Synthesis, crystal growth, and structure of Ta$_3$Al$_2$CoC—An ordered quarternary cubic η-carbide and the first single crystal study of a η-carbide

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ABSTRACT

Single crystals of the new carbide Ta$_3$Al$_2$CoC were synthesised from metallic melt and characterized by XRD, EDX and WDX measurements. The crystal structure of Ta$_3$Al$_2$CoC was refined on the basis of single crystal data (cF112, $Fd\bar{3}m$, $a = 11.6153(13)$ Å, $Z = 16$, 169 reflections, 13 parameters, $R_1(F) = 0.0315$, w$R_2(F^2) = 0.0857$). Ta$_3$Al$_2$CoC belongs to the great family of η-carbides M_3M_3'C or M_4M_2'C which are important components for cermets. Its crystal structure is characterised by TaC$_6$-octahedra, which are connected to a three-dimensional net. Co and Al have icosahedral surroundings without contacts to C-atoms. All positions show full occupation. Ta$_3$Al$_2$CoC represents the first η-carbide with a complete structure refinement on the basis of single crystal data.

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1. Introduction

Binary carbides of "early" transition metals like TiC and WC are important hard materials [1]. In combination with a metallic binder like Co they are used as ceramic metals ("cermets") for many applications [2]. The metallic binder is important for two reasons. Firstly the brittleness of the TM-carbide (high hardness) is counterbalanced by the ductility of the metal (plastic deformation). Secondly the formation of a dense body by sintering is favoured. As a result material properties and behaviour of cermets strongly depend on the interaction between TM-carbide and the metallic binder. In this context the crystal chemistry of multinary carbides of transition metals with low carbon content plays a key role for its understanding.

Usually the carbon atoms show octahedral coordination but in difference to the binary carbides, the perowskite-related phases M_3M'C, and the so-called "MAX"-phases $(MC)_nMM'$ ($n = 1, 2, 3$) their crystal structures are not based on a closest sphere packing of metal atoms. According to Toth [3] and Nowotny [4] the following structure families can be classified which can be described as filled variants of an intermetallic compound:

- Cubic carbides M_3M_2'C with filled ß-Mn structure [5] (i.e. Ta$_3$Al$_2$C, $P4_132$, $a = 7.039$ Å [6]).
- Hexagonal χ-carbides with filled Mn$_3$Al$_{10}$ structure [5] (i.e. W$_{10}$Co$_3$C$_4$, $P6_3/mmc$, $a = 7.85$ Å, $c = 7.85$ Å [7]).
- Hexagonal carbides M_5M_3'C$_{1-x}$ with filled Mn$_5$Si$_3$ structure [5] (i.e. V$_5$Si$_3$C$_{1-x}$, $P6_3/mcm$, $a = 7.14$ Å, $c = 4.84$ Å [8]).
- Cubic η-carbides with filled Ti$_2$Ni structure [5] (i.e. W$_3$Co$_3$C, $Fd\bar{3}m$, $a = 10.898$ Å [9]).

The class of η-carbides can be subdivided [10] into different sub-groups according to the occupation of different Wyckoff-positions (48f, 32e, 16d, 16c, 8a) $M_6^fM_4^eM_2^dX_n^cX_m^a$ (M^f = Ta, Mo, W; M^e = Fe, Co, Ni; M^d = Mo, W, Fe, Co, Ni; X = C, N; n, m = 2, 1; 2, 0; 0, 1) [10]. Another classification refers to the order of metals (η_1-carbide: W$_3$Co$_3$C; η_2-carbide: W$_4$Co$_2$C [3]) and the carbon content (η-6-carbide: M_3M_3'C, C on site 16c; η-12-carbide: M_6M_6'C, C on site 8a [11]).

The crystal structures of Fe$_6$W$_6$C and Fe$_3$W$_3$C were derived from neutron diffraction data [12,13] confirming the localisation of carbon on site 8a and 16c, respectively. Later on [11] Rietveld refinement of neutron powder data confirmed the crystal

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structures of the η-12-carbides Ni_6Mo_6C and Co_6Mo_6C (C on site 8a), and the η-6-carbide Co_3Mo_3C (C on site 16c).

Quarternary η-carbides of the system Ta/Al/M/C (M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn) were already investigated by Reiffenberg et al. [14]. Mixtures of the elements were sintered at 1350 °C and characterized by powder methods. With M = Co they observed at a composition of 3:2:1:1 a homogenous phase with $a = 11.56$ Å and assigned it on the basis of model calculations to a η_1-carbide. According to the limitations of the experiment (X-ray powder data, film methods) a detailed analysis of site occupations was not possible. Later on Sridharan et al. [15] reported on Ti_3Al_2NiC as a η-carbide with a small range of homogeneity ($a = 11.40–11.46$ Å).

All the X-ray investigations had been done on powder samples. This is sufficient for the assignment, but for detection and characterisation of incompletely occupied sites, super-structures, the localisation of light atom positions (C/N) and the formation of solid solutions (TM/TM′; C/N) single crystal data supply more reliable results. But the growth of single crystals is difficult for η-carbides because the high melting points prevent the easy access to single crystals by conventional high temperature syntheses. Up to now no single crystal studies have been published. For η-carbides detailed investigations including a refinement of structure parameters were done only for powder samples using neutron scattering.

Recently we have shown for the systems Ta/Al/C [16] and V/Al/C [17] that the application of the auxiliary metal technique enables the synthesis of high quality single crystals, which allows an unambiguous localisation of the carbon sites and clear statements on occupation factors and mixed occupations. Furthermore analyses by EDX and WDX give compositions of the single crystals which were used for the X-ray data collection.

In the course of these investigations we used Co/Al-mixtures for the crystal growth of the ternary carbides ("MAX-phases") V_4AlC_{3-x} and $V_{12}Al_3C_8$ [17]. For the system Ta/Co/Al/C cobalt was taken up and we observed the formation of single crystals of the quaternary compound Ta_3Al_2CoC, an ordered η-carbide. Despite the great technical importance of η-carbides this is the first report on the growth of single crystals and a structure refinement basing on single crystal data.

2. Experimental

2.1. Syntheses, crystal growth, and characterisation

Single crystals of Ta_3Al_2CoC were obtained from the elements by the following procedure. An excess of Al/Co was used to obtain a metallic melt for the single crystal growth. Commercially available powders of the elements Ta (Acros, 99.5%), Al (Riedel-de Haen, 99.9%), Co (Chempur 99.5%), and C (graphite, Chempur, 99.9+%), were intimately mixed in a ratio 2:10:3:1.5 and pressed into a pellet (total mass: ca. 350 mg). The pellet was put into a corundum crucible and quickly (200 K/h) heated up to 1500 °C under an argon atmosphere. The sample was held for 50 h at 1500 °C, cooled to 1000 °C with a cooling rate of 5 K/h, held for 30 h and then cooled with 30 K/h to RT. The excess metal of the melt was removed by dissolving the regulus in 5n aqueous HCl. The residue was washed and dried. Small truncated octahedra (Fig. 1) were characterised as Ta_3Al_2CoC.

The X-ray powder diffraction pattern showed TaC [5] as the main fraction. Minor parts were $TaAl_3$ [5] and Ta_3Al_2CoC. The refinement of the indexed lines yielded a lattice constant of $a = 11.580(5)$ Å in good agreement with the single crystal results.

EDX and WDX measurements on single crystals were performed to ensure the correct composition. By EDX the ratio Ta:Al:Co was quantified as 54:31:15 (calculated: 50:33:17).
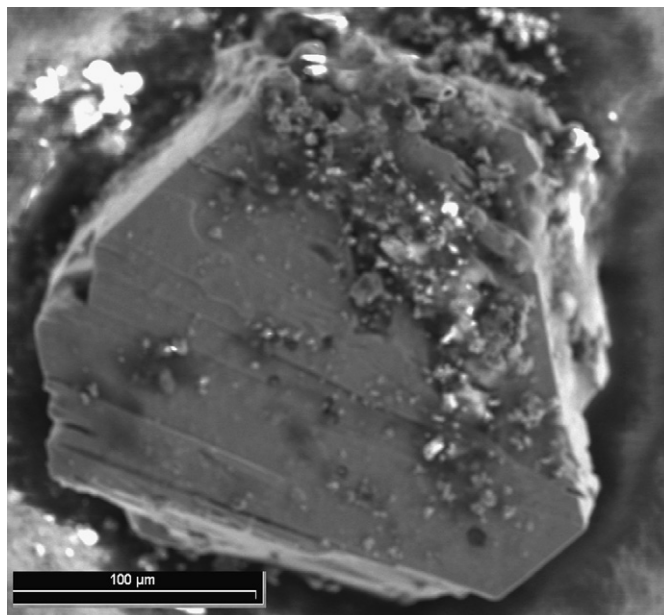

Fig. 1. SEM picture of Ta_3Al_2CoC.

Furthermore WDX measurements are necessary to exclude the incorporation of light elements with $4 < Z < 13$. Especially nitrogen is able to substitute carbon in TM-carbides [12] and cannot reliably be determined from X-ray data. For Ta_3Al_2CoC carbon was confirmed as the only light element.

XRD patterns were recorded with a Siemens D5000 ($CuK_{\alpha1}$-radiation, Ge-monochromator, gas-filled PSD, Debye-Scherrer geometry, transmission). SEM pictures and EDX measurements were done using a Jeol SM 6400 (Ge detector). For WDX investigations a Cameca SX 50 (analyser crystal PC2, diamond and c-BN as standards) was used.

2.2. Structure determination

A black polyhedron was isolated from the Co/Al-melt and investigated by using a single-crystal diffractometer equipped with an image plate detector (STOE, IPDS I, MoK_{α}-radiation). All reflections were indexed with an F-centred cubic unit cell with a lattice parameter of $a = 11.61$ Å. Unit cell dimensions and reflection conditions (hhl with $2h+l = 4n$) were characteristic for a η-carbide. The refinement was started with the parameters of Ta_3Co_3C [5,18] in space group $Fd\bar{3}m$. According to the value of the displacement parameter it turned out that the 32e-site is occupied by Al. The position of C is easily detected in the difference Fourier synthesis by its high residual electron density of 12 e$^-$/Å^3. With 169 unique reflections (154 with $I > 2\sigma(I)$) and 13 parameters R-factors of $R_1(F) = 0.0315$ and $wR_2(F^2) = 0.0857$ were obtained. The refinement of the site occupation factors showed no significant deviations. Therefore an ordered and stoichiometric structure can be assumed. Details are listed in Tables 1–3. Further details on the structure refinements (complete list of distances and angles, F_o/F_c-list) may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (fax: +49724-808-666: e-mail: crysdata@fiz-karlsruhe.de) on quoting the registry number CSD-418908.

3. Results and discussion

The crystal structure of Ta_3Al_2CoC represents an ordered variant of a quarternary η-carbide (Fig. 2). As pointed out in

previous work [11,21] the metal atom positions can be derived from the Ti_2Ni-structure. Carbon is located in octahedral voids formed exclusively by Ta-atoms. C-Ta-distances of 2.1811(3) Å are shorter than in binary TaC (2.228 Å [22]) but similar to Ta_4AlC_3 (2.17–2.23 Å [16]) and Ta_3AlC_2 (2.18–2.21 Å) [16]). These CTa_6-octahedra are liked by common corners to six other octahedra (Fig. 3) resulting in a three-dimensional net. Similar to many multinary carbides (for example anti-perowskite phases, $M_3M'C$, MAX-phases $(MC)_nMM'$) there is a separation between "intermetallic" and "carbidic" interaction. In the case of Ta_3Al_2CoC carbon has only contact to Ta.

The surroundings of the metal atoms are shown in Fig. 4. Within the "carbidic" framework Al and Co have both icosahedral coordinations solely to metal atoms. The surrounding of Al is formed by 3 Co-atoms (Al–Co: 2.509(2) Å), 3 Al-atoms (Al–Al: 2.708(11) Å), and 2 × 3 Ta-atom (Al–Ta: 2.763(5)/2.987(1) Å). Co is coordinated by 6 Al-atoms (2.509(2) Å) and 6 Ta-atoms (2.9861(6) Å). Despite the different atomic radii of Al and Co (r_{Al} = 1.43 Å; r_{Co} = 1.26 Å [23]) the averaged distanced are nearly the same. The calculation of the valence sum according to Brown

[24] gives values of 4.65 (Al) and 4.21(Co), respectively. Ta shows CN 16 which is in agreement to its larger radius. Additionally to the two Ta–C bonds there are contacts to 2 Co-, 4 Al-, and 8 Ta-atoms (3.0765(5)/3.0942(5) Å) forming an irregular polyhedron (symmetry $mm2$). The valence sum of Ta is significantly higher (7.35) because of the additional Ta–C bonds (0.92) and the higher metal coordination. It should be mentioned that the valence sums calculated according to Brown can serve only as a rough measure. η-carbides are typical interstitial compounds and the standard parameters used for the calculations will yield too high values.

While the C-atom is easily localised on the 16c-site with full occupation no residual density is found for the 8a-site. Although coordination (octahedron of 6 Ta-atoms) and distances (2.188 Å)

Table 3
Selected distances (in Å) and angles (in °) in Ta_3Al_2CoC, esd's in parentheses

Ta–C	2.1810(4) 2 ×	Al–Al	2.708(13) 3 ×
Ta–Al	2.763(6)/2.988(2) 4 ×	Al–Co	2.509(3) 3 ×
Ta–Co	2.9864(6) 2 ×	Al–Ta	2.763(6)/2.988(2) 6 ×
Ta–Ta	3.0756(5)/3.0942(5) 8 ×		
		Co–Al	2.509(3) 6 ×
C–Ta	2.1810(4) 6 ×	Co–Ta	2.9864(4) 6 ×
Ta–C–Ta	89.63(3)/90.33(3)		

Table 1
Structure refinement of Ta_3Al_2CoC

Compound	$Ta_3Al_2Co_2C$
Crystal shape	Truncated octahedron
Crystal color	Metallic lustrous
Crystal size	$0.08 \times 0.08 \times 0.02\ mm^3$
Formula weight	667.75 g/mol
Crystal system	Cubic
Space group	$Fd\bar{3}m$
Lattice constants	$a = 11.6153(13)$ Å
Cell volume	1567.08 Å^3
Formula units	16
Density, calculated	11.321 g/cm^3
Radiation	$MoK_{\alpha 1}$
θ-range	$-17 \leqslant h \leqslant 17, -17 \leqslant k \leqslant 17, -17 \leqslant l \leqslant 17$
Temperature	23 °C
$2\theta_{max}$	65°
Diffractometer	IPDS I
	$0° \leqslant \omega \leqslant 200°$
	$\psi = 0°, \Delta\omega = 2°$
Exposure time	120 s
Reflections measured	5613
Independent reflections	169
Reflections $I > 2\sigma(I)$	154
Absorption correction	Numerical; equivalent method [20]
R_{int}, R_{sigma}	0.123; 0.029
Absorption coefficient	87.89 mm^{-1}
Extinction coefficient [19]	0.00033(4)
Max/min transmission	0.051, 0.004
Structure solution	Known model
Refinement	SHELXL 97 [20]
Residual electron e$^-$/Å^3 min, max, sigma	+1.95, −2.74, 0.57
Weighting function [20]	0.035; 34.1
Number of parameters	13
R-factors	$R_1(F) = 0.0315, wR_2(F^2) = 0.0857$
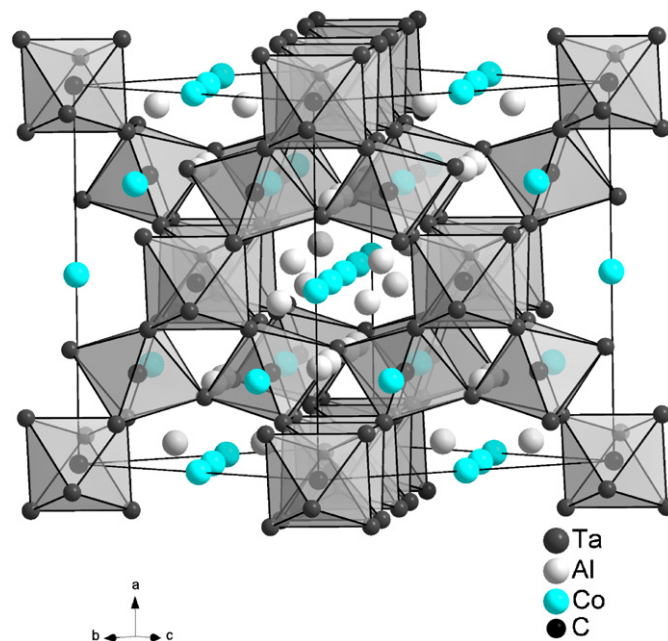
Fig. 2. Crystal structure of Ta_3Al_2CoC.

Table 2
Coordinates, displacement parameters (in Å$^2 \times 10^4$), and site occupation factors in Ta_3Al_2CoC

Atom	Site	x	y	z	U_{eq}	Sof[a]	U_{11}	U_{22}	U_{23}	U_{13}/U_{12}
Ta	48f	0.93670(6)	0.125	0.125	77(4)	1.01(2)	85(4)	72(4)[b]	−3(2)	[b]
Al	32e	0.2926(4)	x	x	94(13)	1.03(4)	94(13)	[c]	9(16)	[c]
Co	16d	0.5	0.5	0.5	102(9)	0.98(2)	102(18)	[c]	−8(10)	[c]
C	16c	0	0	0	99(51)	1.15(14)	99(51)	[c]	−37(64)	[c]

[a] In order to check for mixed occupations and/or vacancies site occupation factors were treated by turns as free variables at the end of the refinement.
[b] $U_{22} = U_{33}$; $U_{12} = U_{13} = 0$.
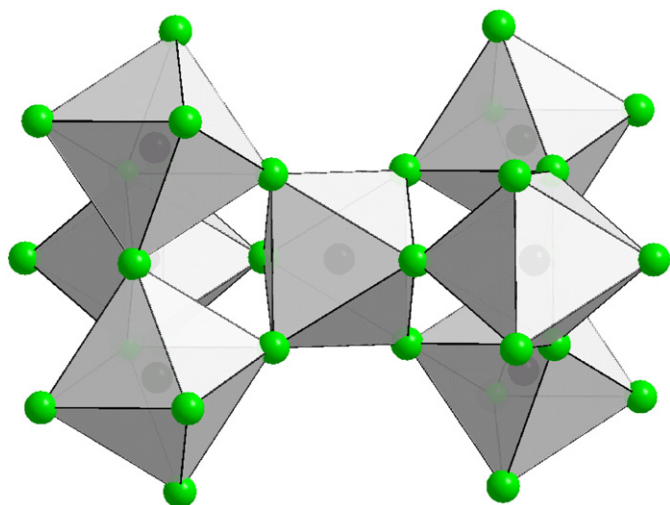[c] $U_{11} = U_{22} = U_{33}$; $U_{12} = U_{13} = U_{23}$.

Fig. 3. Connection of CTa_6-octahedra via common corners in Ta_3Al_2CoC.

are suitable for carbon this site is not occupied. Obviously there is no tendency to form a carbon-poor η-carbide of the type $M_6M'_6C$. This was observed for the system Co/Mo/C where two different η-carbides (i.e. Co_6Mo_6C and $Co_6Mo_6C_2$) were characterised. Also the simultaneous occupation of the sites 8*a* and 16*c*, as it was proposed for $Nb_8Zn_4C_3$ [25], was not observed. This can be explained by the observation that CTM_6-octahedra are usually not connected via common faces [3,4]. Furthermore there is no evidence for deviations from the ordered metal distribution. In $Co_6Mo_6C_2$ the 16*d*-site (Co2) is partially occupied (6.3%) by Mo ($\equiv Co_{5.87}Mo_{6.13}C_2$). Fraker and Stadelmaier [26] give compositions between $Co_{2.94}Mo_{9.06}C_2$ and $Co_{5.45}Mo_{6.54}C_2$. According to our experience the auxiliary metal technique for synthesis and single crystal growth favours the formation of ordered and stoichiometric compounds [16,17,27].

Analyses by EDX and WDX confirm the stoichiometric composition. Especially the exclusion of N and O is important, as they are frequently observed as impurities. Furthermore the clear identification of the light element is necessary, because compounds related to a η-carbide (or Ti_2Ni) are known for borides ($Sc_{4.3}Cr_{0.69}B_{0.4}$ [28], $Nb_4Ni_2B_{0.32}$ [29]), boride oxides (Zr_4Fe_2 $B_{0.4}O_{0.6}$) [30]), nitrides (Fe_4W_2N [31], V_4Co_2N [32,33], Nb_4Co_2N [32], Ta_4Ni_2N [34] and oxides (Ti_4Pd_2O [35], $Zr_4Fe_2O_{0.45}$ [36], Ti_4Fe_2O [37].

4. Conclusions

Well-shaped single crystals of the η-carbide Ta_3Al_2CoC can be grown from a Co/Al-melt by the auxiliary metal technique. The good quality of the single crystals enables for the first time the clear localisation of all atoms in a η-carbide by X-ray diffraction. It turns out that within the small standard deviations all sites are fully occupied by only one kind of atoms. If the labelling system of Parthé and Jeitschko [10] with the formula $M_6^fM_2^dM_4^eX_n^cX_m^a$ is applied to Ta_3Al_2CoC there is $M^f = Ta$; $M^d = Co$; $M^e = Al$; $X = C$; $n = 2$, and $m = 0$. The uptake of light elements like N and O was excluded by WDX measurements. Ta_3Al_2CoC represents the first well-characterized ordered quarternary η-carbide.

The example of Ta_3Al_2CoC shows that the auxiliary metal technique is not only suitable for the single crystal growth of metal-rich borides (τ-borides $Ni_{20}Al_3B_6$ [38]), oxides $Ti_{12}Sn_3O_{10}$ [39] and boride carbides (Al_3BC [40]) but also for carbides. Because of the high importance of η-carbides for cermets and abrasives we will perform measurements of the micro-hardness
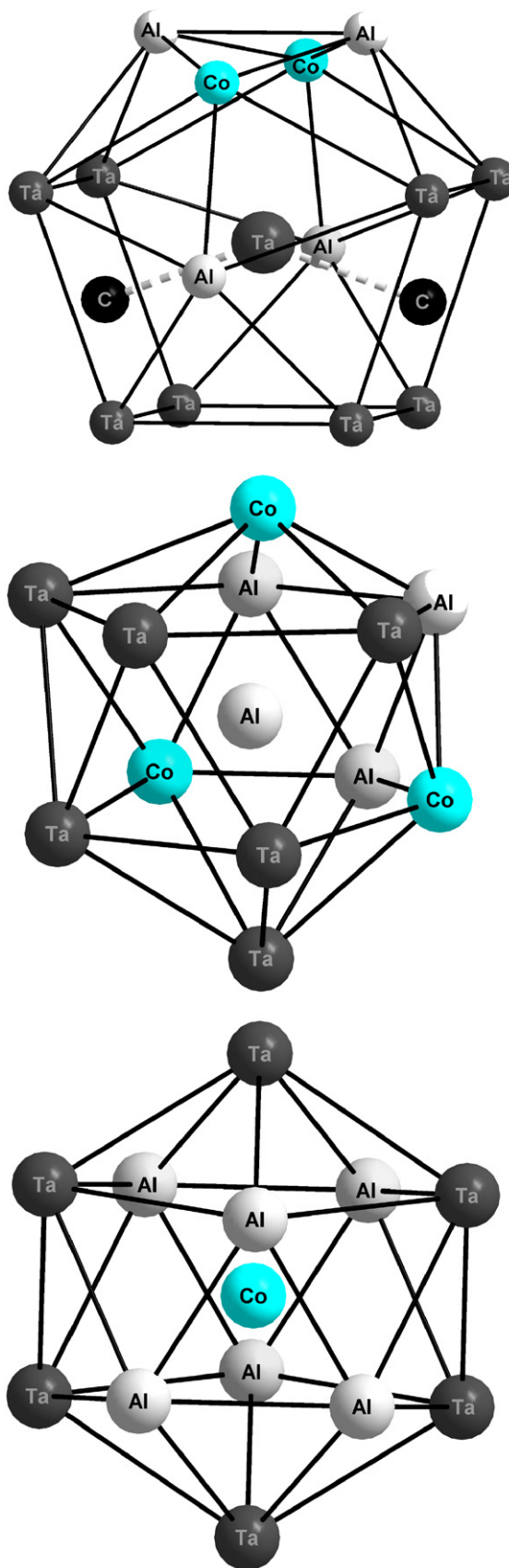

Fig. 4. Surroundings of metal atoms in Ta_3Al_2CoC.

(Vickers, Knoop). The availability of single crystals allows the comparison of these values to those of sintered samples. In this connection it is of special interest that recently for Co_6W_6C a bulk modulus of 462 GPa was measured [41] which is even higher than for diamond (444 [42]) and c-BN (400 [43]).

Acknowledgments

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