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First-principles prediction of the stacking fault energy of gold at finite temperature

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ABSTRACT

The intrinsic stacking fault energy (ISFE) γ is a material parameter fundamental to the discussion of plastic deformation mechanisms in metals. Here, we scrutinize the temperature dependence of the ISFE of Au through accurate first-principles derived Helmholtz free energies employing both the super cell approach and the axial Ising model (AIM). A significant decrease of the ISFE with temperature, $-(36-39)\%$ from 0 to 890 K depending on the treatment of thermal expansion, is revealed, which matches the estimate based on the experimental temperature coefficient $d\gamma/dT$ closely. We make evident that this decrease predominantly originates from the excess vibrational entropy at the stacking fault layer, although the contribution arising from the static lattice expansion compensates it by approximately 60%. Electronic excitations are found to be of minor importance for the ISFE change with temperature. We show that the Debye model in combination with the AIM captures the correct sign but significantly underestimates the magnitude of the vibrational contribution to $\gamma(T)$. The hexagonal close-packed (hcp) and double hcp structures are established as metastable phases of Au. Our results demonstrate that quantitative agreement with experiments can be obtained if all relevant temperature-induced excitations are considered in first-principles modeling and that the temperature dependence of the ISFE is substantial enough to be taken into account in crystal plasticity modeling.

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1. Introduction

Crystal plasticity in materials with face-centered cubic (fcc) structure is overwhelmingly a result of the translation of dislocations, twinning, and cross-slip. Because of the significance of the intrinsic stacking fault energy (ISFE) in connection to the mechanical response, a considerable amount of research has been devoted to the measurement of this parameter (for an overview, see Refs. [1–3]). In spite of these efforts, the fundamental understanding of the physics of the ISFE in relation to the effects of alloying additions and temperature is far from satisfactory, which limits capturing and predicting the deformation mechanisms in close-packed elements and alloys.

Of necessity, an intrinsic stacking fault (ISF) in a fcc crystal is created by splitting a perfect dislocation into two Shockley partial dislocations. The energy cost of this process is roughly proportional to the ISFE γ and an interaction term between the partials that

balances the energy gain due to the splitting [4]. Like other planar fault energies, the ISFE is an intrinsic material property that may depend on temperature. For single-component systems, the temperature coefficient is simply related to the excess entropy of the stacking fault (SF) ΔS [2,5],

$$d\gamma = -\frac{\Delta S}{A} dT, \quad (1)$$

where A is the SF area. On thermodynamic grounds, one expects a positive excess entropy indicating that the ISFE will lower with temperature [2]. The available experimental values of $d\gamma/dT$ for fcc transition metal and noble elements, often obtained through direct observation of the size variation of the Shockley partials bounding the ISF, has generally affirmed a negative temperature coefficient [1–3]. A known exception is the increase of γ with T for the high-temperature ferromagnetic fcc phase of Co, a result that was rationalized in terms of an increasing stability of the fcc phase over the hcp phase above the hcp to fcc allotropic transition in Co at 695 K [3].

The complexity of thermodynamics at planar faults rises in the

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presence of vacancies and for alloys, where, e.g., the segregation of vacancies, interstitial and substitutional components, and clustering may occur [to account for such phenomena, terms containing the chemical potential enter Eq. (1) [2,5]]. In single-component systems, it is expected that for an equilibrium concentration of weakly segregating thermal vacancies (i.e., no significant vacancy excess at the fault) the entropy term would still dominate the temperature dependence [2]. In alloys, the aforementioned phenomena may lead to coefficients $d\gamma/dT$ with positive or negative sign depending on their type and extent, and the magnitude of the excess entropy associated with the ISF. Indeed, experimental values of $d\gamma/dT$ vary considerably from one alloy system to another and show both signs [1,2].

With the advent of density-functional theory (DFT), first-principles computations of the ISFE at 0 K have become feasible. Because ISFEs are typically very small quantities (10–300 mJ/m²) [6,7], such calculations represent a challenge to methodology and numerical precision rather than being routine. Observed discrepancies between experimentally and theoretically determined ISFEs for unary systems, on the one hand, have been attributed to both temperature and impurities, whereas, on the other hand, experimental estimates of the ISFE and its change with temperature are often less reliable due to various difficulties encountered in practice [1,3]. Thus, it is expected that careful theoretical studies of the ISFE at finite temperature could not only reconcile this discrepancy, at least in parts, but also provide an alternative route to access its variation with temperature, assuming an accurate prediction of the thermodynamic properties.

The aim of this work is to use first-principles based modeling of the Helmholtz free energy to rigorously study the ISFE of fcc Au at finite temperature beyond the quasistatic approximation, employing both the super cell approach and the axial Ising model (AIM), and to shed light on the relative importance of the various thermally induced degrees of freedom. We chose Au since it is not only a prominent example of a system with low ISFE at ambient conditions, similar to the isoelectronic Cu and Ag, but it has also attracted recent attention in connection to the formation and electronic properties of SF tetrahedra in Au nanocrystals [8,9].

Before investigating and analyzing the temperature effect on the ISFE of Au in detail (Secs. 4.3 and 4.4), we establish the metastability of hcp and dhcp Au (Sec. 4.1), which is a prerequisite to determine their vibrational free energy through the AIM, and briefly compare our 0 K results for γ to available literature data (Sec. 4.2).

2. Theory and methodology

2.1. Intrinsic stacking fault energy

We employed both the AIM [10] and the super cell approach to study the temperature dependence of the ideal ISFE γ of fcc Au. The ISFs were modeled as coherently embedded layers in the fcc matrix and assumed to be infinitely extended. A typically small and positive elastic strain energy contribution to the ISFE [11,12], which arises from partial dislocations at the SF boundaries, was neglected, but its magnitude at 0 K is estimated in Sec. 4.2.

The AIM draws upon a systematic parameterization of the total energy of polytypes with different stacking sequences in interactions between close-packed layers. It enables the derivation of SF energies in a computationally inexpensive way assuming that the interaction energies decay quickly with distance along the stacking axis. Here, interaction energies up to the next-nearest neighbor layer were included in the calculations. Considering only the interaction between the nearest neighbor atomic planes, the ISFE can be approximated by the axial nearest neighbor Ising (ANNI) model [10,13]

$$\gamma_{\text{ANNI}} = \frac{2(F_{\text{hcp}} - F_{\text{fcc}})}{A}, \quad (2)$$

where F_{hcp} and F_{fcc} are the Helmholtz free energies (per atom) of the hcp and fcc structures, respectively. A denotes the area per atom in a close-packed layer,

$$A = \frac{\sqrt{3}}{4} a_{\text{fcc}}^2 = \frac{\sqrt{3}}{2} (a_{\text{fcc}}^{(111)})^2, \quad (3)$$

a_{fcc} being the lattice parameter of the fcc structure and $a_{\text{fcc}}^{(111)}$ the length of the hexagon that defines the unit cell in a fcc (111) close-packed layer. If additionally the interactions between next-nearest neighbor close-packed planes are taken into account, the ISFE is approximately given by the axial next-nearest neighbor Ising (ANNNI) model [10,13]

$$\gamma_{\text{ANNNI}} = \frac{(F_{\text{hcp}} + 2F_{\text{dhcp}} - 3F_{\text{fcc}})}{A}. \quad (4)$$

F_{dhcp} denotes the free energy of the dhcp structure (per atom). In the previous equations, F_{hcp} and F_{dhcp} do not correspond to energies of equilibrium states rather than to those derived for constrained in-plane lattice parameters, $a_{\text{hcp}} = a_{\text{dhcp}} = a_{\text{fcc}}^{(111)}$ by virtue of coherency with the fcc matrix, and relaxed out-of-plane lattice parameter $c_{(\text{d})\text{hcp}}$ aligned parallel to the stacking axis.

By modeling an ISF through a super cell, the excess energy of the fault relative to the pristine fcc host yields the ISFE and may be obtained from

$$\gamma^{\text{SC}} = \frac{F_{\text{fault}}^m - \frac{m}{n} F_{\text{fcc}}^n}{A}. \quad (5)$$

here, F_{fault}^m and F_{fcc}^n are the free energies of an m -layers super cell containing the SF and an n -layers defect-free fcc super cell, respectively. The inter layer distances in the cell with fault are allowed to relax, subject to the constrained in-plane lattice parameter $a_{\text{fault}} = a_{\text{fcc}}^{(111)}$. Since for a single ISF per super cell we have $m = 3i - 1$, $i > 1$, we may choose for the fcc super cell $n = m + 1$ or $n = m - 2$ to ensure cancellation of numerical noise, which may arise due to employing different cell sizes.

2.2. Helmholtz free energy

The primary goal is to compute the Helmholtz free energy for structures employed in the SF calculations. In the quasiharmonic approximation (QHA), a free-energy function F for nonmagnetic crystals may be defined as [14]

$$F(\{d_{ij}\}, T) = E_{\text{sta}}(\{d_{ij}\}) + \Delta F_{\text{ele}}(\{d_{ij}\}, T) + F_{\text{vib}}(\{d_{ij}\}, T). \quad (6)$$

here, E_{sta} is the static electronic energy at 0 K, ΔF_{ele} is the electronic contribution due to thermal excitations ($\Delta F_{\text{ele}} \equiv F_{\text{ele}} - E_{\text{sta}}$), and F_{vib} is the contribution due to lattice vibrations. The $\{d_{ij}\}$ is the set of interatomic distances between atoms i and j in the unit cell that are variable and independent parameters as a function of temperature, i.e., lattice parameters and interlayer distances.

The Helmholtz free energy of the equilibrium state at temperature T and the equilibrium distances $\{d_{ij}^0(T)\}$ may be obtained by minimizing $F(\{d_{ij}\}, T)$, viz.

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