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The Mackay-type cluster $[Cu_{43}Al_{12}](Cp^*)_{12}$: Open-shell 67 electron superatom with emerging metal-like electronic structure.

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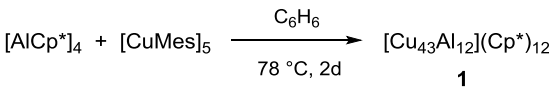
Abstract: *The paramagnetic cluster $[Cu_{43}Al_{12}](Cp^*)_{12}$ was obtained from the reaction of $[CuMes]_5$ and $[AlCp^*]_4$ ($Cp^* = \eta^5$-C_5Me_5; Mes = mesityl). This all-hydrocarbon ligand-stabilized M_{55} magic atom-number cluster features a Mackay-type nested icosahedral structure. Its open-shell 67 electron superatom configuration is unique. Three unpaired electrons occupy weakly antibonding jellium states. The situation prefigures the formation of a conduction band, which is in line with the measured temperature independent magnetism. Steric protection by twelve Cp* ligands annihilates the intrinsic polyradicalar reactivity of the $Cu_{43}Al_{12}$ core.*

The superatom theory, based on the spherical jellium model, has evolved to a concept of choice for understanding stability and chemistry of a wide range of naked and also ligated metal clusters.[1-3] Superatoms feature atom-like cluster orbital shells following the energy order 1S<1P<1D<2S<1F<2P<1G<2D… for which particular stability is related to electronic shell closing at the jellium electron counts of 2, 8, 18, 20, 34, 40, 58, 68 and so on. Accordingly, Schnöckel´s cluster $[Al_{50}(Cp^*)_{12}]$, discovered in 2004, can be described as a Cp*-ligated complex of the *homometallic* $[Al_{50}]^{12+}$ superatom with a 138-electron closed shell.[4-6] We have been fascinated by this compound. Its formula can be written as $[Al_{38}](AlCp^*)_{12}$, leading to the heuristic view of an Al_{38} core protected by twelve $2e^-$ donating AlCp* ligands. Accordingly, we anticipated that other metal cluster cores $[M_a]$ may also be stabilized by AlCp* to yield *heterometallic* superatom complexes.

We, and others, have been exploring the coordination chemistry of AlCp* and related group-12 and group-13 low valent species at transition metal centers (TM), and, over time, derived a library of heterometallic complexes and clusters $[TM_aE_b](L_c)$ (a+b ~ c; E = Zn, Cd, Al, Ga, In; L = Me, Cp*, H, Cl, CO, CN^tBu, PR_3).[7-11] One of our long term targets has been obtaining large, truly *intermetalloid* clusters $[TM_aE_b](L_c)$ with a+b >> c. Herein, we finally wish to communicate success along this research enterprise (figure 1, scheme 1): The title compound, $[Cu_{43}(AlCp^*)_{12}] = [Cu_{43}Al_{12}](Cp^*)_{12}$ (**1**), is the very first example of a ligated *hetero*-metallic Mackay-type M_{55} magic atom-number cluster with a perfect two-shell icosahedral structure. Magnetic data and analysis at the DFT level of theory reveal the unique electronic structure of the cluster which can be described as a heterometallic superatom complex with a 67 electron open jellium shell $[Cu_{43}Al_{12}]^{12+}$ core, protected by twelve Cp* ligands.



Scheme 1. Synthesis of $[Cu_{43}Al_{12}](Cp^*)_{12}$ (**1**).

The non-stoichiometric reaction of $[AlCp^*]_4$ with $[CuMes]_5$ in benzene at 78°C reproducibly yields analytically pure **1** as a black crystalline solid, albeit in low yields of 10-17 % (scheme 1). The compound is highly air and moisture sensitive, whereat the isolated crystals are pyrophoric upon exposure to air. Isolated **1** cannot be re-dissolved in any solvent without decomposition, a property which prohibited its extensive characterization with high-resolution mass spectrometry or solution NMR spectroscopy. Single-crystals suitable for X-ray diffraction structural analysis were obtained by carefully tuning the reaction conditions in order to allow for a slow crystallization of pure **1** directly from the reaction mixture. However, the compound notoriously forms relatively small, weakly diffracting cubes. Despite all efforts, thus obtained crystallographic data falls short of routinely accepted, high quality requirements. Accordingly, the following, quantitative discussions provide an approximation, only, and given bond lengths and angles are to be considered carefully, whereas the proposed core composition of $Cu_{43}Al_{12}$, as well as the overall molecular structure of **1** are unambiguously supported by the compiled experimental data, as well as structure optimizations on the DFT level of theory.

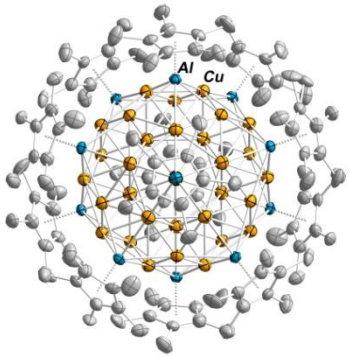


Figure 1. Molecular structure of **1** in the solid state, viewed along the five-fold rotational axis. H atoms and co-crystallized benzene molecules have been omitted for clarity, ellipsoids are drawn at the 30 % probability level. Al, Cu, C are depicted in blue, orange and grey, respectively.

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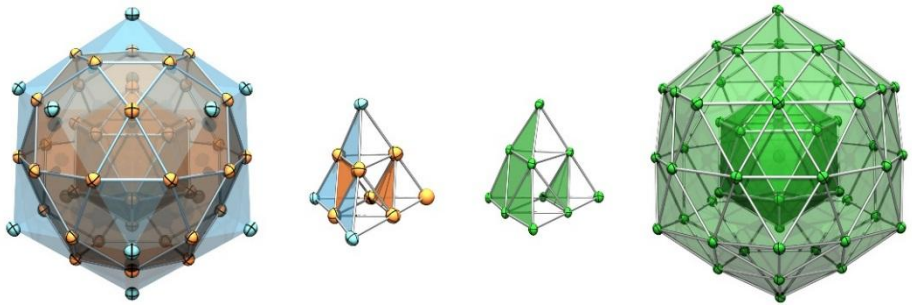

Figure 2. Naked metal cores and underlying tetrahedral M_{10} subunits of $[Cu_{43}Al_{12}](Cp^*)_{12}$ (**1**, left) and $[Pd_{55}(P^iPr_3)_{12}(\mu_3\text{-}CO)_{20}]$ (right) with highlighted M@12M@42M polyhedral shell geometries. The Mackay-type two-shell icosahedra are essentially isostructural. For $[Cu_{43}Al_{12}](Cp^*)_{12}$, the outer shell is constructed from a Cu_{30} icosidodecahedron embedded inside an Al_{12} icosahedron.

Cluster **1** crystallizes in the cubic space group *Im-3* with two molecules per unit cell along with twelve solvate molecules of benzene. Its molecular structure features a unique highly symmetric, discrete heterometallic M_{55} unit which is embedded into the all-enclosing hydrocarbon shell of twelve Cp* ligands. To date, the only other example of a crystallographically characterized, icosahedral M_{55} magic atom-number ligated metal cluster is the recently reported homometallic $[Pd_{55}(P^iPr_3)_{12}(\mu_3\text{-}CO)_{20}]$.[12] Similar to this Pd_{55} core, the $Cu_{43}Al_{12}$ core adopts a Mackay-type two-shell icosahedron (figure 2),[13] an arrangement which is considered to be particularly stable owing to its high sphericity and the accompanying minimization of surface energies according to classical Wulff construction principles.[14] It has been predicted the preferred structure for M_{55} clusters of a variety of metals by quantum chemical calculations[15, 16] and was also experimentally observed in the interior shells of the rare examples of structurally elucidated multi-shell TM_a clusters, like $[Pd_{145}(CO)_{72}(PEt_3)_{30}]$,[17] $[(\mu_{12}\text{-}Pt)Pd_{164-x}Pt_x(CO)_{72}(PPh_3)_{20}]$[18] or $[Au_{133}(SC_6H_4\text{-}p\text{-}^tBu)_{52}]$.[19] Accordingly, the $Cu_{43}Al_{12}$ core of **1** is composed of a body-centered Cu_{13} icosahedron (Cu_A@12Cu_B) that is encapsulated by a second, heterometallic $(Cu_C/Al)_{42}$ shell. Herein, the Al-atoms are symmetrically distributed on the outer sphere of the Cu core to occupy the icosahedral vertices, a geometrical preference which has also been reported for ligand-free 55 and 561 atom Cu/Al clusters based on quantum chemical calculations.[20] While the lower surface energy of Al with regard to Cu was held responsible for the latter, in the case of **1**, the symmetric arrangement of the aluminum atoms is certainly strongly influenced by the steric demand of the Al-bound Cp* ligand. The Al atoms are thus embedded into an almost ideal pentagonal bipyramidal environment between the η^5-Cp* and the η^5-Cu_5 face with $d_{CuC\text{-}Al}$ of 2.622(3) to 2.655(4) Å. These values are similar to the typical $d_{Cu\text{-}Al}$ of the intermetallic solid state reference compounds $CuAl_2$ (2.587(4) Å)[21] and Cu_9Al_4 (2.468(2)-2.737(3)).[22, 23] The Al-Cp*$_{centr.}$ distance of 1.923 Å is within the expected range,[24-26] and only slightly elongated with regards to the smaller cluster $[Cu_6(AlCp^*)_6(N{=}CHPh)H_3]$,[27] probably due to the higher steric crowding in case of **1.** The Cu_B-Al-Cp*$_{centr.}$ angle of 179.4° is almost linear.

Following the formal description of a two-shell Mackay cluster in terms of face-sharing distorted tetrahedra, twenty tetrahedral 10-atom units can be defined, which are constructed from the innermost central Cu_A atom and three neighboring Al vertices of the outer shell (figure 2, middle). The radial Cu_A-Al edges are 5.006 Å in length and slightly shorter than the tangential Al-Al distances of av. 5.270 Å. This distortion of 5.3 % is in good agreement with the 5 % deviation predicted by Mackay based on angular strain considerations,[13] and was also found for the cluster $[Pd_{55}(P^iPr_3)_{12}(\mu_3\text{-}CO)^{20}]$.[12] Deviations from the distorted tetrahedron predicted by Mackay in terms of angles and edge ratios are small, and assumed to result from the packing of distinguishable spheres with different atomic radii (Cu 140 ppm, Al 184 ppm).[28, 29] The interatomic Cu-Cu distances range from 2.430(2) to 2.569(5) Å, which values are considerably shorter than the sum of the *van der Waals* radii for Cu atoms (2.80 Å),[28] and match well with the Cu contacts of the ccp structure of elemental copper (2.55 Å).[30] These contacts are also similar to those of ligated homometallic Cu (nano)clusters, like $[Cu_{25}(PPh_3)_{12}H_{22}]Cl$ (av. 2.635 Å)[31] or $[Cu_{29}Cl_4H_{22}(Ph_2phen)_{12}]Cl$ (av. 2.65 Å).[32] The shortest $d_{Cu\text{-}Cu}$ found for **1** are the radial spacings between the central Cu atom and the inner Cu_{12} shell ($d_{CuA\text{-}CuB}$ 2.434(2) Å), along with those of the inner Cu_B atoms and the outer $Cu_{30}Al_{12}$ shell ($d_{CuB\text{-}CuC}$ 2.430(2)-2.436(3) Å), a situation which is in full agreement with the strain-induced compression discussed above. In contrast, the tangential $d_{Cu\text{-}Cu}$ within the icosahedral shells are slightly elongated ($d_{CuB\text{-}CuB}$/$d_{CuC\text{-}CuC}$ 2.555(2)-2.569(5) Å).

Elemental analysis and X-ray powder diffraction studies (SI), along with solid-state MAS NMR and IR spectroscopy confirm the composition of the bulk sample as deduced from single crystal X-ray diffraction. The ^{1}H MAS NMR spectrum shows one broad singlet at 1.72 ppm, assigned to the methyl groups of the 12 Cp* ligands, in accordance with the icosahedral symmetry. The additional signal at 6.95 ppm arises from co-crystallization of benzene (see SI for matching ^{13}C MAS NMR data). As we were unable to reproducibly detect a broad feature around -97 ppm in the ^{27}Al MAS NMR experiment, we hesitate to unambiguously assign this signal to the AlCp* ligands. Note that the ^{27}Al chemical shifts of the pertinent reference compounds $[AlCp^*]_4$ and $[Al_{38}(AlCp^*)_{12}]$ are -90 ppm and 200 ppm, respectively.[33] IR spectroscopic analysis reveals the characteristic set of bands for Cp* ligands, being the $\nu_{C\text{-}H}$ and $\nu_{C\text{-}C}$ vibrational modes at 2872 and 2818 cm^{-1}, and 1412 and 1358 cm^{-1}. An additional very strong absorption is observed at 391 cm^{-1} which is assigned to the Al-Cp* vibration.[34] Note, neither NMR nor IR data gave us hints for the presence of hydride ligands. The total elemental analysis (determined values for Al, Cu, C, H; Σ = 99.64%) supports the composition of the compound as a benzene solvate of cluster **1** with the empirical formula of $[Cu_{43}(AlCp^*)_{12}]\cdot 3C_6H_6$ (4885.30 g·mol^{-1}) (Table S4).

The electron-count of **1** is somehow disconcerting. Looking at the $[Cu@Cu_{12}@Cu_{30}@(AlCp^*)_{12}]$ concentric shell description, one is tempted to consider the peripheral AlCp* units as neutral 2-electron ligands, leaving the $[Cu_{43}]$ superatomic core with the "non-magic" 43-electron count. Including the Al atoms as part of the metal core, the resulting $[Cu_{43}Al_{12}]^{12+}$ electron count reaches

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67, a value close to the "magic" number 68. However, this cluster electron count appears rather unlikely at first sight, owing to the fact that in a first approximation only one orbital per atom, *i.e.* one 4s(Cu) and one sp(Al) hybrid AO, is expected to contribute significantly to the building up of the jellium-type orbitals. Indeed, with only 55 combinations, occupation of antibonding jellium-type orbitals is expected for this electron count. In order to shed some light on the electronic structure of **1**, we have performed spin-polarized density functional theory (DFT) calculations on the simplified model $[Cu_{43}(AlCp)_{12}]$ (**1'**) by replacing Cp* with Cp = C_5H_5. Calculations were performed with the FHI-aims[35, 36] and ADF[37-39] codes using the PBE and BP86 functionals,[40-44] respectively (see SI for computational details). The ground state was found to be a quadruplet with 3 unpaired electrons of $(t_{2u})^2(a_g)^1$ configuration in I_h symmetry. The even-electron $[\mathbf{1'}]^-$ and $[\mathbf{1'}]^+$ ions are not closed-shell, either. Closed-shell situations were found for $[\mathbf{1'}]^{3+}$ with a HOMO-LUMO gap of 0.23 eV (PBE) and 0.41 eV (BP86), respectively, and for $[\mathbf{1'}]^{9+}$, with HOMO-LUMO gaps of 0.77 eV (PBE) eV and 0.80 eV (BP86). These two cations correspond to the "magic" electron counts of 40 and 34, respectively, if the AlCp units are considered as external 2-electron ligands. If such a description was correct, the electronic structures of $[\mathbf{1'}]^{3+}$ and its naked $[Cu_{43}]^{3+}$ kernel should be strongly related. A look at figure 3 indicates, however, important differences. In particular, the g_g and h_g lowest unoccupied orbitals of $[Cu_{43}]^{3+}$, which correspond to the (splitted) 1G jellium level in I_h symmetry, correlate with occupied counterparts in $[\mathbf{1'}]^{3+}$. Moreover, their t_{1u} HOMOs are of different nature. In short, the superatom closed shell electron configuration of $[Cu_{43}]^{3+}$ is $1S^21P^61D^{10}2S^21F^{14}2P^6$ (40 electrons), and that of $[\mathbf{1'}]^{3+}$ is $1S^21P^61D^{10}2S^21F^{14}2P^6\,1G^{18}$ (HOMO-t_{1u})^6 (58 + 6 electrons). Thus in $[\mathbf{1'}]^{3+}$, the Al atoms appear to be full part of the jellium core. In the case of the "real" neutral **1'** cluster, three supplementary unpaired electrons are distributed in the next t_{2u} and a_g levels. Then, the question of the nature of the t_{1u} HOMO and the lowest unoccupied levels of $[\mathbf{1'}]^{3+}$ (or **1'**) arises. An examination of their nature leads to assign them to the 1H (t_{1u} + t_{2u} + h_u), 3S (a_g) and 2D (h_g) jellium levels (Figure 3).

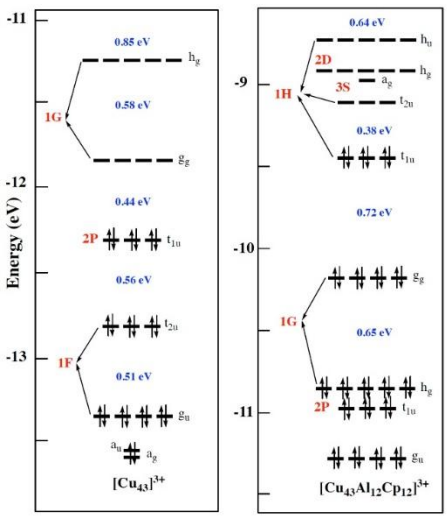

Figure 3. Kohn-Sham orbital diagrams of $[Cu_{43}]^{3+}$ (left) and $[Cu_{43}Al_{12}Cp_{12}]^{3+}$($[\mathbf{1'}]^{3+}$; right) in I_h symmetry. The jellium-type level (1F, 2P, 1G, 1H, 2D, 3S) have been indexed from their atom contributions. The neutral **1'** cluster is found to adopt the $(t_{2u})^2(a_g)^1$ open-shell configuration.

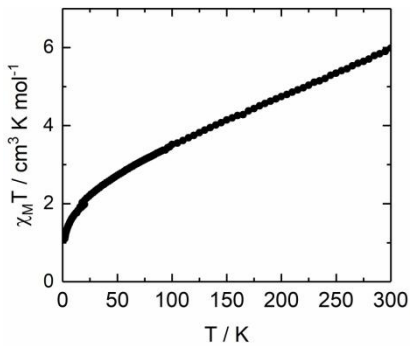

Figure 4. Magnetic properties of **1**. Thermal variation of $\chi_M T$ gives evidence for three unpaired electrons and Temperature Independent Paramagnetism (TIP).

These entangled levels are lying within a range of ~ 0.7 eV and somehow prefigure the formation of a conduction band. Their *a priori* expected antibonding nature (see above) is tempered by the stabilizing participation of 4p(Cu) orbitals. Thus, **1'** (or **1**) can be considered as an open-shell 67 electron superatom complex, made of a $[Cu_{43}Al_{12}]^{12+}$ jellium-type core and "passivated" by 12 Cp^- (or Cp^{*-}) ligands.

It is important to note that the nearest favorable closed-shell situations would be $[\mathbf{1'}]^{3+}$ (64 electrons, "non-magic" number) or $[\mathbf{1'}]^{9+}$ (58 electrons, "magic" number). The possibility for **1** bearing 3 or even 9 additional hydride ligands, thus allowing it to reach such closed-shell configurations has been tested by DFT and it was not possible to find any closed-shell situation for any of the tested models. This result is consistent with the MAS MNR and IR data, which gave no indications for hydrides.

The thermal variation of the magnetization, *M*, of **1** has been investigated between 2 and 300 K at variable magnetic field, *H*. The product of molar magnetic susceptibility, $\chi_M=M/H$, by the temperature, *T*, is plotted in Figure 3. In the low temperature regime, $\chi_M T$ (~1.5 cm^3 K mol^{-1}) approaches the expected value for an isolated spin 3/2 with a Zeeman factor g = 2 (1.875 cm^3 K mol^{-1}). This observation corroborates the existence of three unpaired electrons. $\chi_M T$ increases almost linearly on warming which might be the signature of low lying energy levels coupled with the ground state through Zeeman perturbation, known as the Temperature Independent Paramagnetism (TIP).[45]

To summarize, cluster **1** is the largest Cu superatom reported to date and it is completely new from the point of view of two features. Firstly, it has a very large electron count of 67, as compared to 22 in case of $([Au_{19}Cu_{30}](CCR)_{22}(PPh_3)_6Cl_2)^{3-}$, as the only other heterometallic example,[46] or only 2 for the known homonuclear copper superatoms.[31, 32, 47-49] Secondly, this non-'magic' number is associated with an open-shell configuration (S = 3/2) with an unprecedented electronic structure in which 9 electrons occupy discrete levels prefiguring the bottom of a metallic-like conduction band. Such a situation is largely favored by the presence of a densely packed protecting shell of Cp* ligands which provide the cluster core with sufficient kinetic stability and annihilates the intrinsic polyradicalar reactivity of the superatom core.[50] Together with the emblematic Au_{20}[51] and $[Cu_4Zn_4](Cp^*)_4(CNR)_4$,[52] cluster **1'** is a rare example of a group 11-containing superatom in which the group-11-metal oxidation state is equal to zero. Indeed, such superatom cluster complexes are usually bearing formally anionic ligands (*e.g.*

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thiolates) directly bonded to the metal core, giving rise to metal average oxidation states comprised between +I and 0.[47, 53, 54] Our synthetic approach, which consists in using sources of neutral group 12 and 13 metal ER fragments to saturate and stabilize the cluster is likely to produce a range of other examples of novel electron-rich heterometallic superatoms.

Experimental Section

Synthesis of **1**: A mixture of $[AlCp^*]_4$ (120 mg, 0.740 mmol) and $[CuMes]_5$ (205 mg, 0.961 mmol) in benzene (4 ml) was reacted at 78°C for 2d. The resulting brown-black mixture was cooled to room temperature and allowed to settle for 2d. Filtration afforded **1** as a black crystalline material which was thoroughly washed with benzene and dried in vacuum. Note: A most sensitive adjustment of the conditions is important as even small changes in temperature and time, concentration, purity of starting compounds, and even the surface to volume ratio of the reaction vessel proved to be detrimental to the successful synthesis of **1** (see SI). Yield: 17 mg, 0.004 mmol, 17 %. ^{1}H MAS NMR (r.t., neat): δ_H 1.72 ppm. ^{13}C MAS NMR (r.t., neat): δ_C 117.94 (C_5Me_5), 14.27 ppm (C_5Me_5). IR (neat, r.t.) 2936 (w), 2872 (w), 2818 (w), 1463 (w), 1412 (m), 1358 (m), 1157 (w), 1017 (w), 839 (w), 792 (w), 668 (m), 586 (m), 391 (s) cm^{-1}. Anal. calcd. for $Cu_{43}Al_{12}C_{120}H_{180}\cdot 3C_6H_6$ (M = 4885.30 g/mol): C 33.90, H 4.08, Al 6.63, Cu 55.39; found: C 33.83, H 4.13, Al 6.07, Cu 55.61%.

Keywords: Superatom • Cluster • Aluminum • Copper •

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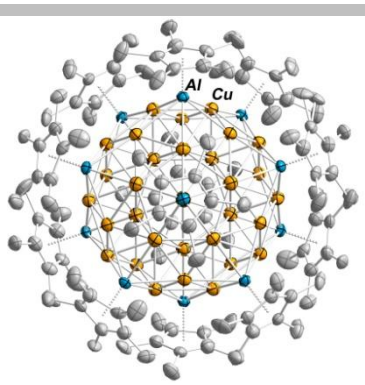
The reaction of $[AlCp^*]_4$ and $[CuMes]_5$ yields the Mackay 55-metal atom two-shell icosahedral $[Cu_{43}Al_{12}](Cp^*)_{12}$. The intermetalloid cluster possesses a unique 67 electron open shell superatomic $[Cu_{43}Al_{12}]^{12+}$ core, embedded inside an all-hydrocarbon shell of twelve Cp^{*-} ligands. Its electronic structure comprises a set of entangled HOMO und low-lying LUMOs, prefiguring the formation of a conduction band.



J. Weßing, C. Ganesamoorthy, S. Kahlal, R. Marchal, C. Gemel, O. Cador, A.C.H. Da Silva, J.L.F. Da Silva, J.-Y. Saillard and R.A. Fischer**

Page No. – Page No.

The Mackay-type cluster $[Cu_{43}Al_{12}](Cp^*)_{12}$: Open-shell 67 electron superatom with emerging metal-like electronic structure.

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