Letters

Comment on the existence of phases $A_xMo_5As_4$ with $A_x = Al_2$, Ga_2, Cu_2 or Cu_4 *

According to Jensen *et al.*[1] there are only three different binary compounds (Mo_5As_4,[2,3] Mo_2As_3[4] and $MoAs_2$[5]) in the Mo/As system. The formation of some non-stoichiometric compounds from Mo and As with transition metals has been explored.[6,7] For example, the phase originally described as 'MoAs' was demonstrated to be stabilized by incorporation of V, Cr or Fe with limiting composition of e.g. $Fe_{0.05}Mo_{0.95}As$.

The compound Mo_5As_4 is isotypic with Ti_5Te_4[8] and its structure was described in terms of the 'condensed metal clusters' concept.[9] The crystal structure from that viewpoint contains infinite strings of Mo built from *trans* vertex-sharing Mo_6 octahedra in Mo_6As_8 clusters. It is synthesised from the elements in quartz glass ampoules at 1270 K. Single crystals are grown by chemical transport reactions with halogens.[3] In contrast to the work of Murray *et al.*[10] we found significant transport with iodine, and succeeded in getting well shaped single crystals using a temperature gradient of 1270–1370 K.

Nanjundaswamy and Gopalakrishnan recently reported[11] the formation of the new compounds '$Al_2Mo_5As_4$', '$Ga_2Mo_5As_4$', '$Cu_2Mo_5As_4$' and '$Cu_4Mo_5As_4$'. This result contradicted our own attempts[12] to insert electropositive metal atoms into the structure of Mo_5As_4. We always found other stable phases like AlAs or GaAs, or we got big crystals of Mo_5As_4 and Mo_2As_3 embedded in metal (Cu). Examination of all molybdenum arsenide crystals by means of electron dispersive analysis of X-rays indicated that Al, Ga or Cu was not incorporated in any sample. Reiss and Renner[13] also observed exclusive formation of Mo_5As_4 besides GaAs in the ternary system Ga/Mo/As.

The proposed new phases were characterized[11] by X-ray powder diffraction, spectroscopic methods and conductivity measurements of pressed powder samples, but no other chemical characterization was provided. Small or no changes in the binding energies of atomic core levels were found compared to Mo_5As_4. Small changes in the kinetic energies of Auger electrons and little chemical shifts in the K absorption edges were interpreted as a consequence of an electron transfer from the guest species (Cu, Ga, Al) to the host (Mo_5As_4). Conductivity measurements showed metallic behaviour for the Cu-containing samples and semiconducting behaviour for the samples with Ga or Al.

The X-ray powder diffraction diagrams of the phases[11] are amazingly similar to that of Mo_5As_4, and the same holds for electron diffraction diagrams of selected crystals. The refined lattice parameters are only increased from 960.0(1) to 964.4(3) pm for the *a* axes (+0.5%) and from 327.8(2) to 328.4(2) pm for the *c* axes (+0.2%) in all cases. In contrast to this, our refined lattice constants for Mo_5As_4-type materials that had been synthesised with or without the presence of Al, Ga or Cu fall in the range of 960.3 ± 0.5 pm for the *a* and 327.8 ± 0.4 pm for the *c* axes, which is at least one order of magnitude smaller for the case of the *a* axes.

Even using the lattice constants of Nanjundaswamy and Gopalakrishnan one calculates a volume increase of only about 1 cm^3 mol^{-1} per formula unit Mo_5As_4 when forming the compounds '$A_xMo_5As_4$'. This change has to be compared with the volume increments[14] of 9.9, 11.7 and and 7.05 cm^3 mol^{-1} for Al, Ga and Cu, respectively! Thus, the suggested compound composition with $x = 2$ or 4 can be rejected from simple volume considerations.

Secondly, any structural model contradicts the observed X-ray intensities. Such models need (*i*) the occupation of positions 4*c* or 4*d* (chains of A atoms), or may be based (*ii*) on the structural principle of $Cu_4Nb_5Si_4$.[15] In any case the intensity of the 1,1,0 reflection should vanish in contrast to observation[11] besides the fact that (*i*) the close approach of A atoms (164 pm) would call for meaningless bond situations (*e.g.* Al–Al bonding with bond order 27). On the other hand, the short Cu–As distances (217–224 pm) in (*ii*) would indicate for three double bonds and a hypothetical copper oxidation state of +6 using Pauling's formalism.[16]

Last, but not least, band-structure arguments strongly contradict the existence of the proposed ternary phases. Fig. 1 shows the results of calculations on the complete three-dimensional Mo_5As_4 structure, which were performed using simple Extended Hückel theory (EHT)[17,18] within the framework of the tight-binding approximation. The empirical energy parameters are in Table 1.

The total density of states (d.o.s.) and the atoms' local contributions are shown in Fig. 1. To begin with, the local d.o.s. on Mo(1) clearly reflects the body-centred cubic surroundings built by the neighbouring Mo atoms. Secondly, the localization of the deepest bonding states at the As atom (peak around −15 eV) is evident. Thirdly, the total d.o.s. is non-zero at the Fermi level in agreement with the metallic character of Mo_5As_4.

The Fermi energies which are indicated by strong lines refer to 50 and 44 valence electrons per formula unit. This region

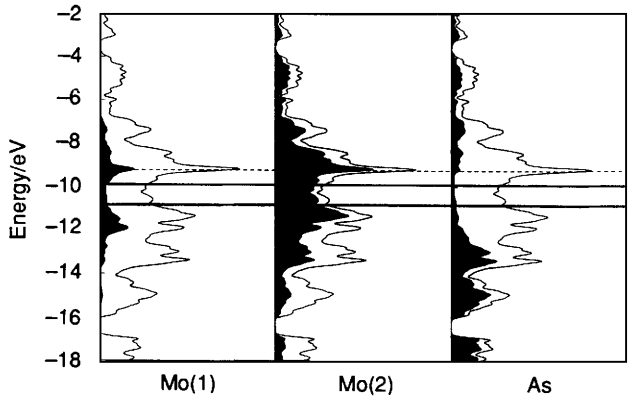

Fig. 1 EHT total density of states for Mo_5As_4. The local d.o.s. for Mo(1) (apex), Mo(2), and As (from left to right) are emphasized in black. The Fermi energies refer to 56 (dashed), 50 and 44 valence electrons per formula unit, respectively

Table 1 EHT energy parameters for Mo_5As_4

Atom	Orbital	H_{ii}/eV	ζ_1
Mo	5s	−9.16	1.96
	5p	−4.94	1.90
	4d *	−10.72	4.54
As	4s	−16.22	2.23
	4p	−12.19	1.89

* $C_1 = C_2 = 0.5899, \zeta_2 = 1.90$.

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

of lowered d.o.s. corresponds to the size of the 'window of existence' for the M_5X_4 structure type. The Fermi energy indicated by the dashed line corresponds to the composition of '$Al_2Mo_5As_4$' with 56 valence electrons. Electronically, the structure turns out to be *maximally destabilized* for the proposed compound composition, because it has the highest global d.o.s. at the Fermi level. Such a phase cannot be stable against distortion (which has not been found) or decomposition into the binary component (Mo_5As_4) and elements (Cu, Ga, Al).

Of course, this argument assumes that a rigid-band approximation is valid to treat the electronic structure of '$Al_2Mo_5As_4$'. We therefore performed EHT calculations for the Mo_5As_4 framework with the Al atoms in 4*d* positions, and obtained the same result: the Fermi level occurs at the position of highest d.o.s.

To summarize, one has to reject the existence of the compounds '$Al_2Mo_5As_4$', '$Ga_2Mo_5As_4$', '$Cu_2Mo_5As_4$' and '$Cu_4Mo_5As_4$'. Together with our findings that the lattice constants of Mo_5As_4 obtained in the absence or presence of Al, Ga and Cu are identical within five standard deviations (0.1 pm) and that no characteristic X-ray emission of Al, Ga and Cu has been found, we conclude that Mo_5As_4 does not incorporate significant amounts of these metals.

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