FIRST-PRINCIPLES INVESTIGATION OF THE INFLUNECE OF ALLOYING ELEMENTS ON THE ELASTIC AND MECHANICAL PROPERTIES OF TUNGSTEN— G. D. Samolyuk, Y. N. Osetskiy, and R. E. Stoller (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this research is to support possible approaches to the design of ductile tungsten alloys through the use of relevant *ab initio* electronic structure calculations.

SUMMARY

The equilibrium lattice parameter, elastic constants and phonon dispersions were calculated for set of binary $W_{1-x}Re_x$ alloys with different Re concentrations within the local density approximation of density functional theory (DFT). Reasonable agreement between results obtained using conventional super-cell and virtual crystal approximation (VCA) approaches has been demonstrated. Increasing the Re concentration leads to reduction of the *c*' elastic constant which becomes negative at a Re concentration of 85%. This change of sign means that the bcc structure is no longer stable at high Re concentrations. In contrast to the *c*' dependence, Poisson's ratio increases with increasing Re concentration. The value of this latter parameter is used as a screening parameter to identify improvement in the alloy ductility.

PROGRESS AND STATUS

Introduction

The alloys of W with Re have been studied extensively both using experiment [1, 2] and theory [3, 4]. Alloying with Re has the effect or ductility improvement of the tungsten. In the present research we are going to investigate the concentration dependence of elastic constants and phonons from first-principles electronic structure calculation. This result will be used in future search for the other alloying elements causing similar changes in tungsten alloy elastic properties.

Formalism

We calculate the electronic structure within the local density approximation of density functional theory using the quantum espresso package [5]. The calculation has been done using plane-wave basis set and ultrasoft pseudo-potential. The Brillouin zone (BZ) summations were carried out over a 24x24x24 BZ grid for the system with one unit cell and 16x16x16 grid for the supercell, representing 2x2x2 unit cells, with Gaussian boarding 0.02 Ry. The plane wave energy cut off at 42 Ry allows reaching accuracy 0.2 mRy/atom. As a realization of VCA for the pseudo potential method we used the scheme proposed in Ref. [6]. The phonon frequencies were calculated using the density-functional linear response method [7, 8].
The elastic constants were calculated from the total energies obtained for the set of unit cell deformations [9] with strain tensor

$$\hat{\varepsilon} = \begin{bmatrix} e_1 & e_6/2 & e_5/2 \\ e_6/2 & e_2 & e_4/2 \\ e_5/2 & e_4/2 & e_3 \end{bmatrix} \qquad (1)$$

Under this strain the change of the energy equals

$$\Delta E = -P(V)\Delta V + V\sum_{i=1}^{6}\sum_{j=1}^{6} c_{ij} e_i e_j / 2 \qquad (2)$$

Thus for the orthorhombic strain

$$e_1 = -e_2 = x, e_3 = x^2/(1-x^2), e_4 = e_5 = e_6 = 0 \qquad (3a)$$

the energy change equals

$$\Delta E = V(c_{11} - c_{12})x^2 \qquad (3b)$$

and for monoclinic strain

$$e_6 = x, e_3 = x^2/(4-x^2), e_1 = e_2 = e_4 = e_5 = 0 \qquad (4a)$$

it equals

$$\Delta E = Vc_{44}x^2/2 \qquad (4b)$$

where c_{ij} are elastic constants.

The Poisson's ratio equals

$$\nu = \frac{c_{12}}{c_{11}+c_{12}} \qquad (5)$$

Results

The results for the density of states calculated for 2x2x2 super cell containing 16 atoms in total, 16 W for pure metal and 15 W and 1 Re for the modeling of W alloy with 6.25 Re atoms alloying, and calculated in VCA approximation are presented on Figures 1a and 1b respectively.

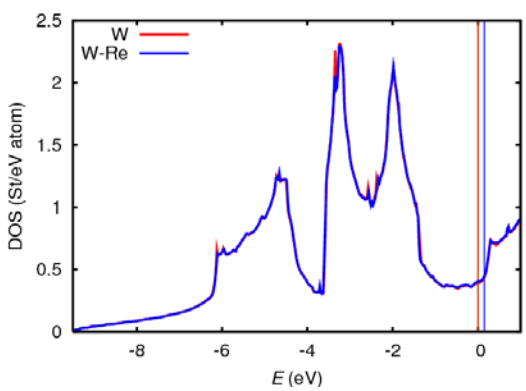

Figure 1a $W_{1-x}Re_x$ DOS for x=0 and x=0.0625 calculated in VCA

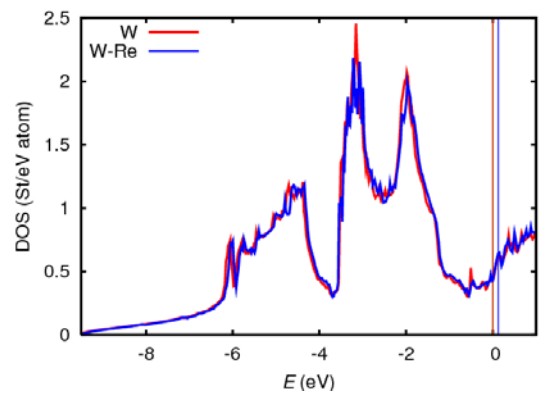

Figure 1b $W_{1-x}Re_x$ DOS for x=0 and x=0.0625 calculated for super cell 2x2x2

The zero energy in these figures corresponds to occupation of valence states by 6 electrons per atom and Fermi energies are shown by the vertical line red for pure metal and blue for the W-Re alloy. Thus for the pure tungsten the Fermi energy is placed at 0 eV. The similarity of the DOS calculated by two methods supports the conclusion of applicability of the VCA approximation for W-Re alloys at low Re concentration. As can be seen from both figures the only effect of Re alloying on the electronic DOS is the shift of the Fermi energy corresponding to occupation of each virtual atom by an additional 0.0625 electrons. It means that the so called rigid band approximation can be applied. Thus, all diluted tungsten based alloys with the same number of electrons per atom (e/a) have the same elastic constants. The concentration of different alloying elements which keep the same (e/a) value can be calculated through the simple expression

$$x = \frac{(e/a)}{Z - Z_W} \qquad (6)$$

where Z is number of valence electrons of the alloying atom and Z_W - of tungsten.

The calculated elastic properties reproduce experimental results with 10% accuracy, as can be seen from the comparison of calculated phonon dispersions with experiment, shown in Figure 1.

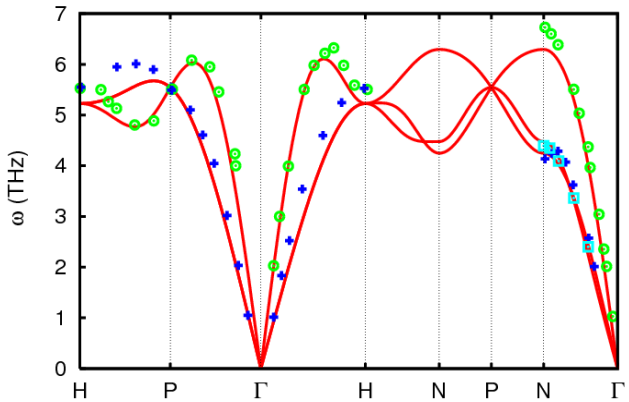

Figure 2 Calculate and experimental [10] phonons in pure W.

In order to check the accuracy of the VCA approximation we calculated the elastic modulus of a $W_{1-x}Re_x$ alloy for the concentration x= 0.0625 by both super cell and VCA methods. The results are presented in Table 1 and figures 2-5.

Table 1. Experimental (first row) and calculated lattice parameter (*a*), bulk modulus (*B*), elastic constants (c_{ij}) in GPa and Poisson's ratio *v*.

		a (a.u.)	*B*	c_{11}-c_{12}	c_{44}	c_{11}	c_{12}	*v*
exp	W	5.98	314	328	163	533	205	0.278
1x1x1	W	6.03	307.1	320.7	141.1	520.9	200.2	0.278
	$W_{1-x}Re_x$, x=0.03	6.024	306.1	311.9	142	514.0	202.1	0.278
	$W_{1-x}Re_x$, x=0.05	6.022	305.5	306.2	142.9	509.6	203.5	0.285
	$W_{1-x}Re_x$, x=1/16	6.020	305.2	302.6	143.5	506.9	204.3	0.287
	$W_{1-x}Re_x$, x=0.10	6.015	303.8	292.0	144.6	498.5	206.5	0.293
	$W_{1-x}Re_x$, x=0.30	5.988	296.0	259.9	155.6	469.3	209.4	0.309
	Re	5.918	338.3	-60.5	162.9	298.0	358.5	0.546
2x2x2	W_{16}	6.019	305.9	308.9	138.6	511.8	202.9	0.284
	$W_{15}Re$	6.015	299.0	295.6	139l3	496.1	200.5	0.288

For the elastic constants the largest difference between calculated and experimental values was obtained for c_{44} and is about 13 % for the one unit cell calculations and slightly larger for 2x2x2 super cell calculations. The VCA and super cell results are in reasonable agreement, except for the c_{44} dependence on Re concentration. c_{44} increases in VCA calculation and decreases in super cell case with addition of 6.25 % of Re to W. However, the VCA result is in agreement with experiment, see Figure 3.

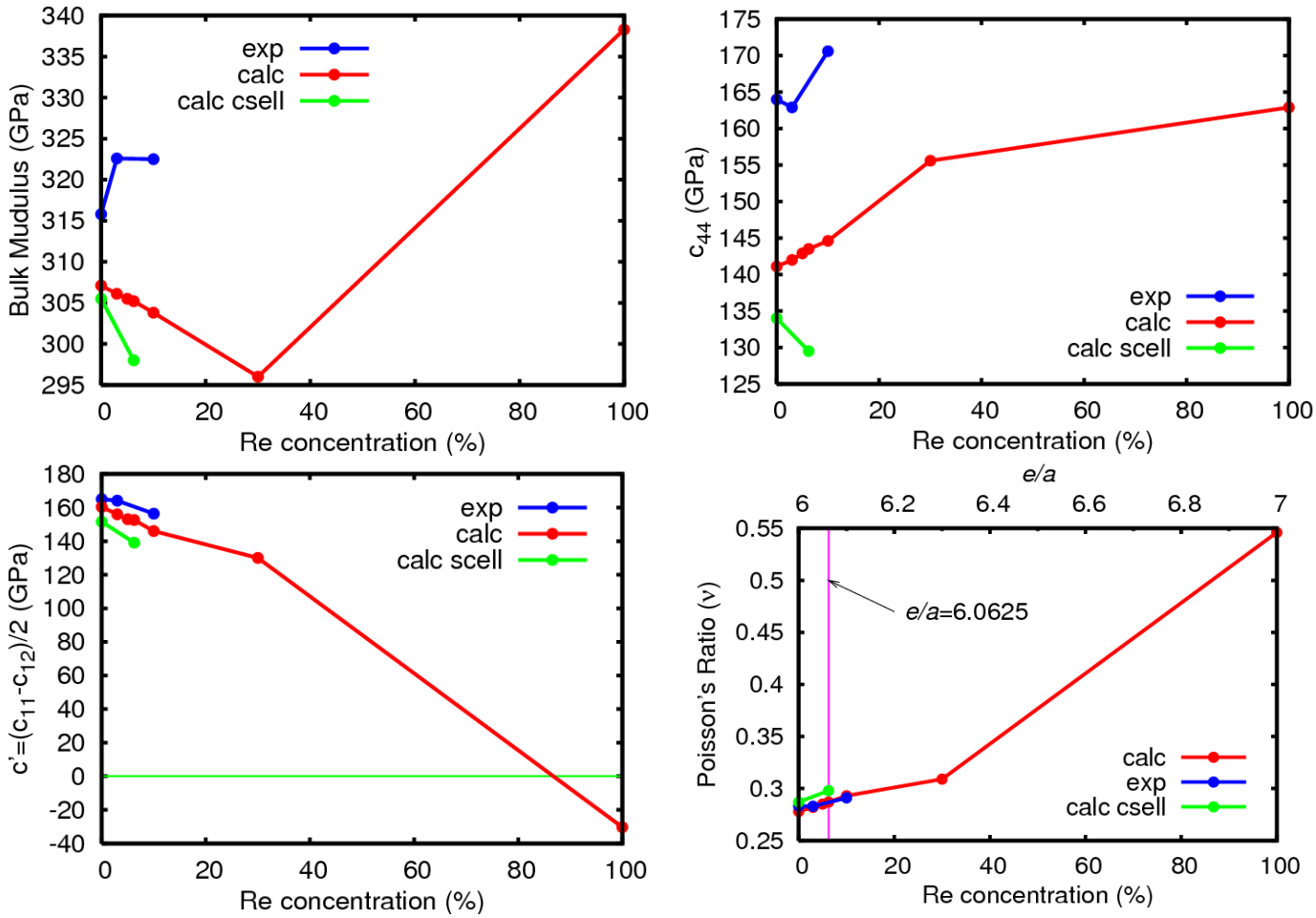

Figure 3 Elastic constant calculated by VCA (red) and super cell (green) methods and experiment [11] (blue) as a function of concentration.

Surprisingly, a large difference in behavior of bulk modulus between VCA result and experiment was obtained. It increases in experiment, see Figure 3, and decreases in our calculations for low Re concentrations. At Re concentrations larger than 30 % the calculated value of *B* starts to increase. However, the applicability of VCA should be checked at such larger alloy concentrations. Also, it should be mentioned that the experimentally observed phase of $W_{1-x}Re_x$ at this concentration is σ-phase not a bcc solid solution. Both *c*' and *v* are in good agreement with experiment and super cell calculations. The *c*' modulus decreases with Re concentration until it turns negative at 85 % Re. This change of *c*' sign corresponds to dynamic lost of stability of the bcc structure. The c' elastic constant corresponds to long-wave transversal phonons branch in [ξξ0] directions ($T_{[1\text{-}10]}$[ξξ0]). The softening of this phonon mode (see Fig. 4) provides a transition path from the bcc to dhcp structure (see discussion in [3]).

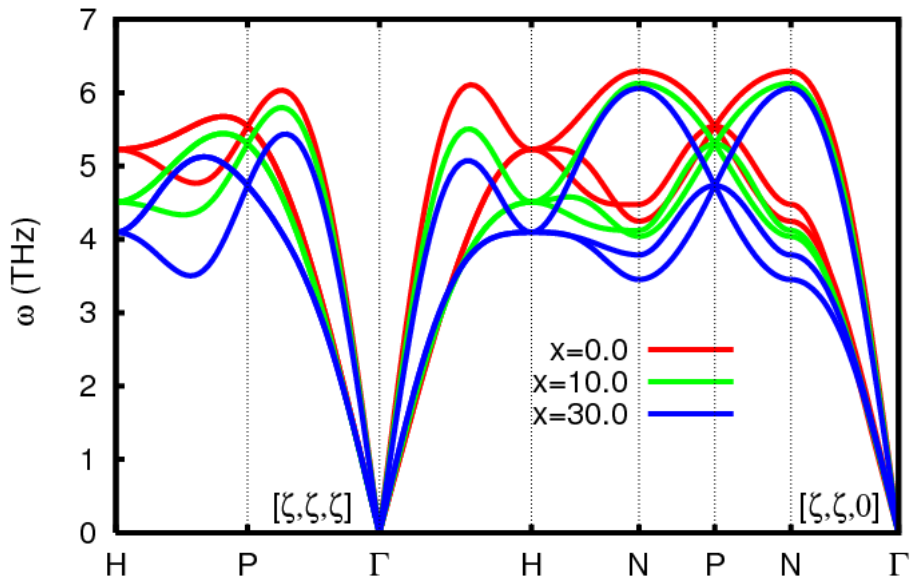

Figure 4 Calculated phonons dispersion in $W_{1-x}Re_x$ calculated in VCA for three Re concentrations.

Experimentally the Re rich W-R alloy is an ordered hcp structure. Such a decrease of bcc crystal could be used as an indicator of the Re ductilizing effect, see discussion in Ref. [2]. Another indicator of ductility improvement discussed in the literature [12] is Poisson's ratio. The author in that publication uses the thesis "the higher the Poisson ratio, the better ductility the crystal has". Within this assumption the authors looked for potential ductilizers in Cr. We found that the Poisson's ratio *v* increases with increase of Re concentration and this result could probably support the point of view of the authors in [12]. According to expression (6) the same change in the elastic properties of tungsten alloy as 6.25 % of Re will result for the concentration of alternate elements shown in Table 2.

Table 2. Equivalent concentrations of alternative alloying elements to produce the same change in elastic properties of tungsten as produced by 6.25% rhenium

e/a=6.0625	Concentration (%) in W
Re	6.25
Os	3.125
Ir	2.08
Pt	1.563

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