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Introduction

The reduced ternary transition metal oxides, or bronzes, are a class of materials with a vast variety of structures and chemistries.1 These materials systems, which include reduced ternary tungsten and molybdenum oxides, have been shown to display remarkable physical phenomena such as superconductivity,^{2,3} charge density waves,⁴⁻¹¹ and electronic properties associated with low dimensionality.¹²⁻¹⁵ These electronic features arise from the combination of hybridization of the Mo 4d states with O p-orbitals and ordered O vacancies that are a function of the structural chemistry of the bronze, leading to a combination of orientation-dependent itinerancy and reduced dimensionality. Here, we discuss such a system that contains a periodic array of Mo₈O₃₆ superatoms-multi-atom clusters, that behave electronically similarly to single atoms-which are electrically isolated and separated from each other by nanometer spacings. Such superatom cluster systems are the subject of increasing research interest as a materials platform

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Interacting nanoscale magnetic superatom cluster arrays in molybdenum oxide bronzes

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In this study, we examine several reduced ternary molybdates in the family of yellow rare earth molybdenum bronzes produced by electrochemical synthesis with composition $LnMo_{16}O_{44}$. These compounds contain an array of electrically isolated but magnetically interacting multi-atom clusters with composition Mo_8O_{36} . These arrayed superatom clusters support a single hole shared among the eight molybdenum atoms in the unit, corresponding to a net spin moment of $1\mu_{B}$, and exhibit magnetic exchange between the units *via* the MoO_4 tetrahedra (containing Mo^{6+} ions) and the LnO_8 cubes (containing Ln^{3+} ions). The findings presented here expand on the physics of the unusual collective properties of multi-atom clusters and extend the discussion of such assemblages to the rich structural chemistry of molybdenum bronzes.

to study how macroscopic matter can mimic atomic behavior $^{16-19}$ with intercluster interactions analogous to interatomic interactions. 20,21

This study describes a system of nanoscale superatom clusters arrayed in a fashion analogous to individual atoms in a crystal lattice, building upon such studies on multi-atom cluster magnet systems in transition metal cluster compounds, such as GaT_4S_8 (where T is a transition metal like V or Mo)^{22,23} and LiZn₂Mo₃O₈.^{24,25} Unlike the former of these systems, the system studied here does not undergo a temperature-dependent structural phase transition,²⁶ but rather the Mo₈O₃₆ clusters are arrayed in rhombohedral lattice at all temperatures with a small relative volume expansion coefficient of the order of approximately $1.1 \times 10^{-5} \text{ K}^{-1}$.²⁷ Furthermore, the magnetic clusters in our system do not exist in a frustrated geometry, such as those in LiZn₂Mo₃O₈. The system studied here displays antiferromagnetic magnetic ordering arising from the exchange between clusters. The clusters themselves are composed of molybdenum and oxygen atoms that, similar to the Mo₄S₄ cluster units in GaMo₄S₈ and the Mo₃O₁₁ cluster units in LiZn₂Mo₃O₈, support a net magnetic moment of $1\mu_{\rm B}$, and the inter-cluster interaction is governed by the collective clusters properties that exhibit physical properties beyond those available from the constituting atoms alone.

To improve our understanding of these unique materials with ordered arrays of nanosized magnetic superatom clusters, we measured the temperature and field dependence of the magnetic susceptibility and the resistance of crystal samples of LaMo₁₆O₄₄, YMo₁₆O₄₄, NdMo₁₆O₄₄ and GdMo₁₆O₄₄. The results reported here show magnetic properties corresponding to predicted magnetic order in these materials,²⁷ providing

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insight into how the remarkable structural chemistry of superatom-based materials contributes to intriguing physical phenomena. The emergent properties of this system reveal that it is an exemplary case of a material in which control of the coupling and exchange between superatom clusters can produce new types of magnetic and conductive materials.

Results and discussion

The yellow molybdenum bronzes, reduced rare earth molybdenum oxides of composition $LnMo_{16}O_{44}$, where Ln is a lanthanide ion such as La, Y, Gd or Nd, have a structure formed from corner shared MoO_4 tetrahedra and MoO_6 octahedra, with the lanthanide ions situated in a cubic cavity formed by eight MoO_4 tetrahedra (Fig. 1a). Key structural features of these compounds are electrically isolated zero-dimensional Mo_8O_{36} clusters that are a subunit of the ReO₃-type structure,²⁸ formed from eight MoO_6 octahedra corner-sharing a total of 12 oxygen atoms (Fig. 1b). These Mo_8O_{36} clusters are linked *via* MoO_4 tetrahedra and LnO_8 cubes to adjacent Mo_8O_{36} clusters in these phases. The ReO₃-type cubic Mo_8O_{36} clusters are arranged as shown in



Fig. 1 a, Structure of LnMo₁₆O₄₄. The green cube is the Ln coordination polyhedron that is corner connected to yellow MoO₄ tetrahedra; linked to the blue MoO₆ octahedra. Eight MoO₆ octahedra form a ReO₃-type Mo₈O₃₆ cluster. b, Detailed view of the Mo₈O₃₆ cluster with the orientation rotated to more easily see the cubic arrangement of the Mo atoms at the centers of the blue MoO₆ octahedra; the oxygen atoms at the corners of the polyhedra are not shown. c, The arrangement of the cubes formed by the eight Mo atoms, where the Mo–Mo contacts are shown in blue and Ln ions shown in green; oxygen atoms and MoO₄ tetrahedra are omitted to show the periodic cluster array. Intracluster and intercluster nearest-neighbor Mo–Mo distances (3.7 Å and 5.9 Å, respectively) and rhombohedral unit cell *a*-lattice constant, 10.8, which represents both Ln–Ln distance and the distance between the centers of nearest-neighbor Mo₈O₃₆ clusters, are shown.

Fig. 1c, where the Mo ions at the centers of the MoO_6 octahedra are shown as blue dots and the Ln ions are shown as green dots. The Mo₈O₃₆ clusters are separated by a distance of 10.8 Å (the value of the rhombohedral unit cell a-lattice constant) and 11.1 Å between the center of the nearest neighbor and next nearest neighbor Mo₈O₃₆ clusters, respectively (changes in these distances for different LnMo16O44 compositions due to different Ln radii are less than 0.02 Å), corresponding to a distance of about 5.9 Å between nearest Mo atoms in different Mo₈O₃₆ clusters. Nearest neighbor Mo atoms within a cluster are separated by distances of about 3.7 Å for all compositions. Details of the crystal structures were given earlier (ref. 27) and the crystallographic information files (CIFs) may be obtained from the Fachinformationszentrum Karlsruhe²⁹ on quoting the deposition numbers CSD 428592-428597. Importantly, within the clusters the Mo ions have a octahedral coordination with three short Mo–O bonds (\approx 1.85 Å) with the oxygen along the cube edges connecting to the next Mo in the cluster and three long bonds (≈ 2.05 Å). The short bonds (*cf.* perovskite BaMoO₃ with a bond length of 2.02 Å) may be expected to lead to enhanced crystal field splitting, which is in fact the case based on our density functional calculations.

The stoichiometry of the compound LnMo₁₆O₄₄ indicates mixed valence Mo: all the molybdenum atoms located in the MoO_4 tetrahedra are clearly hexavalent (Mo^{6+}), whereas the molybdenum atoms located in the Mo₈O₃₆ clusters have an average valence of +4.625, given by bond valence sums calculations, suggesting octahedral sites contain both Mo⁴⁺ and Mo^{5+,27} A magnetic moment is therefore expected with the spins located within the Mo₈O₃₆ clusters. Specifically, a single hole is distributed among the eight Mo atoms in the Mo₈O₃₆ cluster, giving moments of approximately $1/8\mu_{\rm B}$ per octahedral Mo atom. The crystal structure has two symmetry inequivalent octahedral Mo atoms, denoted Mo1 contributing two atoms to each cube and Mo3 contributed the remaining six. We did density functional calculations using the experimental structure of the CeMo₁₆O₄₄ compound from ref. 29, but with Ce substituted by La to simulate the LaMo16O44 studied here and to avoid complications from the Ce moments. These were done with the linearized augmented planewave method similar to our previously reported calculations.²⁷ Fig. 2 shows the electronic density of states (DOS) and a schematic for the formation of the active cluster orbitals. We find that the moments are practically equal on the Mo1 and Mo3 sites. The moments arise from a single hole in set of six bands that comprise the lowest Mo d orbitals. These bands give rise to a narrow 0.5 eV wide peak in the electronic density of states. This peak is well separated by gaps from both the lower lying O p derived bands and higher lying Mo d bands. The peak can be understood as follows using a Cartesian coordinate system where the cube edges form the axes. In this case, octahedral crystal field splits the five d-orbitals into three lower energy t_{2g} orbitals and two higher energy eg orbitals. The t_{2g} orbitals can be labeled xy, xz and yz, and are actually π antibonding combinations of the metal d and O p states. In any case, this gives 24 orbitals from the eight Mo on the cube corners. The orbitals



Fig. 2 a, Calculated electronic density of states without spin polarization with the bonding cluster state labelled "F" and the projections onto the d-orbitals of the octahedral and tetrahedral Mo atoms, as defined by an LAPW sphere radius 1.8 bohr. b, Schematic showing the formation of the bonding orbital on one face of the cube. Note that there are six faces leading to the six bands making up peak "F".

from atoms sharing an edge of the cube hybridize, and this hybridization is important because of the Mo-O bond lengths. This hybridization occurs when orbitals have lobes directed towards each-other, with a common O p π orbital, e.g., xy-p_v-xy, but not for example $xy-p_y-xz$. The result is that each cube face has one maximally bonded orbital, which are the symmetric combinations with 90 degree rotations along an edge as depicted in Fig. 2b, where we consider the z face. This face has a bonded orbital consisting of xy orbitals on the Mo at the four corners, anti-bonding hybridized with O p_x and p_y along the edges running along y and x, respectively. Orbitals of this type on a face are orthogonal to the orbitals along neighboring faces because of the orthogonality of the xy, xz and yz orbitals. The six bonding orbitals, corresponding to the six faces of a cube are the origin of the six bands making up the active DOS peak, occupied by 11 electrons, thus providing a spin moment of $1\mu_{\rm B}$ per cluster.

As temperature decreases, exchange interactions mediated by delocalized carriers within the metallic Mo₈O₃₆ cluster eventually lead to ferromagnetic ordering of the spins on the eight Mo atoms in the Mo₈O₃₆ cluster that gives the cluster a net $1\mu_{\rm B}$ moment below a cross-over temperature, which does not correspond to a true phase transition, but is rather something analogous to the transition at the Burns temperature in relaxor ferroelectrics. Once the spins of individual Mo atoms in an individual cluster are aligned, a magnetic exchange interaction is predicted to occur between Mo₈O₃₆ clusters, with magnetic ordering below a certain temperature, T_N . In addition to intracluster ferromagnetic order within the Mo_8O_{36} cluster and inter-cluster antiferromagnetic order below $T_{\rm N}$, additional paramagnetic behavior is expected to occur for magnetic lanthanides, such as Nd and Gd, at all temperatures according to the Curie-Weiss law.

Magnetometry

Both LaMo₁₆O₄₄ and NdMo₁₆O₄₄ samples were synthesized by electrocrystallization whereas $YMo_{16}O_{44}$ and $GdMo_{16}O_{44}$

samples were synthesized by direct reaction per the procedures described in the methods section. To test that the magnetic ordering in this class of reduced molybdate bronzes arises from Mo_8O_{36} - Mo_8O_{36} intercluster interactions, a collection of very small single crystals of $LaMo_{16}O_{44}$ ($YMo_{16}O_{44}$) were placed together in a non-magnetic glycerin capsule and mounted in a vibrating sample magnetometer (VSM), where the total magnetic moment of the sample as a function of temperature was measured. $LaMo_{16}O_{44}$ and $YMo_{16}O_{44}$ were selected for this measurement because both La and Y are non-magnetic ions; therefore, any observations of magnetic ordering in $LaMo_{16}O_{44}$ ($YMo_{16}O_{44}$) arise from inter-cluster interactions. The magnetic susceptibility, χ , of $LaMo_{16}O_{44}$ and $YMo_{16}O_{44}$ measured at 0.1 T is shown in Fig. 3a. No significant differences between zerofield-cooled and field-cooled measurements were observed.

Both LaMo₁₆O₄₄ and YMo₁₆O₄₄ show increasing magnetic susceptibility as the temperature is decreased from room temperature, with a transition at approximately 6.5 K for LaMo₁₆O₄₄ and 3.1 K for YMo₁₆O₄₄, that is consistent with an antiferromagnetic phase transition, indicative of interactions between Mo₈O₃₆ clusters (Fig. 3a). The broadening of the transition in both LnMo16O44 samples is likely due to the assembly of numerous small crystals instead of an oriented large single crystal, as the axial orientations of the individual crystals comprising the sample will have different orientations relative to the magnetic field. The inverse susceptibility versus temperature, shown in Fig. 3b, reveals a linear relationship above the 6.5 K and 3.1 K transition temperatures for LaMo₁₆O₄₄ and YMo₁₆O₄₄, respectively, signifying paramagnetic behavior in accordance with the Curie-Weiss law. The linear fits to these plots have small non-zero, negative T-intercepts indicative of antiferromagnetic interactions in both materials. Fits of the susceptibility data above the transition temperatures to χ = $C/(T - \theta)$, parameter values for which are given in Table 1, yield Weiss constants of -5.43 K and -3.61 K for LaMo₁₆O₄₄ and YMo₁₆O₄₄, and are in good agreement with the antiferro-



Fig. 3 a, Magnetic susceptibility of LaMo₁₆O₄₄ and YMo₁₆O₄₄, measured at 0.1 T, with temperature shown on a log scale. The magnetic phase transition due to Mo–Mo interactions is visible at 6.5 K for LaMo₁₆O₄₄ and a 3.1 K for YMo₁₆O₄₄ and is labeled. b, The inverse susceptibility *versus* temperature of LaMo₁₆O₄₄ and YMo₁₆O₄₄, showing the paramagnetic behavior down to the transition temperature. The linear fit to the Curie–Weiss law is indicated, together with the Weiss constant, θ .

 Table 1
 Curie–Weiss constants for LnMo₁₆O₄₄ from magnetic susceptibility measurments

LnMo ₁₆ O ₄₄ composition	Curie Constant, C (emu cm ⁻³ K)	Weiss constant, θ (K)	Effective magnetic moment, $\mu_{\rm eff}$
$LaMo_{16}O_{44}$ YMo ₁₆ O ₄₄ NdMo ₁₆ O ₄₄ GdMo ₁₆ O ₄₄	$\begin{array}{l} (4.129\pm0.006)\times10^{-4}\\ (3.334\pm0.006)\times10^{-4}\\ (3.12\pm0.005)\times10^{-3}\\ (2.682\pm0.001)\times10^{-2} \end{array}$	$\begin{array}{c} -5.43 \pm 0.02 \\ -3.61 \pm 0.02 \\ -11.65 \pm 0.08 \\ -1.7 \pm 0.01 \end{array}$	$\begin{array}{l} 1.36 \mu_{\rm B} \\ 1.22 \mu_{\rm B} \\ 3.75 \mu_{\rm B} \\ 10.9 \mu_{\rm B} \end{array}$

magnetic transition temperatures, $T_{\rm N}$, of 6.5 K and 3.1 K labeled in Fig. 3a.

Magnetic susceptibility measurements on NdMo₁₆O₄₄ and GdMo₁₆O₄₄ shown in Fig. 4a are primarily dominated by the paramagnetic signal of the magnetic Ln ions Nd and Gd (local magnetic moments of $3.6\mu_{\rm B}$ and $7.94\mu_{\rm B}$, respectively), as shown in the inverse susceptibility versus temperature plots (Fig. 4b and c); the non-zero, negative T-intercepts indicate antiferromagnetic interactions. Fits of the susceptibility data to the Curie-Weiss law $\chi = C/(T - \theta)$, parameter values for which are given in Table 1, yield negative Weiss constants of -11.65 ± 0.08 K and -1.7 ± 0.01 K for NdMo₁₆O₄₄ and GdMo₁₆O₄₄, respectively. The localized magnetic moments of Nd and Gd are responsible for the order of magnitude increases in the Curie constant for $NdMo_{16}O_{44}$ and $GdMo_{16}O_{44}$ compared to LaMo₁₆O₄₄ and YMo₁₆O₄₄. However, the antiferromagnetic order arising from Mo₈O₃₆-Mo₈O₃₆ interactions, as with LaMo₁₆O₄₄ and YMo₁₆O₄₄ is still present in NdMo₁₆O₄₄ and GdMo₁₆O₄, but is only a small contribution relative to the overall susceptibility that is due to the magnetic ions Nd and Gd.

The effective magnetic moments above $T_{\rm N}$ were calculated from the Curie constants for each sample. LnMo₁₆O₄₄ samples with nonmagnetic lanthanides, LaMo₁₆O₄₄ and YMo₁₆O₄₄, were calculated to support effective magnetic moments, $\mu_{\rm eff}$, of 1.36 $\mu_{\rm B}$ and 1.22 $\mu_{\rm B}$, respectively. These effective magnetic



Fig. 4 a, Magnetic susceptibility of NdMo₁₆O₄₄ and GdMo₁₆O₄₄, measured at 0.1 T, with temperature shown on a log scale; the susceptibility curves for LaMo₁₆O₄₄ and YMo₁₆O₄₄ are shown for reference. b, The inverse susceptibility *versus* temperature of NdMo₁₆O₄₄, showing the paramagnetic behavior, with a linear fit according to the Curie– Weiss law (navy) and the two-sublattice mean field model (red) indicated. c, The inverse susceptibility *versus* temperature of GdMo₁₆O₄₄, showing the paramagnetic behavior, with the Curie–Weiss law fit. The Weiss constant, θ , is shown for both NdMo₁₆O₄₄ and GdMo₁₆O₄₄.

moments correspond with g-factor values of 1.57 and 1.40, respectively, according to $\mu_{\text{eff}} = g(S(S + 1))^{1/2}$, where *S* is the spin of the cluster; here, S = 1/2. Differences in these values are suspected to primarily arise from small uncertainties in the measured sample mass. The reduction in the *g*-factor value relative to the ideal *g*-factor value, $g_e \approx 2$, arises from a partial unquenched orbital spin orbit coupling contribution to the total angular moment of the d¹ and d² electrons in the MoO₆ octahedra.³⁰ No temperature-dependent crossover is expected to occur for these octahedral complexes with few-electron occupation of the d-orbitals, nor is such an effect observed in the magnetometry data.

The net effective magnetic moments above T_N calculated from the Curie constants for NdMo₁₆O₄₄ and GdMo₁₆O₄ are given in Table 1. Assuming the Ln³⁺ moments are uncoupled to the Mo moments, we calculate the magnetic moments on the Mo₈O₃₆ and Ln sublattices, where the total Curie constant, C, is the sum of the contributions from the two sublattices, $C = C_{Mo_8O_{36}} + C_{Ln}$, and, for the purpose of this study, $C_{Mo_8O_{36}}$ is assumed to be the value measured for LaMo₁₆O₄₄. The calculated effective magnetic moments are $3.5\mu_B$ on the Nd³⁺ ions in NdMo₁₆O₄₄—in good agreement with the expected $3.5\mu_B$ the I_{9/2} state of the Nd³⁺ ion. The value of $10.9\mu_B$ for the Gd³⁺ ions in GdMo₁₆O₄₄, while somewhat high relative to the $7.94\mu_B$ expected for the S_{7/2} state of the Gd³⁺ ion, is close to what is expected, and the difference can be ascribed to uncertainties in the sample mass that account for the difference.

The magnetic susceptibility in GdMo₁₆O₄₄ is dominated by paramagnetism associated with Gd³⁺, the effective magnetic moments on which are substantially higher than the Mo₈O₃₆ moments. The hyperbolic shape of the inverse susceptibility *versus* temperature plot for NdMo₁₆O₄₄, however, lends itself to a fit to a the two-sublattice mean field model,³¹ the inverse susceptibility equation for which can be written as $=\frac{T-\theta}{C}-\frac{\sigma}{T-\theta'}.$ Here, $C = C_{MO_8O_{36}} + C_{Nd}$ and θ' and σ are fitting parameters containing information on Mo₈O₃₆-Mo₈O₃₆ exchange, Nd-Nd exchange, and Mo₈O₃₆-Nd exchange in the form of coupling constants. The model fits well to the data, and the calculated magnetic coupling constants from the twosublattice magnetization mean field model for $NdMo_{16}O_{44}$ are given in Table 2. The low value for Mo₈O₃₆-Nd exchange supports the hypothesis that Ln³⁺ moments are uncoupled to the Mo moments, and the modest +11.1 mol emu⁻¹ value for Nd-Nd suggests some ferromagnetic exchange occurs between the lanthanides. The -46 mol emu⁻¹ coupling constant for Mo₈O₃₆-Mo₈O₃₆ indicates that the strongest magnetic

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Table 2 Magnetic coupling constants in NdMo₁₆O₄₄

Mo_8O_{36} -Nd	Nd–Nd	$Mo_8O_{36}-Mo_8O_{36}$
(mol emu ⁻¹)	(mol emu ⁻¹)	(mol emu ⁻¹)
-3.8	+11.1	-46

exchange in $NdMo_{16}O_{44}$ is the antiferromagnetic coupling between the clusters in good agreement with theory and other findings in this study.

Electrical transport

To further explore the physics of these arrayed electrically isolated but magnetically interacting superatom clusters, we pertemperature-dependent two-terminal formed resistance measurements on individual single crystals of LaMo₁₆O₄₄ and NdMo₁₆O₄₄ (Fig. 5a); unfortunately, LnMo₁₆O₄₄ crystals of the other compositions were too small for reliable transport measurements. The low resistances observed at room temperature demonstrate substantial electronic charge transport between metallic clusters, likely via hopping, with room temperature resistivities on the order of $\approx 1 \Omega$ cm. As the temperature is lowered, the resistance increases exponentially for both LaMo₁₆O₄₄ and NdMo₁₆O₄₄, consistent with a decrease in the charge transport between Mo₈O₃₆ clusters and overall semiconducting/insulating behavior. At low temperatures near $T_{\rm N}$, resistance on the order of 10 G Ω demonstrates that these samples are highly insulating at temperatures where Mo₈O₃₆ units are antiferromagnetically coupled, suggesting that, unlike the exchange between Mo₄S₄ units in GaMo₄S₈, the magnetic exchange in LnMo₁₆O₄₄ between Mo₈O₃₆ clusters is not mediated by itinerant electrons,³² but rather is believed to arise via a superexchange mechanism through the insulating MoO₄ tetrahedra separating the Mo₈O₃₆ units. The established method for determining magnetic ordering is by performing a neutron scattering experiment; however, the small sample



Fig. 5 a, Resistance *versus* temperature of LaMo₁₆O₄₄ and NdMo₁₆O₄₄ at 0 T from 300 K to 5 K; (inset) Arrhenius plots showing the temperature dependence of electrical transport through LaMo₁₆O₄₄ and NdMo₁₆O₄₄ given by the Arrhenius equation, $\ln(G) \propto T_0/T$, with red lines showing the fit to the equation and equation parameters shown. b, Resistance *versus* temperature of LaMo₁₆O₄₄ at applied magnetic fields of, 0, 0.1 T, 0.5 T and 1 T, at low temperature; (inset) the height of the resistance feature at T_{peak} . $\Delta R_{\text{peak}} = R(T_{\text{peak}}) - R_{\text{BG}}(T_{\text{peak}})$, as a function of applied magnetic field.

sizes synthesized for this study (on the order of 0.25 mm³) is too small to undertake neutron scattering experiments, making this measurement beyond the scope of the study documented here. Earlier neutron scattering studies on $EuMo_{16}O_{44}$ show no change in the crystallographic structure between 300 K and 1.5 K.²⁶

Transport through both LaMo₁₆O₄₄ and NdMo₁₆O₄₄ at high temperatures is predicted to arise from a hopping transport mechanism, where carriers hop between the electrically insulated Mo₈O₃₆ clusters.²⁷ The bands derived from the tetrahedral Mo sites are energetically below the Fermi level and are not expected to contribute to transport. Nearest-neighbor hopping transport has a resistance versus temperature dependence given by $R_{\text{hopping}}(T) \propto e^{T_0/T}$, where T_0 is a fitting parameter that corresponds to the freeze-out of carriers involved in the hopping process as temperature decreases (and 1/T correspondingly increases).³³ This corresponds to Arrhenius behavior of the thermally activated carrier hopping, $\ln(G) \propto T_0/T$, where G is the conductance given as 1/R. The natural log of the conductance versus inverse temperature fits well to the Arrhenius equation, giving T_0 values of 133 K for LaMo₁₆O₄₄ and 118 K for NdMo₁₆O₄₄. These data support the predicted hopping mechanism: as the temperature decreases, the thermally activated hopping between electrically isolated Mo₈O₃₆ clusters arrayed in the material is reduced, and the conductance decreases

With a magnetic field applied perpendicular to the current through the LaMo₁₆O₄₄ sample, the resistance versus temperature plot reveals a notable magnetic field effect in the form of a local maximum in the resistance *versus* temperature with a peak around 6 K. The peak increases in magnitude with increasing magnetic field (Fig. 5b). Subtracting the resistances given by the measurement taken in zero applied field (R_{BG}) from the resistance measured with an applied magnetic field, gives the magnetic field-dependent feature that has an approximately Gaussian shape, with midpoint T_{peak} and height ΔR_{peak} $= R(T_{\text{peak}}) - R_{\text{BG}}(T_{\text{peak}})$. We note that T_{peak} (approximately 5.7 K and 6.0 K for 0.5 T and 1 T applied fields, respectively) of the magnetic field effect observed in resistance versus temperature measurements coincides with the 6.5 K transition temperature. The magnitude of the magnetic field-dependent resistance feature, ΔR_{peak} versus magnetic field H is plotted in Fig. 5b inset, and exhibits an approximately linear magnetic field dependence. This behavior of an increase in resistance with an applied magnetic field is difficult to explain, as one would expect the suppression of spin fluctuations and disorder with a greater applied magnetic field to lead to a reduction in resistance. A potential mechanism is that a magnetic field produces a misalignment of the energy levels in the ordered state whereby the Zeeman splitting affects the spin up and spin down energy levels differently. With the energy levels misaligned, the hopping integral is expected to decrease, increasing the resistivity. Further research is necessary to better understand the physical mechanism behind this increase in the resistance at T_{peak} with increasing magnetic field in this complicated condensed matter system.

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These data suggest that electronic transport through $LnMo_{16}O_{44}$ systems occur primarily *via* nearest-neighbor hopping *via* Mo_8O_{36} clusters. A magnetic field-dependent effect in $LaMo_{16}O_{44}$ is observed at temperatures corresponding to the onset of antiferromagnetic order in this material that arises from intercluster exchange. As this effect is observed in $LaMo_{16}O_{44}$, which contains no magnetic ions, the effect is not suspected to arise from local atomic magnetic moments, but is rather associated with the odd-valent molybdenum ions in the Mo_8O_{36} clusters.

Summary

In summary, we observe magnetic interactions between periodically arrayed Mo₈O₃₆ clusters in the rare earth molybdenum bronzes LaMo16O44 and NdMo16O44 and in isostructural YMo₁₆O₄₄. Measurements of the temperature dependence of the magnetic moment identify the onset of a magnetic order at around 6.5 K in LaMo₁₆O₄₄ and 3.1 K in YMo₁₆O₄₄. The non-zero, negative Weiss constants derived from the magnetic susceptibility data for all materials confirms overall antiferromagnetic interactions. Differences in temperature onsets of magnetic behavior between these isostructural materials suggests that the intercluster magnetic exchange between Mo₈O₃₆ clusters is sensitive to small structural changes, namely the effect on lattice dimensions-specifically the c-axis -due to different radii of the Ln ions. Temperature-dependent electrical transport measurements support the hypothesis that electronic transport through LnMo₁₆O₄₄ systems occur primarily via nearest-neighbor hopping through Mo₈O₃₆ clusters. Furthermore, we observe a magnetic field effect in LaMo₁₆O₄₄ at temperatures corresponding with the onset of antiferromagnetic order that arises from intercluster exchange between the arrayed Mo₈O₃₆ clusters.

These results are consistent with the theoretical prediction that these eight molybdenum atoms in the Mo₈O₃₆ clusters behave as superatoms with a single hole residing in the cluster, corresponding to a net spin moment of $1\mu_{\rm B}$ and resulting in magnetic exchange between the units. This study is an important step toward understanding interactions between nanoscale periodically arrayed multiple-atom-clusters. Such materials systems have the potential to allow researchers to produce superatoms with tailored properties, which, by controlling the exchange interactions between the superatoms in an array, will have impactful applications and serve as the basis for novel kinds of electronics and sensors. The rich structural chemistry of rare earth molybdenum oxide bronzes affords a wealth of opportunities to study the emergent properties of superatom clusters and better understand such remarkable quantum states in materials.

Experimental

Samples examined in this study were grown by both electrocrystallization and direct reaction methods. Electrocrystallization yields larger crystals that contain fewer defects such as merohedral twinning in comparison with crystals grown by direct reaction of the constituent oxides in sealed fused silica ampoules. Electrocrystallization growth of $LaMo_{16}O_{44}$ and $NdMo_{16}O_{44}$ followed this procedure: a typical charge of approximately 15 grams of MoO_3 and rare earth oxide was vacuum dried before melting. The melt was contained in a high purity recrystallized alumina crucible which was seated in a fire brick support. The assembly was contained in an inert atmosphere within a quartz vessel housed in a furnace. Crystal growth was carried out under galvanostatic control with a Pt foil electrode serving as the anode and a 1 mm Pt wire as the cathode. Traces of the melt were removed by gently heating the crystalline product in 12 M HCl following deposition.

The following procedure was used to grow YMo₁₆O₄₄ and GdMo₁₆O₄₄ by direct reaction: a 1–2 g charge consisting of stoichiometric mixtures of high purity Ln_2O_3 , Mo, and MoO₃ was ground and mixed using an agate mortar and pestle and then was placed in fused silica ampoules and sealed under vacuum. The ampoules were heated in a horizontal tube furnace at a rate of 100 °C h⁻¹ to 700 °C, kept at that temperature for at least 5 days, and then furnace-cooled.

A vibrating sample magnetometer was used to measure the temperature dependence of the total magnetic moment for a collection of single crystals of $LnMo_{16}O_{44}$ with volumes on the order of approximately 0.25 mm³. Samples were weighed before being placed in a non-magnetic glycerin capsule and inserted into the magnetometer sample space. The total magnetic moment was measured from 2 K to 300 K in magnetic fields ranging from 0 T to 1 T under both field-cooled and zero-field-cooled conditions.

Magnetotransport measurements were prepared by gluing a single crystal of adequate size (approximately 1 mm in length and 0.25 mm^2 in cross-sectional area) to an insulating SiO₂ substrate using nonconductive epoxy. Current leads were attached by attaching indium-soldered gold wires to two separate points on the crystal and attaching the other ends to the sample package electrical leads. The assembly was fastened to the end of an insert rod, and loaded into a continuous closedcycle cryostat with a superconducting magnet (maximum field of 12 T). Direct current-voltage (I-V) curve measurements were taken between 5 K and 10 K at 0.5 K steps and 10 K to 300 K at 5 K steps. We ensured accurate high-resistance measurements by using source-measurement units with very high (>10¹⁴ Ω) input impedance and with current accuracies of 0.15% of the reading + 1 pA at 1.0 power line cycles, giving a typical peak-topeak noise of about 2 pA. Appropriate signal integration times were selected along with a long hold at the initial voltage to account for possible charging effects to ensure steady state currents as device contacts. These I-V curves were taken at different magnetic fields, and the resistance was extracted from a linear fit to give an average resistance R = 1 per slope. Observed I–V curves were linear at all temperatures with $R^2 > 1$ 0.96 on all fits. Several samples of each stoichiometry were measured as a function of applied magnetic field to confirm reproducibility.

Density functional calculations were performed using the general potential linearized augmented planewave (LAPW) method as implemented in the WIEN2k code. We used the PBE generalized gradient approximation, and did calculations for both spin polarized (ferromagnetic ordered) and non-spin polarized cases. The calculations were done using the experimental structure of CeMo₁₆O₄₄ with Ce replaced by La for convenience, specifically avoiding complications due to f-electron moments. We used LAPW sphere radii of 2.2 bohr, 1.8 bohr and 1.45 bohr for La, Mo and O. Other aspects of the calculations were similar to those used previously.²⁷

Abbreviations

Ln Lanthanide

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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