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2004 J. Phys.: Condens. Matter 16 5199

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Metastable phases of silver and gold in hexagonal structure

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Received 1 March 2004

Published 2 July 2004

Online at stacks.iop.org/JPhysCM/16/5199

doi:10.1088/0953-8984/16/28/038

Abstract

Metastable phases of silver and gold in hexagonal close-packed structures are investigated by means of first-principles total-energy calculations. Two different methods are employed to find the equilibrium states: determination of the minima along the hexagonal epitaxial Bain path, and direct determination of minima of the total energy by a new minimum-path procedure. Both metals have two equilibrium states at different values of the hexagonal axial ratio c/a . For both metals, the elastic constants show that the high- c/a states are stable, hence, since the ground states are face-centred cubic, these states represent hexagonal close-packed metastable phases. The elastic constants of the low- c/a states show that they are unstable.

1. Introduction

The capability of calculating first-principles total energies of crystals for any structure has made it possible to find metastable phases from theory. A two-stage procedure first finds minima of the total energy with respect to structure, which are equilibrium structures, i.e. structures with zero stress. The elastic constants of the equilibrium structures are then tested to see if they satisfy the stability conditions.

One way to find metastable phases is to find minima of energy in body-centred tetragonal (bct) structures for elements with hexagonal close-packed (hcp) ground states. Structures with one atom per unit cell, such as bct structures, are separated from structures with two atoms per unit cell, such as hcp structures, by high energy barriers. Hence the process of finding minima of energy in the former type of structure will never land to hcp structures. The one-atom per unit cell 'ground state' is then necessarily a metastable phase. In this way face-centred-cubic (fcc) Mg [1] and fcc Ti [2] have been shown to be metastable phases.

In the present work, the inverse situation is considered, i.e. stable equilibrium states in hcp structures are sought for elements that have fcc ground states. Both hcp Ag and hcp Au are each shown to have two equilibrium states, one at high c/a values and one at low c/a values, where a and c are the lattice constants of the hexagonal structure. The high- c/a equilibrium state is

found to be stable in each case, hence it is in a metastable phase. The low- c/a equilibrium state is in both cases unstable. (In common usage the denomination ‘hcp’ is used for these low- c/a states even though they are not close-packed in the c direction.)

Two computational procedures were used to locate the energy minima: one procedure finds the hexagonal epitaxial Bain path (EBP) first and then follows the EBP to minima of energy. The other procedure, called the minimum-path procedure (MNP), goes directly to a minimum from an arbitrary initial structure in a single calculation. By using various starting structures the two minima are found. The MNP has previously been applied to find equilibrium states for yttrium and cadmium [3]. We compare the two procedures.

We briefly describe the calculation procedures in section 2 and the results in section 3. We present a discussion of the results in section 4.

2. Calculations

One method used in this work consists in calculation of the *hexagonal* EBP for both Ag and Au, and determination of the minima of energy E along it. The definition of an EBP for tetragonal states [4] is extended to an EBP for hexagonal close-packed states, defined by lattice vectors $a = b$ at an angle $\gamma = 120^\circ$ to one another, and c perpendicular to both. The EBP is the path defined by the condition that for any value of the $a = b$ parameters the stress σ_3 in the c -direction vanishes, i.e. $\sigma_3 = (2/a^2 \sin \gamma)(\partial E/\partial c)_a = 0$ (this is also called the epitaxial boundary condition, as it is the one that applies to an epitaxial film which satisfies the condition that the normal stress is zero). Hence the value of c that minimizes E for the chosen a is the appropriate value of c . When the total energy is thus calculated for different values of $a = b$ all minima along the EBP correspond to a vanishing first derivative of E in two directions in the hexagonal plane: along c by construction of the EBP and along the EBP itself at the minima. Hence the energy derivative vanishes in all directions and all stresses on the crystal are zero.

The energy calculations in this EBP method were done with the WIEN97 computer program [5] within the relativistic generalized-gradient approximation (GGA) and with the following parameters: a plane-wave cutoff $RK_{\max} = 9$, resulting in about 2040 plane waves; a largest vector in the charge-density Fourier expansion $G_{\max} = 16 \text{ bohr}^{-1}$; a k -point sampling in the Brillouin zone (BZ) of 20 000 points, corresponding to 1040 k -points in the irreducible wedge of the Brillouin zone (IBZ); a muffin-tin radius $R_{\text{MT}} = 2.4 \text{ bohr}$ for both Ag and Au; a criterion for energy convergence $\epsilon_c = 1 \times 10^{-6} \text{ Ryd}$.

The other method, called the minimum path procedure (MNP), involves calculations of the total energy E for an arbitrarily chosen hexagonal structure (which we call the initial state) and for structures derived from it by application of selected strains. The selected strains exclude shears, which break hexagonal symmetry, so that the energy can be expanded in a power series containing only two linear strain terms and three quadratic strain terms. The first goal of the calculations is to establish whether the quadratic terms by themselves are a positive definite quadratic form. This step requires calculations of the elastic constants of the initial state, which are the coefficients of the quadratic terms.

Two cases arise: in the first case the quadratic terms are found to be positive definite by themselves. In this case the next step is to minimize the coefficients of the linear terms, which is done by putting the two strain derivatives of E equal to zero, thus obtaining two linear equations in the strains which define a new structure. The procedure is repeated for this new structure until the linear coefficients are sufficiently small. The structure thus found is an equilibrium state in hexagonal structure of the material under study. This procedure for determining the minimum is exact if higher-order terms than quadratic in the energy expansion are negligible.

If the quadratic terms are not positive definite, then a direction can be found along which E decreases, eventually reaching a new minimum. The procedure is repeated for the a and c values of this new minimum, seeking positive definiteness of the quadratic terms. If these are now positive definite, the procedure aimed at reducing the linear terms is repeated; if they are not positive definite the procedure aimed at finding a new minimum is repeated. A minimum must exist, because E cannot become lower than the ground state, which in this case is fcc for both Ag and Au.

Several initial states are chosen and the whole procedure is repeated. Thus, this procedure requires a large number of total-energy calculations, for which we used again the WIEN97 program [5]. To speed up the process, in the early stages only 2000 k -points were chosen in the whole BZ, corresponding to 144 points in the IBZ, and a less stringent criterion for energy convergence was adopted ($ec = 1 \times 10^{-5}$ Ryd). For each initial state the structures found at the energy minima are, as expected, close to one another. In the final stage, the average of those structures is chosen as the initial state for a more accurate calculation (12 000 k -points, corresponding to 650 in the IBZ, and $ec = 1 \times 10^{-6}$ Ryd).

In order to establish whether the equilibrium states found with either EBP or MNP represent stable or unstable phases, it is necessary to determine all the elastic constants and test whether they satisfy the stability conditions for hexagonal structures [6]. The procedures are summarized in previous publications [1] and will not be repeated here. We recall only that for hcp structures (as for all noncentrosymmetric structures) some of the elastic constants are composed of a homogeneous and an inhomogeneous contribution. The former is the response of the crystal to a strain in which the extra atom maintains its relative position in the unit cell. The latter takes into account the fact that the extra atom has a different environment from the atom at the origin and is therefore not constrained by symmetry when strains are applied (so-called internal relaxation) and can lower the energy by moving.

3. Results

The MNP procedures required on average 35 total-energy calculations, from a minimum of 18 to a maximum of 52, depending on the choice of initial state. The final, more accurate, step usually required only 12–18 calculations. The EBP method, by taking advantage of the MNP results, required only 3–5 calculations. With either method both Ag and Au are found to exhibit two energy minima, one with high- c/a values (about 1.6) and one with low- c/a values (about 0.6). For both minima the results are summarized in table 1.

The lattice parameters of the equilibrium states found with either method are in satisfactory agreement with one another: the differences vary from 0.03 to 0.1% (or about 0.001–0.006 Å). The corresponding energy minima differ by 0.02–0.5 mRyd.

To check stability we have evaluated the elastic constants of the high- c/a phases with the results displayed in table 2. Note that the internal relaxation reduces the c_{44} and c_{66} constants by 3 and 19%, respectively, for Ag, and 1 and 34%, respectively, for Au. For both metals the elastic constants satisfy the stability conditions [6], hence these hexagonal phases of Ag and Au are metastable. For comparison we have added in table 2 the experimental values of the elastic constants of the corresponding fcc ground states.

We have also evaluated the elastic constants of the low- c/a phases and found results for the c_{66} constants which indicate that these phases are unstable. The nature of this instability, however, is unusual and may be worth noting, as we now explain. The normal procedure for evaluation of the c_{66} of hexagonal crystals requires applying ϵ_6 shears to the equilibrium state (usually shears varying from 0.001 to ± 0.1 or ± 0.2) and for each such shear vary the position of the second atom in the unit cell until the energy is minimized [1]. Thus, for each value of the shear one has two energy values, one (the ‘unrelaxed’ energy E^u) with the second atom

Table 1. Parameters of the hexagonal phases of silver and gold. MNP and EBP refer to the two methods used for finding the equilibrium states (see the text): we distinguish between a high- c/a and a low- c/a state. For each state a and c are the parameters of the hexagonal unit cell, in ångström units, V is the volume per atom, in Å³, and E_{\min} is the total energy per atom in Rydberg.

	hcp Ag		hcp Au	
	MNP	EBP	MNP	EBP
High- c/a phase				
a	2.931	2.932	2.922	2.921
c	4.822	4.816	4.889	4.892
c/a	1.645	1.643	1.673	1.675
V	17.93	17.93	18.08	18.07
E_{\min}	-10 634.612 137	-10 634.612 230	-38 095.852 897	-38 095.853 358
Low- c/a phase				
a	4.228	4.226	4.292	4.290
c	2.881	2.883	2.803	2.804
c/a	0.681	0.682	0.653	0.654
V	22.30	22.30	22.37	22.35
E_{\min}	-10 634.592 112	-10 634.592 136	-38 095.840 355	-38 095.840 423

Table 2. Calculated elastic constants of the hexagonal phases of silver and gold. The elastic constants (c_{ij}) are given in Mb. The superscript u in c_{44}^u and c_{66}^u denotes unrelaxed elastic constants (calculated with homogeneous strain), while the superscript r refers to relaxed elastic constants (inhomogeneous strain considered). For comparison we list also the experimental data for the fcc ground states of both metals: the data stem from [12] (0 K values).

c_{ij}	Ag		Au	
	hcp (calc.)	fcc (expt)	hcp (calc.)	fcc (expt)
c_{11}	1.3183	1.3149	1.7536	2.0163
c_{12}	0.7755	0.9733	1.3644	1.6967
c_{13}	0.5895		1.0423	
c_{33}	1.4281		1.8982	
c_{44}^u	0.2208		0.1388	
c_{44}^r	0.2141	0.5109	0.1374	0.4544
c_{66}^u	0.3348		0.2936	
c_{66}^r	0.2714		0.1946	

in its normal unrelaxed position, and one with the second atom in the position that minimizes the energy for that particular value of ϵ_6 (the ‘relaxed’ energy E^r). Usually, a plot of E^u and E^r versus ϵ_6 shows minima at or very close to $\epsilon_6 = 0$. An example is depicted in figure 1(a) for the case of the high- c/a phase of hcp Ag: the fact that for finite shear strain the relaxed energy is lower than the unrelaxed is a clear demonstration of the effect of internal relaxation. Both curves in figure 1 have positive curvatures, hence the corresponding c_{66} constants are both positive (as shown in table 2).

In other cases (not shown here) the curves exhibit maxima at $\epsilon_6 = 0$ (or the relaxed curve exhibits a maximum), so that the curvature and therefore the c_{66} constant is negative, proving that the phase under study is unstable. This is the behaviour typical of instability produced by ϵ_6 shears. However, in the present study we found that while for both low- c/a phases of Ag and Au the unrelaxed energy curves have minima at about $\epsilon_6 = 0$, the relaxed curves have negative slope: the energy decreases with increasing negative value of the shear and the second

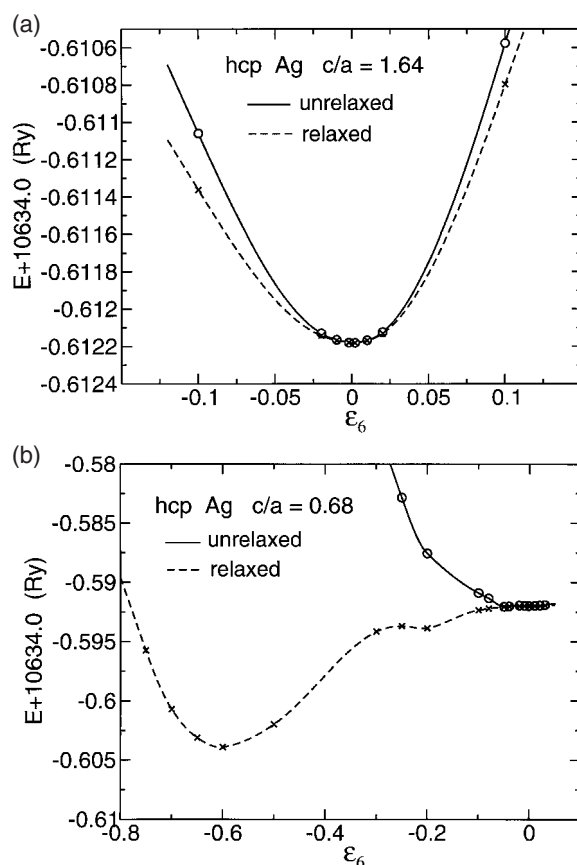


Figure 1. Total energy per atom as a function of shear strain ϵ_6 . In the unrelaxed case, the second atom keeps its relative position in the unit cell. In the relaxed case, the second atom moves to minimize the energy. (a) For the high- c/a phase of hcp Ag; (b) for the low- c/a phase of hcp Ag.

atom relaxes increasingly away from its unrelaxed position in the cell. Figure 1(b) shows the example of the low- c/a phase of hcp Ag, for which we have extended the calculations to find where a minimum occurs. At the minimum, $\epsilon_6 \simeq -0.6$, the structure is orthorhombic. We do not assign a value to the c_{66} constant of the unstrained phase, but it is obvious that the phase is unstable. By contrast, both the unrelaxed and the relaxed c_{44} constants exhibit a normal behaviour and are both positive.

4. Discussion

As pointed out elsewhere in the study of tetragonal structures [3] the EBP and the MNP methods have different features, but both find the same minima of the total energy as a function of the lattice parameters. The MNP procedure usually requires a large number of total-energy evaluations, since three elastic constants are calculated at every step of the path to the minima. The EBP method may require fewer calculations, but only if information is available from elsewhere about the approximate location (i.e. the lattice parameters) of the equilibrium states. The advantage of MNP is that it is fully automated and completes the sequence of steps at electronic speed without human intervention. It is also suitable for generalization to lower-symmetry structures, whereas the EBP procedure is limited to tetragonal or hexagonal

structures. But the EBP can also provide information about energy *maxima* in the tetragonal or hexagonal plane, thus identifying unstable states.

The significant physical result of the present study is the success of first-principles calculations in identifying the existence of a metastable hexagonal-close-packed phase in both Ag and Au, which have fcc ground states. This result confirms in an explicit way the finding suggested by calculations of Rosengaard and Skriver [7]. These authors performed *ab initio* calculations of stacking-fault energies in all 3d, 4d and 5d transition metals, and also of the energy differences between the fcc and hcp phases of these metals. They found that the d-band occupancy determines the formation of stacking faults in such a way that in elements with filled d-bands those differences are negligibly small. The implication of these results is that Cu, Ag and Au could possibly be grown in hcp stacking along the [0001] direction. We note, however, that in some of our recent work we found that hcp Cu is unstable, although ultrathin films in (11 $\bar{2}$ 0) orientation could surprisingly be grown pseudomorphically on a W{001} substrate [8].

But for Ag and Au the metastability of the hcp phase, found in the present work by evaluation of the elastic constants, indirectly confirms Rosengaard and Skriver's results, and also explains and supports some experimental observations reported in the literature. Thus, Harfenist *et al* [9] produced silver nanocrystals using an aerosol technique, and established by means of electron diffraction that the three-dimensional structure of these crystals was hcp with axial ratio $c/a = 1.79$, about 8% larger than that calculated here (table 1). Wetli *et al* [10] used the technique of secondary-electron imaging and low-energy electron diffraction to investigate the structure of Ag films vapour-deposited onto a (0001) surface of Ag₂Al at room temperature. They found that up to a thickness of 6–8 atomic layers the films had an hcp structure, although no quantitative data were reported. With regard to Au, we found a paper by Bozzini *et al* [11] in which the authors reported that thin films electrodeposited at low current densities on different substrates (annealed or laminated Cu and Ni) exhibited a 'new hexagonal crystalline structure'. The connection between these results and our own, however, is at best vague, because the experiment showed that the hexagonal structure was stabilized by the addition of metal ions such as Cu²⁺ and Tl⁺, and the lattice parameters ($a = 9.93$ Å, $c = 7.10$ Å) differ too much from those found here.

Acknowledgments

We gratefully acknowledge partial support of this work by the National Science Foundation with Grant DMR0089274. PMM thanks IBM for providing facilities as an emeritus member of the Thomas J Watson Research Center.

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