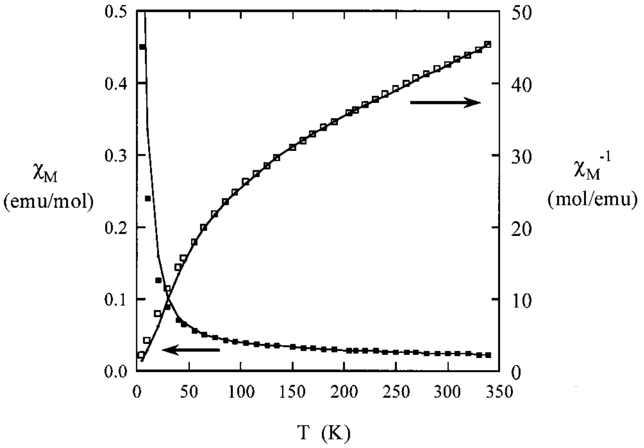

Figure 3. The molar susceptibility (χ_M, solid squares) and reciprocal molar susceptibility (χ_M^{-1}, empty squares) of $La_{15.9(2)}Cr_{5.4(2)}S_{32}$. The solid line represents the fit of the data to the three-term model given in the text.

In $La_{15.9(2)}Cr_{5.4(2)}S_{32}$ and all other compounds of this structure type studied thus far, there is the same –O–D–O′–D– alternation of bioctahedra and octahedral clusters. While the occupancies and atomic constituents in the O′ and D units vary widely from compound to compound, the metal ion positions of O′ are always disordered over at least two sites. The origin of this disorder appears to result from short La–La contacts between the –O–D–O′–D– chains. The La–La separations are all greater than 5.0 Å within each cluster, but there is a very short 2.72(1) Å La3B–La3B separation between adjacent chains (see Figure 1a). To avoid this interaction in the crystal lattice, the La3B site occupancy cannot exceed 50%. Below this concentration, only La3B–La3A (3.27(1) Å) and La3B–Cr3 (4.39(2) Å) are present. In $La_{15.9(2)}Cr_{5.4(2)}S_{32}$, the La3B occupancy is 27.5% and is close to the Cr3 occupancy (21.5%). The interchain La–La distances to cluster O (La2) all exceed 4.1 Å which is consistent with the absence of disorder in this unit.

The magnetic susceptibility of $La_{15.9(2)}Cr_{5.4(2)}S_{32}$ was measured from 5–350 K using a SQUID magnetometer. The data were fit (see Figure 3) by using a three-term model[38,39] that included terms for two antiferromagnetically coupled d^3-d^3 $Cr_2S_9^{12-}$ dimers and a S=3/2 Curie–Weiss ion for the Cr^{3+} in the O′ cluster. The expression for the susceptibility is:

$$\chi = \frac{2N_A g^2 \mu_B^2}{3kT}\left(\frac{2e^{2x} + 10e^{6x} + 28e^{12x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x}}\right) + N\alpha + n'\left(\frac{C}{T}\right)$$

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where $x = -J/kT$, $n' =$ mole fraction of edge-bridged octahedral Cr^{3+} ions per two $Cr_2S_9^{12-}$ units, $N\alpha$ is the temperature independent susceptibility, C is the Curie constant calculated for one mole of Cr^{3+}, N_A is Avogadro's constant, k is the Boltzmann constant, J is the antiferromagnetic exchange constant, and μ_B is the Bohr magneton. In the analysis, g was fixed at 2.0 based on previous studies[28] and three parameters were refined: x, n' and $N\alpha$. Because our analysis neglected intercluster couplings, only the data between 65 and 350 K were used in the least-squares regression as the contributions from these interactions should be negligible above 65 K. The agreement between the calculated and observed susceptibility is excellent above 65 K but deviates slightly below 40 K where intercluster couplings become important.[22] Refinement of the parameters led to the following values: $J = -97(\pm 10)$ K, $n' = 1.5$ (± 0.2), $N\alpha = -0.017(\pm 0.005)$. The value of n' (1.5) gives a total chromium content of 5.5 per formula unit in excellent agreement with the microprobe analysis (5.5) and is only slightly higher than the structural refinement (5.3). This small error may be due to paramagnetic impurities in the sample (i.e., Cr_2S_3), which would be reflected in this term, or a slight deviation in the g value from 2.0. The magnetic exchange constant, J, is an order of magnitude larger than those of the isoelectronic $Cr_2X_9^{3-}$ ions (0 to -16 K)[28] but a factor of ~5 less than the $Mo_2X_9^{3-}$ ions (-300 to -800 K).[5,28] The increase in J relative to the chromium halides is quite reasonable in view of the 0.1–0.2 Å decrease in Cr–Cr separation (the dominant factor in magnetic exchange)[5] and the fact that the larger, more polarizable ions give rise to enhanced M–M overlap[40] and antiferromagnetic exchange.[5] $TlCr_5S_8$, which also has antiferromagnetically coupled $Cr_2S_9^{12-}$ units, has an estimated J value of -84 K and a similar Cr–Cr separation of 2.96 Å.[41]

The combination of structural, magnetic, and microprobe data on the title compound give a consistent composition of $La_{15.9(2)}Cr_{5.4(2)}S_{32}$ which indicates an all-Cr(III) compound. This finding contrasts all earlier reports suggesting an all-Cr(II) compound.[9] The discrepancies in oxidation states arise from differences in composition in the disordered edge-bridged octahedral unit (O′) of the $La_{32.66}M_{11}S_{60}$ structure type.[9,10] In the Collin structural model (for M = Mn, Fe), the disordered cluster unit has three partially occupied M atoms in the center of an La_6 octahedron. The Cr3 sites in our structure are completely absent in the Collin model. In turn, the three metal atoms inside the O′ cluster in the Collin model ($d_{Mn-Mn} \approx 2.0$ Å) are refined as a 6-fold disordered sulfur atom in our model. In subsequent publications,[17] we shall show that the FSBO dimers and the partially occupied edge-bridged octahedra O′ can be completely devoid of transition metals as the situation warrants. The 6-fold disordered sulfur atoms in the O and O′ clusters are also absent in some cases. In addition, we have found that the structure type can accommodate extensive amounts of chloride when prepared in chloride fluxes.[17]

Acknowledgment. We thank the NSF-DMR (# 9223060) for financial support of this work.

Supporting Information Available: A complete listing of positional parameters, thermal parameters, bond distances and angles for $La_{15.9(2)}Cr_{5.4(2)}S_{32}$, and powder XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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