Synthesis and Characterization of Ti_5Te_4-Type Molybdenum Cluster Compounds, $A_xMo_5As_4$ (A = Cu, Al, or Ga)†

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A new series of molybdenum cluster compounds of the general formula $A_xMo_5As_4$ (A = Cu, Al, or Ga) has been synthesized. They are isostructural with the host Mo_5As_4 (Ti_5Te_4-type) consisting of *trans*-vertex shared Mo_6 octahedral chains. Investigations by *X*-ray photoelectron and Auger electron spectroscopies revealed a charge transfer from A to Mo_5As_4 in $A_xMo_5As_4$. The occurrence of metallic ($Cu_xMo_5As_4$) and non-metallic ($Al_2Mo_5As_4$ and $Ga_2Mo_5As_4$) properties in this isostructural series of solids is consistent with the electronic structure of Ti_5Te_4-type solids involving M–M bonding in the cluster chains.

Transition-metal compounds containing metal–metal bonded clusters are of current interest in view of their unique structures and properties.[1,2] Well known among this class of solids are the Chevrel phases[3,4] $A_xMo_6X_8$ (A = Pb, Sn, Cu, Li, *etc.*; X = S, Se, or Te) where the binary chalcogenides Mo_6X_8 act as the hosts. The host structure[4] consists of a three-dimensional arrangement of cubic Mo_6X_8 units which contain distorted octahedral Mo_6 metal clusters. This arrangement produces intersecting channels of vacant lattice positions, which are occupied by the A atoms. Recently it has been shown[5,6] that Mo_6X_8 clusters can condense through opposite faces of the Mo_6 octahedra to give a new family of condensed metal cluster compounds, $Mo_{3(n+1)}X_{3(n+1)+2}$ ($n \geqslant 1$), which also form Chevrel-phase analogues. The end member of the series is the infinite chain anion, $[Mo_3X_3]^-$ which is present for example in KMo_3S_3.[6] Condensation of M_6X_8 (M = transition metal) clusters can also occur through corners and edges of M_6 octahedra.[2,7,8] A typical example of a *trans*-vertex condensed molybdenum cluster compound containing a Mo_6X_8 unit is Mo_5As_4 which crystallizes in the Ti_5Te_4 structure.[9] We envisaged that Mo_5As_4 could act as host for the insertion of electropositive metal atoms giving rise to a new family of solids, $A_xMo_5As_4$, just as Mo_6X_8 chalcogenides act as hosts for the Chevrel-phase compounds. The existence of compounds such as $Cu_4Nb_5Si_4$[10] and $Ni_4Nb_5P_4$[11] adopting the Ti_5Te_4 structure, wherein Cu/Ni atoms are inserted in the voids between the cluster chains, strengthens this viewpoint. The objective of the present work has been to synthesize and characterize such insertion compounds of Mo_5As_4.

We have been able to synthesize new $A_xMo_5As_4$ with A = Cu ($1 \leqslant x \leqslant 4$) and Fe, Ga, or Al ($x = 2$). Characterization of these solids by *X*-ray photoelectron spectroscopy (x.p.s.), Auger electron spectroscopy (a.e.s.), *X*-ray absorption spectroscopy (x.a.s.), and electrical conductivity measurements shows that there is a charge transfer from A to Mo_5As_4 in these solids and that their electronic properties are determined by the valence-electron count (v.e.c.) on the cluster molybdenum atoms.

Experimental

The clusters $A_xMo_5As_4$ (A = Cu, $1 \leqslant x \leqslant 4$; A = Fe, Al, or Ga, $x = 2$) were prepared by reaction of the corresponding elements in the required stoicheiometry in evacuated sealed silica ampoules at 1 000—1 050 °C for about 15 d with one grinding in between. Experimental procedures for recording

† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

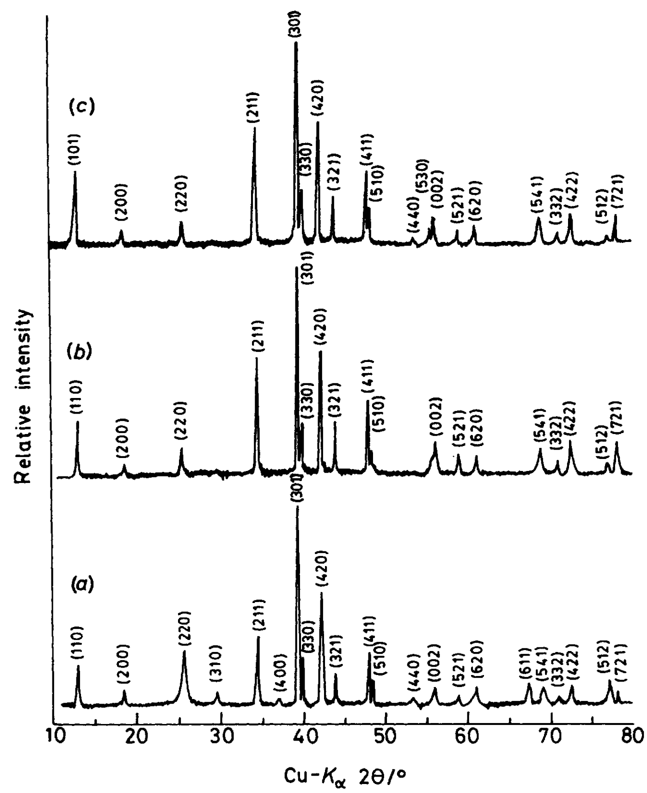

Figure 1. *X*-Ray powder diffraction patterns of (*a*) $Cu_4Mo_5As_4$, (*b*) $Al_2Mo_5As_4$, and (*c*) $Ga_2Mo_5As_4$

X-ray powder diffraction patterns and measuring electrical conductivity were as reported in an earlier paper.[12] Electron diffraction patterns were recorded on a Philips EM 301 electron microscope.

An ESCA-3 Mark II spectrometer (VG Scientific Ltd.) was used to record *X*-ray photoelectron spectra and *X*-ray initiated Auger electron spectra. Freshly prepared samples were used and exposure to the atmosphere was kept to a minimum. Powdered samples pressed into thin pellets and coated with silver paint were mounted on the P8 probe in an argon atmosphere. Since we were interested in determining the charge state of the metal atoms, etching with argon ion was avoided. The compounds are fairly good conductors, therefore there was no shift in binding energies due to charging. The peak energies reported here are

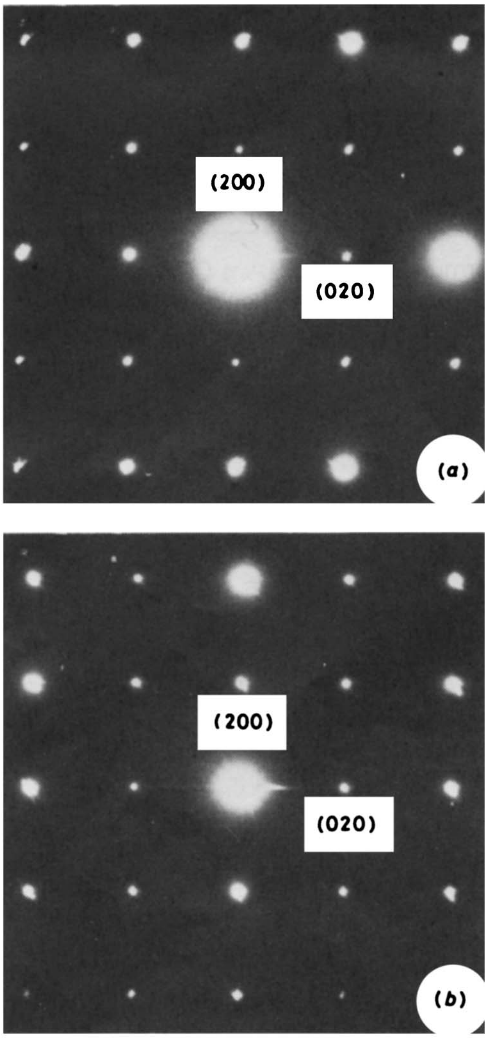

Figure 2. Electron-diffraction patterns of (*a*) Mo_5As_4 and (*b*) $Cu_4Mo_5As_4$ along the [001] zone axes

with reference to Au($4f_{\frac{7}{2}}$) which occurs at 83.7 eV and are accurate within ± 0.2 eV. The Cu-*K* and Mo-*K* edges were recorded with a bent-crystal spectrograph[13] and energy analysis of the spectra was carried out with the help of a Carl-Zeiss G-II type photometer.

Results and Discussion

We have investigated the formation of $A_xMo_5As_4$ phases for A = Pb, Cu, Fe, Co, Ni, Al, or Ga with different values of *x* by allowing the elements to react in evacuated sealed silica tubes at elevated temperatures. Powder *X*-ray diffraction of the products (Figure 1) revealed that $A_xMo_5As_4$ isostructural with Mo_5As_4 are formed only with Cu($0 < x \leqslant 4$), Fe($x = 2$), Al($x = 2$), and Ga($x = 2$). Refined lattice parameters for the new phases are listed in Table 1. We have examined $Cu_4Mo_5As_4$ and Mo_5As_4 by electron diffraction to provide further evidence for the structural similarity. Several crystals of both compounds were examined in the microscope. The most common orientation was [001] of the tetragonal cell; the diffraction patterns (Figure 2) are similar showing the tetragonal symmetry of $Cu_4Mo_5As_4$. Lattice parameters of $A_xMo_5As_4$ (Table 1) reveal that, while the *c* remains nearly the same, there

Table 1. Lattice parameters, v.e.c., and room-temperature resistivities of $A_xMo_5As_4$

Compound	Lattice parameters/Å *a*	*c*	v.e.c.	ρ (300 K)/ ohm cm
Mo_5As_4	9.600(1)	3.278(2)	3.6	2.0×10^{-2}
$Cu_2Mo_5As_4$	9.642(2)	3.282(2)	4.0	1.8×10^{-2}
$Cu_4Mo_5As_4$	9.644(3)	3.284(2)	4.4	1.0×10^{-2}
$Al_2Mo_5As_4$	9.643(2)	3.283(3)	4.8	2.0
$Ga_2Mo_5As_4$	9.641(2)	3.282(3)	4.8	1.0

Table 2. Core-level binding energies (eV) of $A_xMo_5As_4$ compounds

Compound	Core level	Binding energy
Mo_5As_4	Mo $3d_{5/2}$	228.6
	Mo $3d_{3/2}$	231.8
	As $3d$	41.6
$Cu_4Mo_5As_4$	Cu $2p_{3/2}$	933.0
	Mo $3d_{5/2}$	228.5
	Mo $3d_{3/2}$	231.7
	As $3d$	41.6
$Ga_2Mo_5As_4$	Ga $3d$	19.6
	Mo $3d_{5/2}$	228.4
	Mo $3d_{3/2}$	231.5
	As $3d$	41.6

Table 3. L_3VV ($L_3M_{45}M_{45}$) Auger-electron kinetic energies (eV) of Cu and Ga in $Cu_4Mo_5As_4$, $Ga_2Mo_5As_4$, and related solids*

Compound	L_3VV energy	Compound	L_3VV energy
Cu	918.8	Ga	1 068.1
$Cu_4Mo_5As_4$	918.0	$Ga_2Mo_5As_4$	1 066.9
CuAgSe	917.6	GaAs	1 066.4
Cu_2Se	917.5	GaP	1 066.2
Cu_2S	917.4		

* L_3VV energies of elemental Cu, Ga, and related solids are taken from ref. 15.

is an increase in *a* as compared to Mo_5As_4, on insertion of A atoms.

By analogy with Chevrel phases, one would expect a charge transfer from A to the molybdenum cluster in these solids. We have investigated the charge transfer and oxidation states of the metal atoms in $A_xMo_5As_4$ by x.p.s., a.e.s., and x.a.s. The core-level binding energies of Mo, As, Cu, or Ga in Mo_5As_4, $Cu_4Mo_5As_4$, and $Ga_2Mo_5As_4$ as determined by x.p.s. are given in Table 2. The core-level shifts relative to elemental solids provide information about the charge transfer and oxidation states in favourable cases.[14,15] The Cu $2p_{\frac{3}{2}}$ binding energy in $Cu_4Mo_5As_4$ (933 eV) is higher than that of elemental copper (932.6 eV). We see no shake-up satellite in the Cu 2*p* spectrum of $Cu_4Mo_5As_4$ (Figure 3). A similar shift in Ga 3*d* binding energy is noticed in $Ga_2Mo_5As_4$. That the charge transfer from A atoms is essentially to the Mo is seen from the shift of the Mo 3*d* binding energy as compared to that in Mo_5As_4 (Figure 4). The arsenic levels essentially remain unaffected; for instance, the As 3*d* binding energy is 41.6 eV in Mo_5As_4 as well as in $Cu_4Mo_5As_4$ and $Ga_2Mo_5As_4$.

The changes in chemical state which give rise to a shift in the core-level x.p.s. also produce a shift in the Auger spectra.[15] These shifts which are much larger than x.p.s. shifts and are mainly determined by changes in the polarizability of the environment of the ionized atom have been used to characterize the chemical state of atoms in solids.[15–17] L_3VV Auger electron[15] energies of Cu and Ga in $Cu_4Mo_5As_4$ and $Ga_2Mo_5As_4$

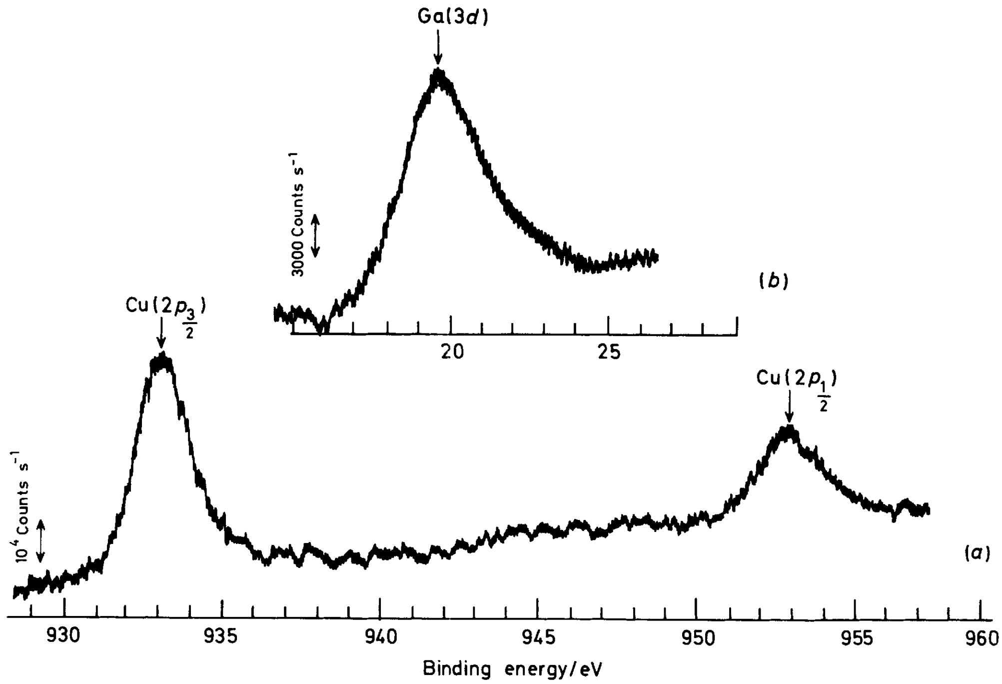

Figure 3. X.p.s. of (*a*) Cu 2*p* and (*b*) Ga 3*d* core levels in $Cu_4Mo_5As_4$ and $Ga_2Mo_5As_4$ respectively

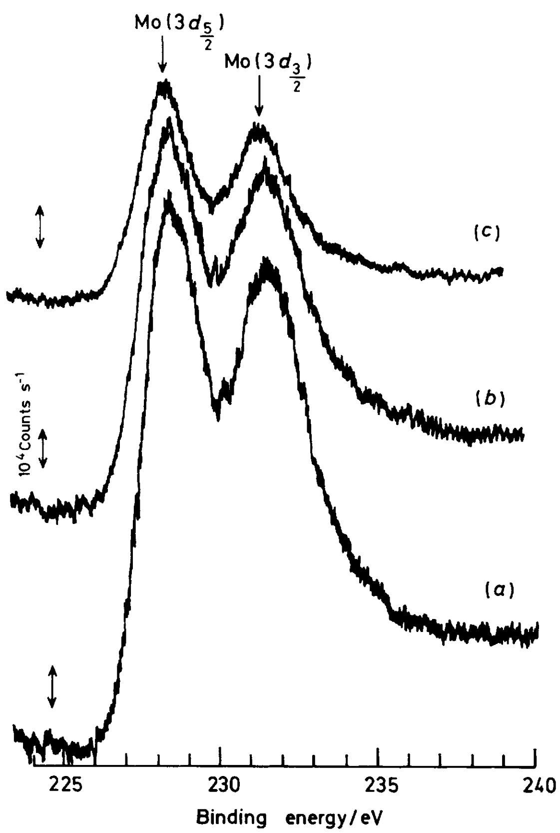

Figure 4. X.p.s. of Mo 3*d* in (*a*) Mo_5As_4, (*b*) $Cu_4Mo_5As_4$, and (*c*) $Ga_2Mo_5As_4$

recorded by using Al-K_α radiation in the $N(E)$ *vs.* E mode are given in Table 3 [$N(E)$ = Auger electron counts, E = kinetic energy]. For comparison, corresponding data for similar Cu- and Ga-containing solids are also listed. It is seen that the L_3VV energy of Cu in $Cu_4Mo_5As_4$ is lower than that of Cu metal but is comparable to the Cu(L_3VV) values of CuAgSe and Cu_2Se. Similarly, the Ga(L_3VV) energy of $Ga_2Mo_5As_4$ is significantly lower than that of elemental gallium but is comparable to the corresponding value for GaAs. These results may be taken to indicate that the chemical nature of Cu in $Cu_4Mo_5As_4$ is similar to that in CuAgSe, and that of Ga in $Ga_2Mo_5As_4$ is similar to the nature of Ga in GaAs. Further evidence was provided by chemical shifts in the *K*-absorption edge (Table 4). The *K*-edge shift of Cu in $Cu_4Mo_5As_4$ is of the same order of magnitude as in the Chevrel phases, $Cu_{1.6}Mo_6S_8$ and $Cu_{1.8}Mo_6Se_8$. Thus it is reasonable to assume that in $A_xMo_5As_4$ the A atoms act as electron donors 'transferring' their valence electrons to Mo atoms of the Mo_5As_4 host; the electrons result in an increase in the v.e.c.* of the molybdenum atom in the cluster. Although it is difficult to determine quantitatively the extent of electron transfer and the

Table 4. Chemical shifts[a] in the *K*-absorption edges of Mo and Cu in $A_xMo_5As_4$ and related solids[b]

	Chemical shift (eV) in	
	Mo-*K* edge	Cu-*K* edge
Mo_5As_4	4.8	—
$Cu_4Mo_5As_4$	4.5	1.92
Mo_6S_8	6.5	—
$Cu_{1.8}Mo_6S_8$	6.1	2.10
Mo_6Se_8	5.2	—
$Cu_{1.8}Mo_6Se_8$	4.9	1.77

[a] Measured relative to the metals. [b] The data for Mo_6X_8 and $Cu_xMo_6X_8$ (X = S or Se) are taken from S. Yashonath, M. S. Hegde, P. R. Sarode, C. N. R. Rao, A. M. Umarji, and G. V. Subba Rao, *Solid State Commun.*, 1981, **37**, 325.

* The valence electron count (number of valence electrons) per metal atom in the cluster which participate in M–M bonding.

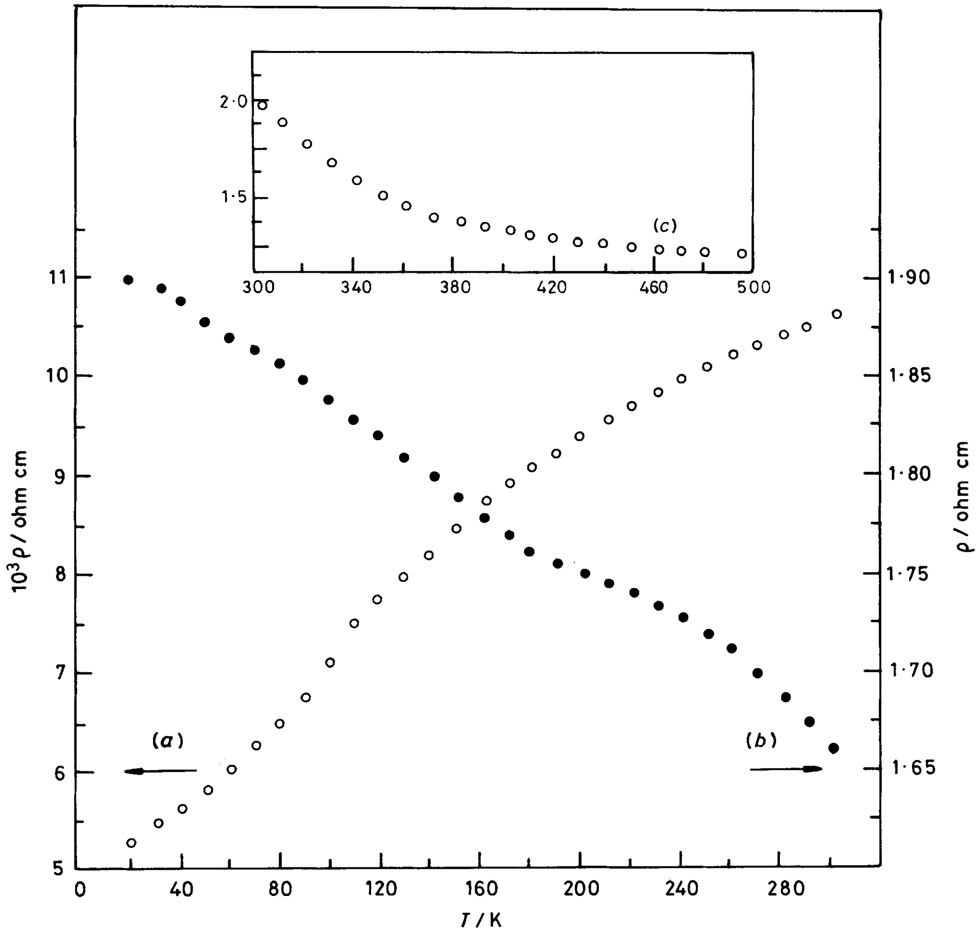

Figure 5. Resistivity *vs.* temperature plots of (*a*) $Cu_4Mo_5As_4$, (*b*) $Al_2Mo_5As_4$, and (*c*) $Ga_2Mo_5As_4$

oxidation states of the insertion atoms in $A_xMo_5As_4$, it is most likely that the formal oxidation states of Cu and Ga in $Cu_xMo_5As_4$ and $Ga_2Mo_5As_4$ are I and III respectively.

Electrical resistivity measurements indicate that Mo_5As_4 and $Cu_xMo_5As_4$ are metallic but $Al_2Mo_5As_4$ and $Ga_2Mo_5As_4$ are semiconducting. While the room-temperature resistivities of Mo_5As_4 and $Cu_xMo_5As_4$, measured on sintered polycrystalline pellets, are around 10^{-2} ohm cm, those of $Al_2Mo_5As_4$ and $Ga_2Mo_5As_4$ are around 1—2 ohm cm (Table 1). The temperature dependence of the resistivities (Figure 5) clearly shows that $Cu_4Mo_5As_4$ is metallic and $Ga_2Mo_5As_4$ and $Al_2Mo_5As_4$ are semiconducting. The occurrence of metallic and non-metallic behaviour in this isostructural series of solids probably signals the influence of cluster v.e.c. on the electronic properties. This behaviour may be understood in terms of the electronic band structure of Ti_5Te_4-type solids.[7] In this model (Figure 6), which emphasizes the M–M bonding in the cluster chain, each cluster forms four normal M–M bonds in the equatorial plane; in addition, there are four three-centre M–M bonds involving the bridging M atoms at the vertex. The ordering of metal *d*-like states shows gaps at 8, 16, and 24 electrons per cluster. This picture is consistent with the generally observed v.e.c. of 2.4—3.6 for the Ti_5Te_4 structure.[2] It also explains the formation and properties of $A_xMo_5As_4$ reported in this paper. The cluster Mo_5As_4 has a v.e.c. of 3.6 at molybdenum [$(5 \times 6 - 12)/5$] assuming that each molybdenum atom 'transfers' three of its valence electrons to arsenic in forming the compound. Thus, with 18 electrons per cluster available for M–M bonding, the highest occupied M–M band is partially filled and therefore Mo_5As_4 is metallic. Insertion of four copper atoms in Mo_5As_4 in forming $Cu_4Mo_5As_4$ would increase the v.e.c. to 4.4, making available 22 electrons per cluster for M–M bonding. (This assumes that copper is formally 1+ in the solid.) With 22 electrons per cluster, the highest occupied M–M band is still partially filled in $Cu_4Mo_5As_4$. In $Al_2Mo_5As_4$ and $Ga_2Mo_5As_4$ the v.e.c. would be 4.8 (assuming that each Al/Ga provides three electrons to the cluster). With 24 electrons per Mo_5 cluster, the highest occupied band would be full and therefore the aluminium and gallium derivatives are semiconducting. It is significant that a similar behaviour is seen in the M_6X_8 family of isolated cluster compounds: the 24-electron compounds,[18—20] $Mo_2Re_4S_8$ and $Mo_4Ru_2Se_8$, are semiconducting, while all the other Mo_6X_8 and $A_xMo_6X_8$ Chevrel phases with electron counts less than 24 per cluster are metallic.[4]

The present investigation has shown that using Mo_5As_4 as the host it is possible to prepare metal insertion compounds of formula $A_xMo_5As_4$, which are analogous to the Chevrel phases. Just as in the Chevrel phases, the inserted metal atoms 'transfer' their valence electrons to the host, increasing the number of electrons available on molybdenum for M–M bonding. Strikingly, when this number is 24, as in $Al_2Mo_5As_4$ and $Ga_2Mo_5As_4$, the material becomes semiconducting, the behaviour being reminiscent of M_6X_8 cluster compounds with 24 electrons.

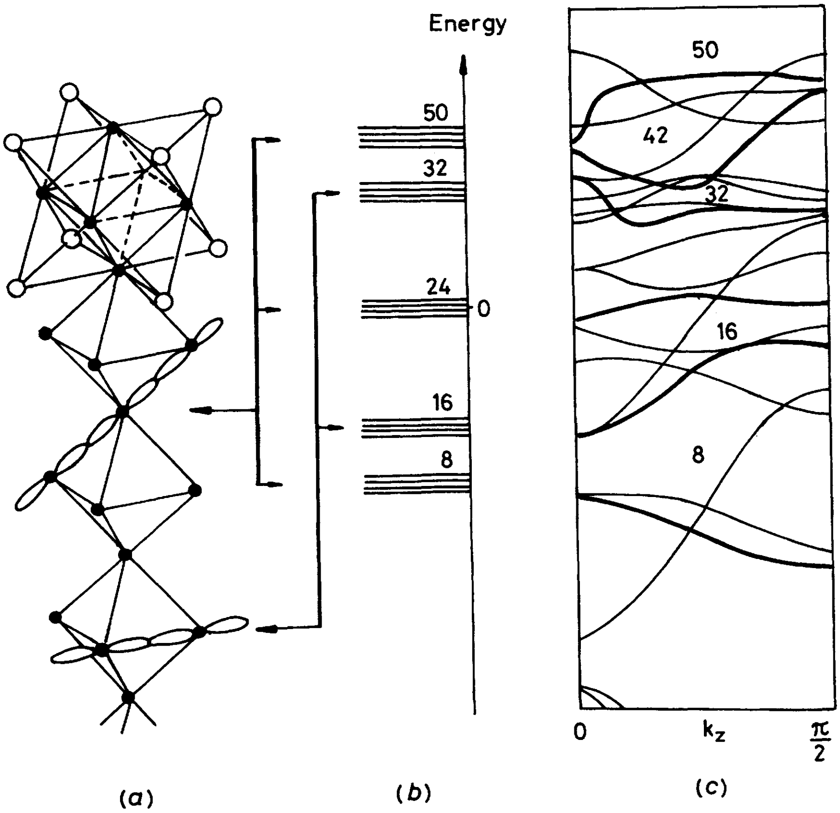

Figure 6. Electronic structure of Ti_5Te_4-type condensed metal cluster compounds. (*a*) Atomic structure of M_5X_4 chain resulting from the condensation of M_6X_8 units. (*b*) Schematic energy levels of the *d* states involved in M–M bonding. (*c*) Band structure of a typical M_5X_4 solid for the wave vector along the chain, k_z. The number of electrons per unit cell is indicated (from ref. 7)

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