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# Electronic properties of hexagonal tungsten monocarbide (*h*-WC) with 3*d* impurities from first-principles calculations

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First-principles FLAPW-GGA calculations have been performed to predict the structural, electronic, cohesive and magnetic properties for hexagonal tungsten monocarbide (*h*-WC) doped with all 3*d* metals. The optimized lattice parameters, density of states, cohesive and formation energies have been obtained and analyzed for ternary solid solutions with nominal compositions $W_{0.875}M_{0.125}C$ (where M = Sc, Ti…Ni, Cu). In addition, the magnetic properties of these solid solutions have been examined, and magnetization has been established for $W_{0.875}Co_{0.125}C$.

## 1. Introduction

Tungsten monocarbide (WC) attracts much attention owing to its unique physical and chemical properties such as extreme hardness, high melting point, chemical inertness, interesting catalytic behavior etc., and belongs to the most promising engineering materials with a wide range of industrial applications [1–4]. Simultaneously, much attention is given to the crystalline and nano-sized WC-based composites comprising other transition metals (WC/M, where M are *d* metals) and related materials suitable for many technological applications.

Today, for WC–M systems a set of various materials has been prepared.

An important group of such materials includes the above-mentioned WC/M composites (termed also as metallo-carbides or cemented carbides), namely, heterogeneous systems that consist of grains of WC glued with a binder metal to combine the hardness of the carbide with the toughness of the metal, see [5–7].

Another group involves the so-called intermediate metal-rich phases such as $Fe_3W_3C$, $Co_3W_3C$ or $Co_6W_6C$. These phases (which adopt individual crystal structures and properties) may arise due to mutual solution in the interface region between WC and transition metals (or their alloys or carbides) or may be prepared using special synthetic routes [8,9].

Finally, a set of restricted solid solutions (SSs) $W_{1-x}M_xC$ ($x \ll 1$) may be formed, where *d* atoms are partially substituted for tungsten atoms. This situation can arise at the contact of WC with metals or their carbides, during mechanical alloying from elemental powders or liquid-phase sintering, see [1–4,10,11].

While extensive theoretical studies have been performed for WC [12–20], much less information is available for the electronic structure, stability and physical properties of the above-mentioned SSs $W_{1-x}M_xC$. To our knowledge, only WC with 25% substitution of Mo or Ti for tungsten and WC-12% M (M = Cr, Co, Zr) alloys have been considered in earlier works [10,11].

In this paper we have performed a systematic study of the effect of substitutional impurities—all transition 3*d* metal ions (Sc, Ti,…,Cu, Zn) on the structural, electronic, cohesive and magnetic properties of hexagonal WC (*h*-WC).

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## 2. Models and computational method

The basic phase in the WC system is the *h*-WC. This material has a hexagonal structure (space group *P*-6*m*2), where tungsten and carbon atoms form simple hexagonal layers, their stacking is of the *ABAB*… type. Both W and C sites are trigonal prismatic. On the other hand, systematic data on SSs in WC–M systems, where M are 3*d* transition metals, are not available in the literature up to now.

In our simulations we examine the structural, electronic and magnetic properties of *h*-WC-based SSs $W_{1-x}M_xC$ in the doping limit ~12%. For this purpose we use the periodic 16-atomic $W_8C_8$ supercell, in which one tungsten atom is replaced by M atoms (supercells $W_7MC_8$). In this way we model ternary SSs, which correspond to the nominal compositions of $W_{0.875}M_{0.125}C$.

Our band-structure calculations for all $W_{0.875}M_{0.125}C$ SSs (where M = Sc, Ti,…,Ni and Cu) were performed with the full potential method with mixed basis APW+lo (LAPW) implemented in the WIEN2k suite of programs [21]. The generalized gradient correction (GGA) to exchange-correlation potential of Perdew, Burke and Ernzerhof [22] was used. The electronic configurations were taken to be [Xe] $6s^25d^4$ for W, [Ar] $4s^23d^n$ for M and [He] $2s^22p^2$ for carbon. Here, the noble gas cores were distinguished from the subshells of valence electrons. The basis set inside each muffin tin (MT) sphere was split into core and valence subsets. The core states were treated within the spherical part of the potential only, and were assumed to have a spherically symmetric charge density in MT spheres. The valence part was treated with the potential expanded into spherical harmonics to $l = 4$. The valence wave functions inside the spheres were expanded to $l = 12$. The plane-wave expansion with $R_{MT} \times K_{MAX}$ was equal to 7, and *k* sampling with $10 \times 10 \times 10$ *k*-points mesh in the Brillouin zone was used. Relativistic effects were taken into account within the scalar-relativistic approximation.

The self-consistent calculations were considered to have converged when the difference in the total energy ($E_{tot}$) of the crystal did not exceed 0.01 mRy as calculated at consecutive steps. In this way we have used a standard optimization regime as was described in the original version WIEN2k [21]; this means a minimization of the $E_{tot}$ by variation on the lattice parameters (*a* and *c*) and the minimization of the atomic forces (<0.05 mRy/a.u.). The density of states (DOS) was obtained using a modified tetrahedron method [23].

## 3. Results and discussion

### 3.1. Structural properties and density

As the first step, $E_{tot}$ versus cell volume (*V*) calculations were carried out for the *h*-WC to determine the equilibrium structural parameters. The calculated values ($a = 0.2926$ nm and $c = 0.2849$ nm) are consistent with those measured experimentally ($a = 0.2906$ nm and $c = 0.2837$ nm, see [4]). Our theoretical values are slightly higher (at about 1%) as compared to the experimental data. This is a well-known fact of overestimation of structural parameters for GGA calculations. The theoretical density ($\rho$, 15.395 g/cm$^3$) also agrees with the experiment: $\rho = 15.5$–$15.7$ g/cm$^3$ [24].

**Table 1**
Optimized lattice parameters (*a* and *c*, in nm) for ternary $W_{0.875}M_{0.125}C$ alloys in comparison with *h*-WC.

| Phase | WC | $W_{0.875}Sc_{0.125}C$ | $W_{0.875}Ti_{0.125}C$ | $W_{0.875}V_{0.125}C$ | $W_{0.875}Cr_{0.125}C$ |
|---|---|---|---|---|---|
| *a* | 0.2926 | 0.2952 | 0.2927 | 0.2912 | 0.2905 |
| *c* | 0.2849 | 0.2856 | 0.2838 | 0.2830 | 0.2824 |
| *Phase* | $W_{0.875}Mn_{0.125}C$ | $W_{0.875}Fe_{0.125}C$ | $W_{0.875}Co_{0.125}C$ | $W_{0.875}Ni_{0.125}C$ | $W_{0.875}Cu_{0.125}C$ |
| *a* | 0.2905 | 0.2909 | 0.2912 | 0.2920 | 0.2929 |
| *c* | 0.2818 | 0.2812 | 0.2819 | 0.2820 | 0.2828 |

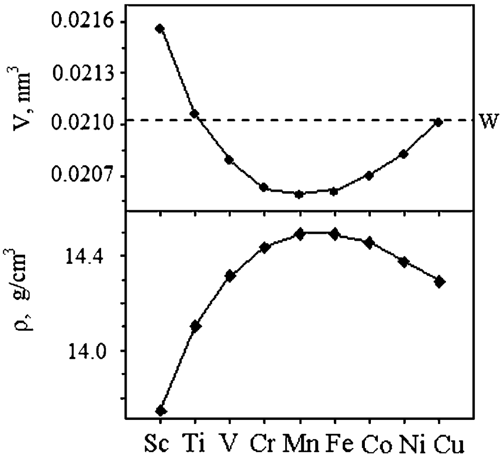

**Fig. 1.** Cell volumes (*V*, nm$^3$) and density ($\rho$, g/cm$^3$) for ternary $W_{0.875}M_{0.125}C$ SSs. Cell volume for *h*-WC is also given.

Let us discuss the same parameters as obtained for the ternary $W_{0.875}M_{0.125}C$ SSs, Table 1 and Fig. 1. Note that our lattice parameters are in reasonable agreement with other available data. For example, our values for $W_{0.875}Ti_{0.125}C$ are $a = 0.2927$ nm and $c/a = 0.9696$ as compared with $a = 0.289$ nm and $c/a = 0.961$ for $W_{0.750}Ti_{0.250}C$ [10]. According to our FLAPW-GGA calculations, the parameters *a* and *c*/*a* for $W_{0.875}Cr_{0.125}C$ and $W_{0.875}Co_{0.125}C$ are 0.2905, 0.972 nm and 0.2912, 0.968 nm, respectively, as compared with $a = 0.2905$ nm and $c/a = 0.972$ (for $W_{0.875}Cr_{0.125}C$) and $a = 0.2901$ nm and $c/a = 0.976$ (for $W_{0.875}Co_{0.125}C$) as obtained by means of the LDA approach (VASP code) [11]. Interestingly, a non-monotonous behavior of *a* and *c* parameters was established in our systematic calculations when going from $W_{0.875}Sc_{0.125}C$ to $W_{0.875}Cu_{0.125}C$. In addition, for various $W_{0.875}M_{0.125}C$ SSs the trends of *a* or *c* parameter variations were different, Table 1. In fact, the parameter *a* decreased from $W_{0.875}Sc_{0.125}C$ to $W_{0.875}Cr_{0.125}C$ and then increased as going to $W_{0.875}Cu_{0.125}C$, whereas the minimal value for the constant *c* was obtained for $W_{0.875}Fe_{0.125}C$, see Table 1. Thus, *anisotropic deformation* of the crystal structure of the matrix (*h*-WC) took place when tungsten was replaced by 3*d* atoms.

Naturally, it should be expected that all $W_{0.875}M_{0.125}C$ alloys containing more light 3*d* atoms will adopt lower density as compared with WC. The lowering of $\rho$ change from 6% (for $W_{0.875}Fe_{0.125}C$) to 11% (for $W_{0.875}Sc_{0.125}C$). However, if the atomic masses of substitutional M atoms increase when going from Sc to Cu, the cell volumes (*V*) change non-monotonously, and the density of the SSs also changes non-monotonously and adopts the maximal values for compositions with Mn and Fe, as shown in Fig. 1.

### 3.2. Cohesive properties and energies of formation

To provide an insight into the fundamental aspects of phase relations in the W–M–C systems, some estimations based on the $E_{tot}$ calculations were performed.