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Thermal Stabilization of the HCP Phase in Titanium

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Abstract

We have used a tight-binding model that is fit to first-principles electronic-structure calculations for titanium to calculate quasi-harmonic phonons and the Gibbs free energy of the hexagonal close-packed (hcp) and omega (ω) crystal structures. We show that the true zero-temperature ground-state is the ω structure, although this has never been observed experimentally at normal pressure, and that it is the entropy from the thermal population of phonon states which stabilizes the hcp structure at room temperature. We present the first completely theoretical prediction of the temperature- and pressure-dependence of the hcp-ω phase transformation and show that it is in good agreement with experiment. The quasi-harmonic approximation fails to adequately treat the bcc phase because the zero-temperature phonons of this structure are not all stable.

The experimentally observed ground state of titanium at room temperature is the hexagonal close-packed (hcp) structure[1], even though zero-temperature first-principles electronic-structure calculations[2, 3, 4, 5, 6] predict the omega (ω) structure to be the energetically favored ground state. There are two possible causes for this discrepancy: (1) this is another failure of the local-density approximation (LDA) for calculating electronic-structure of solids, or (2) thermal effects stabilize the hcp phase. In this paper we show that the second argument is correct: the thermal occupation of phonon states favors the hcp structure above a pressure-dependent transition temperature. Only by including the vibrational entropy in the first-principles calculations can theory be brought into agreement with experiment.

Titanium is a good case for testing our ability to predict solid-solid phase transformations with first-principles methods. It is an element that displays a rich phase diagram with several recently discovered high-pressure phases[7, 8]. When alloyed with other elements, it leads to materials of major technical importance for the airline, space, and other industries.

It is possible to use first-principles methods to calculate the zero-temperature internal energy, $\Phi_0(V)$, as well as the free energy contributions from the ions, $F_I(T, V)$, and the electrons, $F_E(T, V)$, to give the complete equation of state

$$F(T, V) = \Phi_0(V) + F_I(T, V) + F_E(T, V). \tag{1}$$

Because of the large computational effort required to calculate the free energy of Eq. 1 over a significant range of volumes and temperatures, we have chosen to use a tight-binding model instead of conventional first-principles electronic-structure methods. We will demonstrate the high accuracy of our model and believe that it should be essentially identical with the best available first-principles methods.

The model's accurate emulation of first-principles calculations (in this case the Wien97 code[9]) requires optimization of a single tight-binding parameterization such that the model closely reproduces the relative total energies of selected crystal structures. The structures are chosen to be both simple and representative: simple enough to make the first-principles calculations feasible, and representative of all microscopic environments the model is aimed at describing. A comparison of total energies as a function of volume with structures fulfilling these requirements are shown in Fig. 1. Not shown but included in the fit as independent structures are fcc crystals distorted to correspond to the longitudinal and transverse phonons at the reciprocal-space high-symmetry point X. These additional structures fine-

tune the model's ability to correctly describe lattice vibrations[10]. Crucial for convergence of the fitting procedure is to fit the cubic-structure energy bands at high-symmetry points in reciprocal space[11, 12].

The electronic contribution to the free energy depends on the electronic density of states (DOS) as a function of volume, $n(E,V)$. The occupation of these states, given by the Fermi distribution $f(E,T) = [e^{(E-E_f)/(k_BT)} + 1]^{-1}$, determines their entropy[13],

$$S_{el}(T,V) = -k_B \int [f \ln f + (1-f) \ln(1-f)] n(E,V) dE, \tag{2}$$

and hence the electronic contribution to the free energy $F_E(T,V) = -TS_{el}(T,V)$. This contribution is small compared to that of the ions but is included for completeness.

The ionic contribution to the free energy depends on the phonon DOS, $g(\omega,V)$, through the zero-point energy,

$$U_{zero}(V) = \frac{1}{2} \int_\Omega \hbar\omega g(\omega,V) d\omega, \tag{3}$$

as well as the temperature-dependent, quasi-harmonic free energy,[13]

$$F_H(T,V) = k_BT \int_\Omega \ln[1 - e^{-\hbar\omega/k_BT}] g(\omega,V) d\omega. \tag{4}$$

This differs from the volume-independent harmonic approximation in that the quasi-harmonic approximation uses phonons calculated for small displacements (i.e., harmonic) at each volume. The resulting phonon frequencies are therefore volume dependent but temperature independent (they are calculated at zero temperature). The approximation requires that the phonons for any given crystal structure and volume are stable at zero temperature, which may not be true if the crystal can lower its total energy by spontaneously and continuously distorting into another crystal structure. At elevated temperatures (near melting) this approximation also neglects some important anharmonic contributions to the free energy that can be responsible for stabilizing some high-temperature phases.

We have used the tight-binding model to calculate the electronic and the phonon DOS by evaluating the relevant energy eigenvalues and dynamical matrices on a fine mesh of wave vectors in the first Brillouin zone. In both cases the spectrum is smeared with a Gaussian, chosen to be as small as possible while keeping the DOS smooth and continuous. The mesh is refined until the free energy converges.

The dynamical matrix at a given wave vector $\mathbf{q}$ is the Fourier transform of the force constants, which we calculate from the tight-binding model by the direct-force method[14,

15, 16, 17]. This method requires large simulation cells consisting of repeated unit cells transposed by vectors ℓ, the forces on all atoms are calculated in response to the displacement of the atom(s) in one unit cell. Our simulation cells contain 54 (hcp), 81 (ω), and 128 atoms (bcc); for more details we refer the reader to Ref.[10].

Figure 2 compares our calculated phonon dispersion for the hcp structure to experimental data[18]. The overall agreement is good, in particular near the zone center (around Γ) and along the vertical direction (parallel to the c-axis). Frequencies of modes in horizontal directions (perpendicular to the c-axis) away from the zone center are somewhat high compared to experiment. The main characteristics, which the tight-binding model captures, give a reliable DOS, the relevant entity used in Eqs. 3 and 4 to calculate the phonon contribution to the free energy.

The phonon density of states is calculated for the hcp[23], ω, and bcc structures at a dozen volumes corresponding to pressures in the range from zero to 170 GPa and is then used to evaluate the Gibbs free energy[13], $G(T,P) = F(T,V) + PV$.

Comparison of the Gibbs free energies as a function of pressure and temperature for the hcp and ω crystal structures allows us to identify the phase transformation line. This approach is extremely demanding because tiny errors in the relative free energies can dramatically alter the phase boundary. Figure 3 shows good agreement between our theoretically calculated $\alpha \rightarrow \omega$ phase transformation line with the experimental phase diagram[19]. The calculated transition temperature at zero pressure is approximately 280 K.

At normal pressure we know of no experimental data that shows that the ω phase is the correct zero-temperature ground state. However, it has recently been shown that energy barriers exist for this phase transformation[20] that may make it extremely difficult to verify at low temperatures. Thus the kinetics may be just too sluggish for the system to bring itself into true thermodynamic equilibrium.

We were not able to similarly calculate and include in Fig. 3 the transition into the bcc structure. The open bcc structure appears to be dynamically stabilized by entropy and anharmonic effects. At zero temperature some phonon modes are unstable due to a spontaneous instability of the bcc crystal structure into the ω phase. There is no energy barrier to this continuous transformation. In particular, this causes the longitudinal phonon mode with wave vector $\mathbf{q} = \frac{2}{3}(1,1,1)$, which distorts the bcc crystal into the ω phase, to be unstable below pressures of roughly 40 GPa. The mechanical instability of this phonon

mode at low temperatures is also seen experimentally; the martensitic phase transition from the bcc phase to the hcp phase prevents the high-temperature bcc phase from being quenched to room temperature[21]. One branch of transverse phonon modes with wave vectors $(\xi, \xi, 0)$, which are related to the bcc to hcp transition, also appears unstable in our treatment. Both of these instabilities are consistent with strictly first-principles calculations of zero-temperature phonons[22].

Figure 4a shows the relevant segment of the (ξ, ξ, ξ) branch. The energy of the corresponding pathway from the bcc phase to the ω phase, shown in Fig. 4b, develops a local minima for the bcc phase at pressures of roughly 40 GPa, but at lower pressures the crystal can deform from bcc to ω without encountering an energy barrier. This pathway can be viewed as planes moving in accordance with the wave vector $\mathbf{q} = \frac{2}{3}(1, 1, 1)$ or as chains of atoms along the body diagonal moving with respect to each other. Calculations of the energy needed to move such a single chain of atoms indicate that for small displacements the movement is energetically favored, whereas the movement of a single atom is not.

If only the stable phonons are included in the evaluation of Eq. 4, the bcc structure is calculated to be lowest in Gibbs free energy at pressures that are an order of magnitude higher than experimentally observed. A correct calculation requires a more sophisticated treatment that includes phonon-phonon interactions, i.e., anharmonic contributions to the free energy.

In conclusion, we have for the first time used a completely theoretical approach, without any experimental input, to calculate the Gibbs free energies of competing crystal phases in titanium. Comparison of the hcp and ω Gibbs free energies results in a pressure- and temperature-dependence of the structural phase transition in good agreement with experiment and serves to explain how finite-temperature entropy effects stabilize the experimentally found room-temperature hcp crystal structure over the theoretically found zero-temperature ω-phase ground state.

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[23] The c over a ratio of the hcp structure is varied to give the lowest zero-temperature energy, i.e., in particular at high pressures the calculation is done for a hexagonal crystal with a c/a larger than the ideal value.
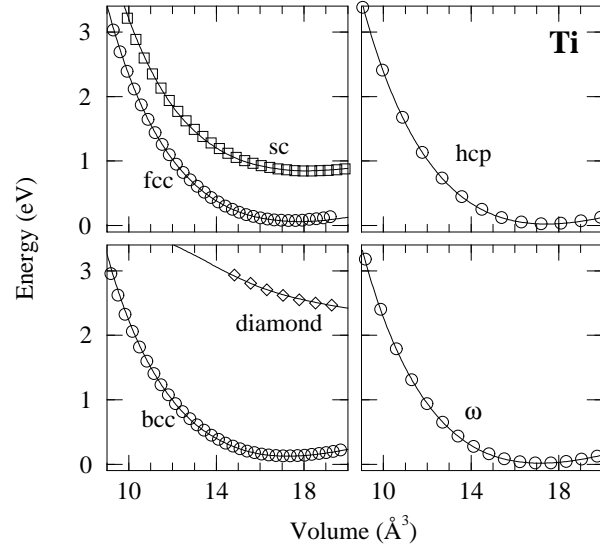
FIG. 1: Calculated energies for the crystal structures in the fitting database. Symbols are the first-principles results, solid lines are calculated from the fitted tight-binding model. Also included in the fit (but not shown here) are the fcc crystal with distortions corresponding to the longitudinal and transverse phonons at the reciprocal-space high-symmetry point X. The ω structure lies lowest in energy, in contrast to the experimentally found ground state, hcp.
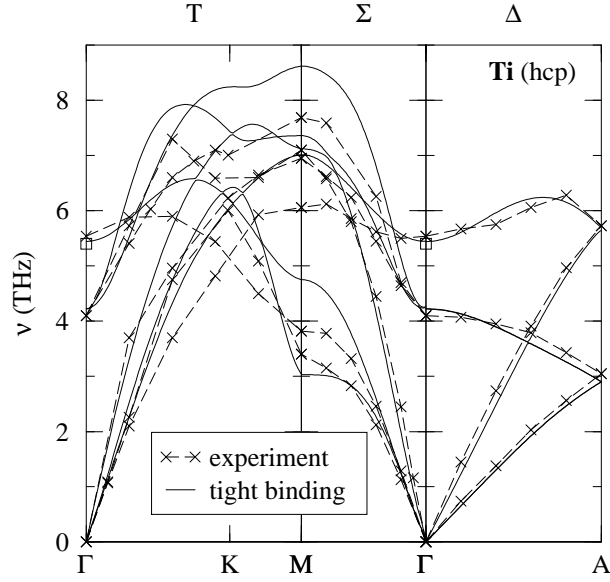
FIG. 2: Experimental (crosses)[18] and tight-binding (solid lines) phonon dispersion of titanium in the hcp crystal structure at ambient pressure. Although some experimental details are not reproduced by our tight-binding model, the overall agreement is quite good. The phonon DOS that is relevant for the calculation of the Gibbs free energy should still be highly accurate. The square at Γ is from a first-principles frozen-phonon calculation.
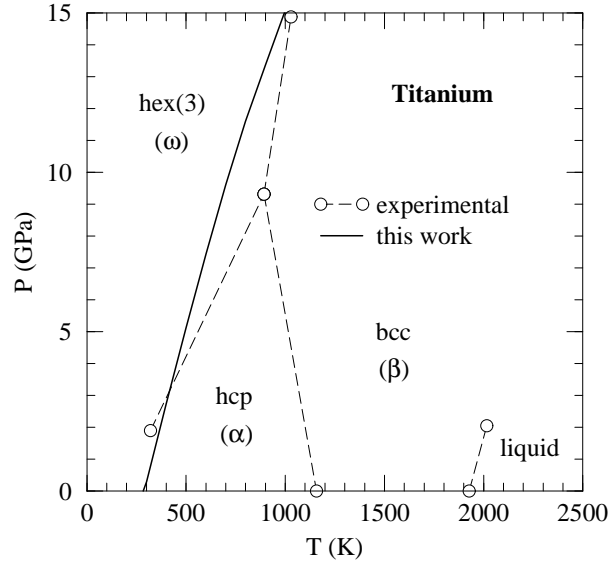
FIG. 3: The phase diagram of titanium. The dashed lines connect the experimental data points given by Young[19]; the solid line shows our calculated $\alpha \to \omega$ transformation. Thermal stabilization explains why at room temperature the experimentally observed hcp structure is favored over the ω structure (the calculated zero-temperature ground state).
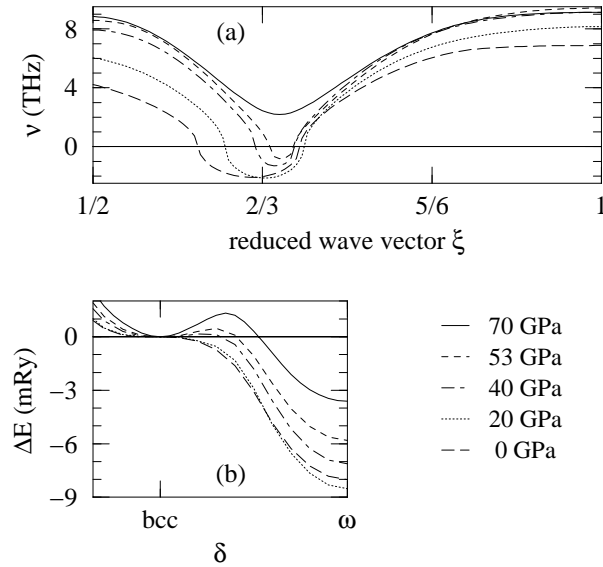

FIG. 4: (a) Calculated zero-temperature longitudinal phonon modes around the wave vector $\mathbf{q} = \frac{2}{3}(1,1,1)$, which distorts the bcc crystal into the ω phase. (b) Calculated zero-temperature energy landscape for the bcc to ω pathway.