Materials Science-Poland, Vol. 23, No. 2, 2005

Atomic modelling of point defects in B2-RuAl

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Ab initio calculations based on density functional theory (DFT) and the pseudopotential method have been used to study B2-structured RuAl. The structural parameters, volume changes of single defects and pressure caused by the presence of point defects in B2-RuAl intermetallic compound were computed by the ab initio pseudopotential method with the plane-wave basis set and a generalized gradient approximation (GGA). The calculated structural parameters are in good agreement with available experimental data.

Key words: *Ab initio calculations; density functional calculations*

1. Introduction

In recent years, ab initio computations have become one of the tools in modern computational materials science. These calculations, based on the concept of DFT developed by Walter Kohn [1] in 1960s, can be used to predict the positions of individual atoms in cells (super-cells) of various systems and in particular in intermetallic compounds. By this method the inter-planar distances, energy of cohesion and relative energies of point defects, such as vacancies and foreign atoms can also be estimated. These in turn can be used to explain most of the likely crystal structures and the positions of defects which are relevant to modelling mesoscopic properties of crystalline materials.

In the present work, calculations from first principles have been performed for B2-RuAl. This compound is known to crystallize in a cubic lattice, of the CsCl type, with the space group *Pm*3*m*. B2-structured RuAl has been considered to be one of the potential materials for high temperature applications in aggressive environments because of its high temperature strength, oxidation and corosion resistance and good room temperature toughness [2].

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2. Computations

For the computations of the crystal structure of RuAl ultrasoft pseudopotentials under the assumption of the gradient generalized approximation (GGA) has been adopted. CASTEP [3] and VASP [4, 5] packages have been employed and the computations have been carried out at the ICM of Warsaw University. CASTEP and VASP are a DFT pseudopotential total-energy codes. The Monkhorst–Pack scheme was used to sample the Brillouin zone. The calculations were considered to have converged when forces acting on the atoms were less then 0.01 eV/atom and the residual bulk stress was smaller than 0.02 GPa.

3. Results

3.1. Structural parameters

The cell constant and the cohesion energy have been calculated. The cohesive energy of a solid is defined as the energy required to separate the condensed material into isolated free atoms. The total energy for the supercell and for free atoms has also been determined. The results of computations are plotted in Fig. 1 in the form of graph of cohesion energy E_c against the cell constant. It should be noted that the energy minimum $E_c = -6.44$ eV/at) is attained for $a = b = c = 2.9825$ Å. This value agrees well with the literature data (e.g., $a = b = c = 2.967$ Å [6], 2.95–3.03 Å [7]).

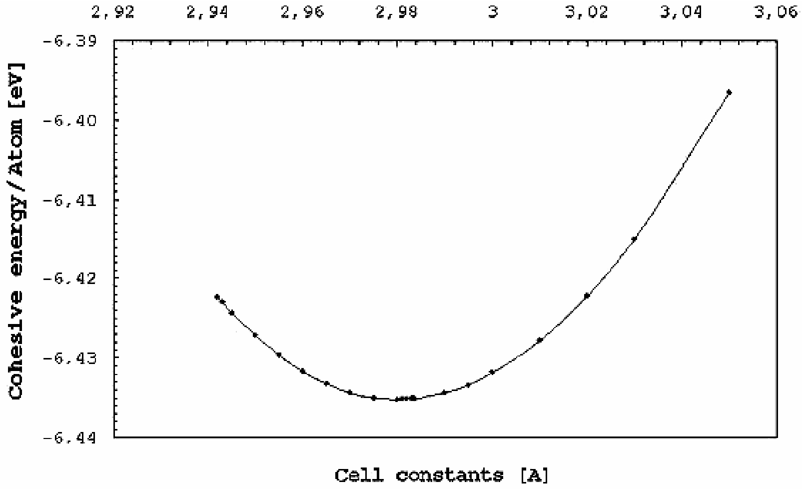

Fig. 1. Cohesion energy [eV] against the cell constant [Å]

First principles computations have been used to calculate the formation energy, E_{form}, of the B2-RuAl. This alloy is formed directly from the constituent Ru and Al crystals. As the first step, the energies of Ru (hcp) and Al (fcc) in the most stable crystalline states were calculated. As the second step, the energies of the compound described above were obtained. The variation of E_{form} with supercell size is given in Table 1.

Table 1. VASP calculations of the variation of E_{form} with supercell size

Supercell size	1×1×1	2×2×2	3×3×3	Experimental
E_{form} [eV/at]	–0.6689	–0.6699	–0.6645	0.64 [8]

Ab initio computations have been also used to calculate the bulk modulus of the system B which is equal to 203 GPa. Again this is close to the literature value of 208 GPa [9].

3.2. Point defects in B2-RuAl

Ab-inito computations of crystal lattice defects can be carried out by following two routes. Firstly, it can be estimated how a given defect changes the cell size of the respective crystal lattice. In this case, the cell structure is numerically optimized after the defect in question is generated (e.g., one atom is removed to form a vacancy). The new positions of atoms are subsequently computed and the change in crystal volume is determined. The second computational route of concerns the local pressure induced by a point defect. The stresses in the unit cell containing the given defect are computed with the assumption that atoms are frozen in the same positions as in defect-free structure. For computations based on 2×2×2 super-cells the latter approach seems to be more appropriate, as the defect coordination zones are "submerged" into the crystal with the equilibrium positions of atoms. The useful information which can be obtained with this assumption is an estimate of the energy needed to generate the defects of interest and their preferential positions.

3.3. Volume changes of single defects

Ab-initio computations were also carried out for vacancy and substitutional atoms of Cr, Fe and Co. In the ground state energy calculations, the primitive unit cell was used. The elements Al, Co, and the alloy RuAl were treated as being non-magnetic, Cr as antiferromagnetic and Fe(α) was considered as ferromagnetic. Since RuAl is non-magnetic the defect ground state energies were also calculated as non-magnetic. For this case 2×2×2 and 3×3×3 super-cells have been used. The vacancy, antisite atoms and the ternary alloying elements have been studied in the position of Al and Ru atoms. The results are summarized in Table 2 which lists super-cell ground state energies E_c and single defect volume changes, $\Delta V/V$.

Table 2. Calculated ground state energies E(A,B), volume V and relative to RuAl volume change $\Delta V/V$ of a single defect in the 2×2×2 and 3×3×3 supercells. VASP calculations

System (A, B)	E(A, B) [eV]	V [Å^3]	$\Delta V/V$ [%]
(8Ru, 8Al)	–113.216	217.83	0.0
(27Ru, 27Al)	–381.810	735.41	0.0
(8Ru, 7Al Ru)	–116.660	219.22	0.638
(27Ru, 26Al Ru)	–385.127	737.10	0.229
(7Ru Al, 8Al)	–107.479	221.08	1.492
(26Ru Al, 27Al)	–376.438	738.36	0.399
(8Ru, 7Al vac.)	–105.236	212.24	–2.566
(27Ru, 26Al vac.)	–373.837	729.40	–0.817
(7Ru vac., 8Al)	–107.479	221.08	–1.196
(26Ru vac., 27Al)	–371.107	732.81	–0.355
(8Ru, 7Al Cr)	–117.795	215.94	–0.868
(27Ru, 26Al Cr)	–386.545	732.84	–0.349
(7Ru Cr, 8Al)	–111.743	217.32	–0.234
(26Ru Cr, 27Al)	–380.644	734.51	–0.122
(8Ru, 7Al Fe)	–115.682	215.02	–1.290
(27Ru, 26Al Fe)	–384.227	732.17	–0.441
(7Ru Fe, 8Al)	–111.505	214.56	–1.501
(26Ru Fe, 27Al)	–380.095	731.64	–0.513
(8Ru, 7Al Co)	–114.572	215.00	–1.299
(27Ru, 26Al Co)	–383.145	732.13	–0.446
(7Ru Co, 8Al)	–110.978	214.24	–1.648
(26Ru Co, 27Al)	–379.583	731.26	–0.564

3.4. Pressure caused by the presence of a point defect

The pressure, P [GPa] caused by the presence of a point defect in 2×2×2 super-cell were determined. The results are summarized in Table 3.

Table 3. The cohesive energy (in eV) per a supercell composed of 2×2×2 cells and having its constants as in an equillibrium crystal, and the pressure P, in GPa, caused by a presence of a point defect. CASTEP calculations

System (A, B)	E_{koh} (A, B) [eV]	P [GPa]
(8Ru, 8Al)	–104.67	0.0
(8Ru, 7Al Ru)	–106.88	2.76
(7Ru Al, 8Al)	–99.13	1.65
(8Ru, 7Al vacans)	–96.12	–2.04
(7Ru vacans, 8Al)	–95.11	–2.45

4. Conclusions

Ab initio calculations have been used to determine cohesion energy E_c against the cell constant, formation energy, E_{form}, of the B2-RuAl. First principles computations of crystal lattice defects were carried out following two routes. Firstly, changes the size of the respective crystal lattice cell caused by the presence of a given defect have been estimated. The second computational route concerned the local pressure induced by a point defect.

Acknowledgements

The simulations were performed at the Interdisciplinary Centre for Mathematical and Computational Modelling, Pawińskiego 5A, PL-02-106 Warsaw.

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Received 6 September 2004
Revised 13 January 2005