Apparent Sizes of Solute Atoms in Aluminium from First Principles

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Structural changes upon the introduction of substitutional defects in fcc aluminium were investigated in *ab initio* calculations within the framework of density functional theory. Calculations show that the addition of copper or tin impurities results in contraction or expansion of the crystal lattice, respectively, while the presence of silver has little effect on the equilibrium geometry. The theoretical results show good agreement with experiment.

1. Introduction

Density functional theory (DFT) [1,2] and the performance of computers of recent years has made it possible to study the quantum mechanical origins of many macroscopic properties of condensed matter systems. Such systems include not only pure crystalline materials, but crystals with defects or dislocations, as well as precipitate phases embedded in a host material. The present study considers substitutional defects in aluminium and their effect on the geometry of the crystal lattice. The theoretical results are compared with experimental data.

2. Method

The ground state valence electron densities in periodic structures were obtained by numerical solution of the Kohn-Sham equations [2] within the frozen-core approximation. The nuclei and core electrons were treated using either the pseudopotential (PP) approximation [3] as implemented in the ABINIT software package [4], or the full-potential linearised augmented planewave (FLAPW) method implemented in the WIEN2k package [5]. The Perdew-Burke-Ernzerhof generalised gradient approximation (GGA) [6] for the exchange-correlation functional was used in all calculations.

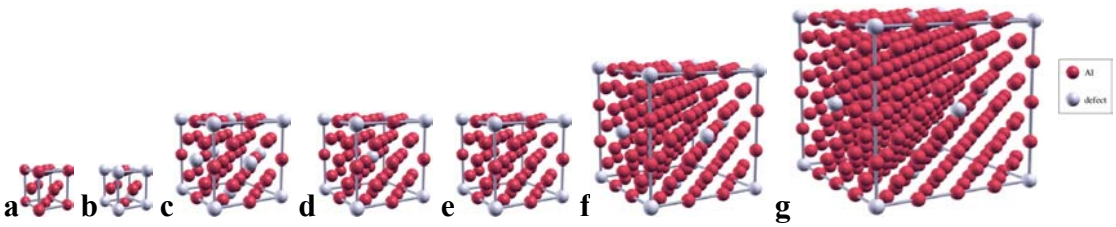

Figure 1. Supercells used to model substitutional defects in face-centred cubic aluminium. Defect concentrations (number of defects per lattice site) are (a) 0, (b) 1:4, (c) 1:8, (d) 1:16, (e) 1:32, (f) 1:27, (g) 1:64.

Defects were studied using periodic structures defined by supercells consisting of up to 64 conventional face-centred cubic (fcc) unit cells of aluminium, where one or more aluminium atoms were replaced with impurity atoms or vacancies. Supercells used in the present study are shown in Fig. 1. To determine the equilibrium geometry for supercells with defects, the total energy per unit cell was minimised numerically with respect to supercell volume and the positions of all atoms in the cell. For supercells containing only aluminium or aluminium and copper, thorough studies of the convergence of supercell geometry and total energy with respect to numerical parameters were carried out. For the sake of brevity, details will be presented elsewhere.

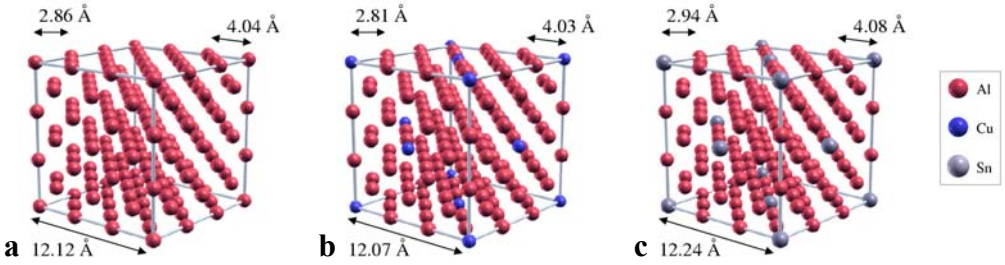

Figure 2. Equilibrium geometries calculated using the FLAPW method. (a) Pure aluminium. (b) Aluminium with copper impurities. (c) Aluminium with tin impurities.

3. Results

Typical changes in fcc supercell geometry upon the introduction of a defect are illustrated in Fig. 2 that shows equilibrium structures for fcc aluminium [Fig. 2(a)] with substitutional copper [Fig. 2(b)] or tin [Fig. 2(c)].

The replacement of one in 27 aluminium atoms with copper [Fig. 2(b)] results in a reduction of supercell volume, and local lattice strain in the direction of the defects, i.e., aluminium atoms will move towards copper atoms during structural relaxation. The addition of tin was found to have the opposite effect on the fcc geometry. Aluminium atoms move away from tin atoms and the volume of the solid is increased [Fig 2(c)]. The calculations also show that tin is highly insoluble in aluminium with about 0.8 eV of energy required to accommodate a single tin atom. The insolubility of tin in aluminium is well established experimentally [7,8]. Similar results for silver indicate no appreciable change in lattice geometry. This is as expected from experiment [9].

Table 1. Summary of results for substitutional copper and vacancies in aluminium.

Defect type	Method	Defect conc.	r_{defect} / r_{Al}
copper	PP (ABINIT)	1 : 4	0.889 ± 0.003
		1 : 8	0.877 ± 0.006
		1 : 16	0.888 ± 0.012
		1 : 27	0.879 ± 0.020
	FLAPW (WIEN2k)	1 : 27	0.889 ± 0.020
	experimental [9]	1 : 62	0.889 ± 0.026
		1 : 125	0.889 ± 0.015
		1 : 250	0.889 ± 0.025
vacancy	PP (ABINIT)	1 : 8	0.898 ± 0.002
		1 : 16	0.893 ± 0.003
		1 : 27	0.891 ± 0.004
		1 : 32	0.891 ± 0.005
		1 : 64	0.886 ± 0.010

For quantitative comparison of the numerical results with experimental data, let us define the apparent radius of a defect as

$$r_{defect} = r_{Al} \{[<a>^3 - (1 - C)\, a_{Al}^3] / C\}^{1/3} / a_{Al} ,$$

where a_{Al} is the lattice parameter for defect-free aluminium, $\langle a \rangle$ is the mean lattice parameter for the perturbed crystal structure, $r_{Al} = a_{Al} / 2^{3/2}$ is the metallic radius of aluminium, and C is the defect concentration, defined as the mean number of defects per lattice site.

Table 1 shows numerical results for apparent radii of copper atoms at concentrations between 1:27 and 1:4, as well as experimental results from Ref. [11] at lower solute concentrations. Numerical results for vacancies are also shown. The last column of Tab. 1 shows the ratio of defect radius to metallic radius of aluminium corresponding to lattice parameters $a_{Al} = 4.0464 \pm 0.0002$ Å (PP) and $a_{Al} = 4.040 \pm 0.002$ Å (FLAPW), and $a_{Al} = 4.0413 \pm 0.0004$ Å (experimental).

The results show that the effective radii of the defects are largely independent of the defect concentration. Copper impurities are about 11 % smaller than aluminium atoms, and comparable with the size of vacancies in the pure metal. The numerical results for copper show good agreement with experimental data. To better facilitate comparison between theory and experiment, data on the effect of copper concentration on the mean lattice constant are presented in Fig. 3.

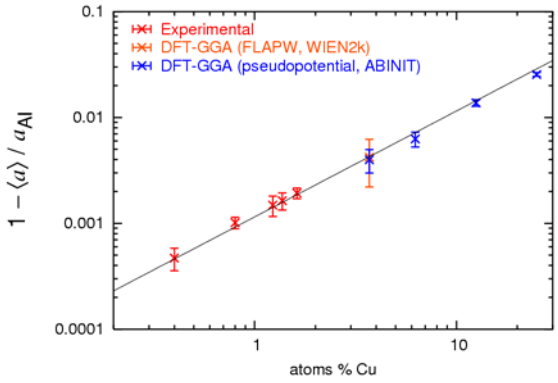

Figure 3. Numerical and experimental [9] results for the mean lattice parameter $\langle a \rangle$ of solid solutions of copper in aluminium.

Acknowledgments

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References

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