

$\alpha \leftrightarrow \beta$ phase transition in tin: A theoretical study based on density-functional perturbation theory

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The free energies of the α and β phases of tin are calculated in the harmonic approximation using density-functional theory and density-functional perturbation theory, within the local-density approximation. At $T=0$ K the free energy of the β phase lies ≈ 359 cal/mole above that of the α structure. The narrower frequency range spanned by the vibrational band in the β phase makes its entropy larger at high temperature. As a consequence, the free energies of the two phases equal each other at a temperature of 38°C , in close agreement with the observed transition temperature $T_c \approx 13^\circ\text{C}$. [S0163-1829(98)03714-X]

Tin is commonly found in one of two allotropic forms: At ambient pressure, the stable phase at low temperature is α -Sn (gray tin) which is a zero-gap semiconductor having the diamond structure; when the temperature is raised above $T_c \approx 13^\circ\text{C}$, the crystal transforms into the β phase (white tin) which is a body-centered tetragonal metal.¹ The $\alpha \leftrightarrow \beta$ transition in tin is possibly the simplest and prototypical case of an entropy-driven structural transformation which is determined by the (harmonic) vibrational properties of the two phases of the material. Vibrational entropies are relevant in many other situations such as, for instance, the commonly observed stability of the body-centered cubic phase of metals at high temperature² and the description of martensitic transformations in transition-metal alloys.^{3,4} The existing theoretical investigations of the temperature-induced $\alpha \leftrightarrow \beta$ phase transition rely on semiempirical lattice-dynamical models fitted to neutron-diffraction data and on other experimental inputs such as the specific heats which are used to estimate the value of the free-energy difference at $T=0$.⁵⁻⁷ In this paper the $\alpha \leftrightarrow \beta$ transition in tin is studied by using modern electronic-structure techniques without making use of any experimental inputs. The relevant free-energies are obtained in the harmonic approximation from static internal energies and vibrational frequencies in the two different phases, as computed by density-functional theory (DFT)⁸ and density-functional perturbation theory (DFPT),⁹ respectively. Our results show that the combination of the (quasi)harmonic approximation and DFPT provides an accurate and efficient tool for the study of finite-temperature solid-solid phase transformations.

Over the past twenty years, structural phase transitions in simple solids have been among the most successful benchmarks of modern electronic-structure techniques based on density-functional theory.⁸ Because of the difficulties of

properly accounting for dynamical effects, however, these investigations have been mainly limited to pressure-induced (zero-temperature) transitions. The free-energy calculations necessary to evaluate the relative stability of two different phases of a material at finite temperature have long escaped any *ab initio* approach and only a few attempts have appeared in the literature which make use of first-principles molecular dynamics and thermodynamic-integration techniques.¹⁰ Well below the melting point, however, the lattice contribution to the free energy is mainly determined by the harmonic vibrational frequencies of the system and can be easily calculated without any thermodynamic integration, once the latter are known. Recently, the *ab initio* calculation of free energies in the harmonic (or, more generally, quasiharmonic) approximation has been successfully applied to the study of the lattice expansion in simple semiconductors,¹¹ of the temperature dependence of the surface relaxation in some metals,¹² as well as to some related phenomena such as the dependence of the crystal volume upon isotopic composition.¹³ At low temperatures, the estimate of free energies via molecular dynamics is plagued by ergodicity problems and furthermore it cannot account for quantum zero-point effects which may be important in some cases. In a sense, free-energy calculations based on the harmonic approximation or on molecular dynamics and thermodynamic integration are complementary in that near or above the melting point the latter technique naturally accounts for anharmonic effects, and it is the only possible choice, while at low temperature the former is both less expensive and more accurate. The predictive power of free-energy calculations based on the harmonic approximation has been greatly enhanced by DFPT which is now allowing the determination of the vibrational properties of solids with an unprecedented degree of accuracy.¹⁴

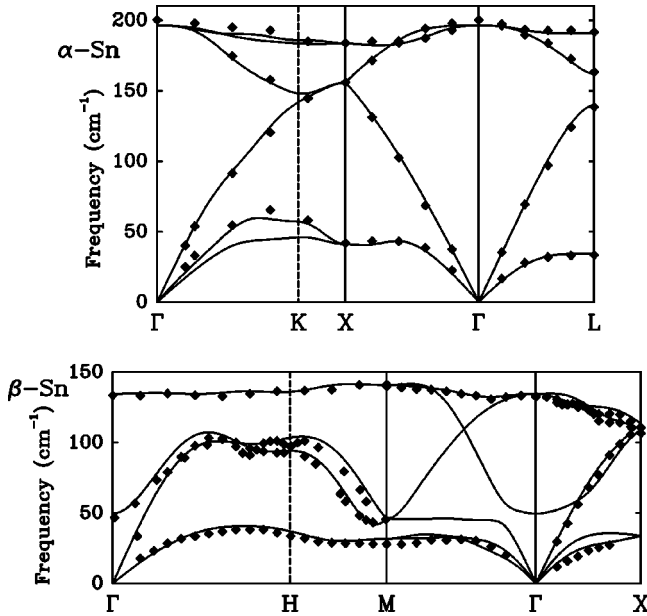


FIG. 1. Calculated phonon dispersions (continuous lines) for the α (upper panel) and β (lower panel) phases of tin. Experimental data from neutron diffraction (from Refs. 23 and 24 for the α and β phases, respectively) are reported with diamonds.

As the transition temperature of the $\alpha \leftrightarrow \beta$ transition in tin is $\approx 60\%$ of the melting temperature, we do not expect, in this case, anharmonic effects to play any important role. The free energies of the two phases have been thus calculated in the harmonic approximation which reads

$$F(V, T) = E_0(V) + k_B T \sum_{\nu} \ln \left[2 \sinh \left(\frac{\hbar \omega_{\nu}}{2k_B T} \right) \right], \quad (1)$$

where $E_0(V)$ is the static crystal energy—easily accessible to standard local-density-functional calculations⁸— k_B is the Boltzmann's constant, and the ω 's are normal-mode frequencies which have been calculated using DFPT.

Our calculations have been performed within the plane-wave (PW) pseudopotential method,⁸ using norm-conserving pseudopotentials from Ref. 15 and basis sets including PW's up to a kinetic-energy cutoff of 14 Ry. Brillouin-zone (BZ) integrations have been performed with the Gaussian-smearing special-point technique,^{16,17} using a Gaussian width of 0.01 and 0.02 Ry for the α and β structures, respectively, which at convergence require 60 and 163 special points in the irreducible wedge of the BZ.

The calculated equilibrium lattice parameters of the two phases are (experimental data from Ref. 18 are reported in parenthesis): $a_{\alpha} = 6.38 \text{ \AA}$ (6.48), $a_{\beta} = 5.70 \text{ \AA}$ (5.82), $(c/a)_{\beta} = 0.544$ (0.546). The corresponding bulk moduli are (experimental data from Refs. 19 and 20): $B_{\alpha} = 47 \text{ GPa}$ (53) and $B_{\beta} = 61 \text{ GPa}$ (55). The static energy of the α structure lies 516 cal/mole below that of the β phase. Taking into account zero-point contributions to the internal energy, at $T = 0 \text{ K}$ the α phase results to be more stable than the β one by 359 cal/mole. An indirect estimate of the experimental value for this quantity was obtained by integrating the experimentally known constant-pressure specific heats with respect to temperature, and resulted to be 339 cal/mole.⁷ As one can see,

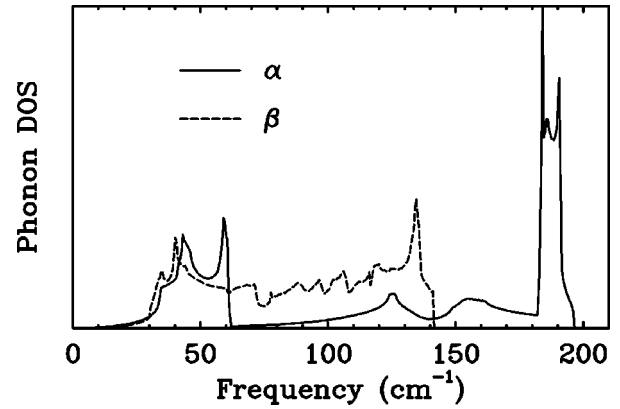


FIG. 2. Calculated vibrational density of states for the α (continuous line) and β (dashed line) structures of tin.

all these data are in close agreement with available experimental values, as well as with previous calculations made using the pseudopotential^{7,21} or the linear muffin-tin orbital²² methods.

In Fig. 1 we display our calculated phonon dispersions for the α and β phases of tin. Besides the excellent agreement with available neutron-diffraction experimental data,^{23,24} the main feature to be noticed is the different range spanned by the vibrational bands in the two phases, which extend up to $\approx 200 \text{ cm}^{-1}$ in gray tin, while it is limited to $\approx 140 \text{ cm}^{-1}$ in white tin. The corresponding phonon density of states are displayed in Fig. 2.

The fact that the structure with a larger static energy has smaller vibrational frequencies indicates that a phase transi-

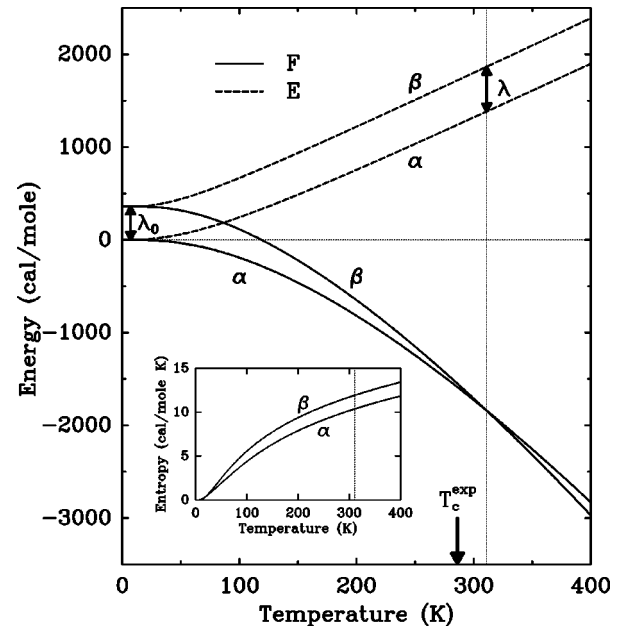


FIG. 3. Zero-pressure free-energy (solid lines) and internal energy (dashed lines) curves for the α and β phases of tin as functions of temperature. The thin vertical dotted line indicates the theoretical transition temperature, while the experimental value for T_c is shown by the arrow. $\lambda_0 = 359 \text{ cal/mole}$ is the $T = 0 \text{ K}$ free-energy difference—including the zero-point contribution—while $\lambda = 482 \text{ cal/mole}$ indicates the latent heat absorbed in the $\alpha \leftrightarrow \beta$ transition. Finally, the inset displays the temperature dependence of the vibrational entropies of the two phases.

tion may occur when raising the temperature, as a consequence of the larger value of its entropy at high temperature. In fact, in this regime the difference between the internal energies of the two phases tends to a constant because of the equipartition law, and hence their relative stability is determined by the difference between the entropies. For the sake of simplicity, suppose that each structure (α or β) is characterized by a single vibrational frequency (Einstein model): the difference between the entropies of the two structures tends then to $\Delta S_\infty \approx 3k_B \ln(\omega_\beta/\omega_\alpha)$. Thus, at sufficiently high temperature the entropic contribution to the free energy difference $-T\Delta S_\infty$ takes over the difference between the internal energies, and the β phase becomes more stable (provided the transition temperature so obtained is well below the melting point of the two phases, so that the harmonic approximation is well justified).

This behavior is clearly illustrated in Fig. 3 where the internal energy and the free energies of the two structures are displayed. The internal energies of the two phases increase with temperature and their difference saturates to a value which is $\approx 35\%$ larger than at $T=0$ K. The free-energy curves bend down, and their difference decrease quasilinearly with temperature vanishing at $T_c=38$ °C. The inset shows the corresponding entropies. The asymptotic value of the difference between the entropies in the two phases corresponds to a ratio $\omega_\alpha/\omega_\beta \approx 1.3$, as defined by the above oversimplified Einstein model, and in fair agreement with the ratio between the vibrational band edges of the two phases. The theoretical value for the transition temperature, $T_c=38$ °C, is in excellent agreement with the experimentally observed value $T_c^{\text{exp}}=13$ °C. This agreement is even better

than one could have expected, and it strongly depends on the accuracy of the calculated value for λ_0 . In fact, the two free-energy curves are almost tangent when they cross and a slight vertical displacement of one of the two (such as it would be determined by a slightly different value of the difference between the static energies of the two structures λ_0) would result in sizable variation of the transition temperature. We estimate the error on λ_0 —as due to the pseudopotential approximation—to be of the order of 30 cal/mole, resulting in an uncertainty of 20° on the predicted transition temperature. At the same time, we find that the calculation of the entropy difference between the two structures is less sensitive to the fine details of the calculation, as it results from its logarithmic dependence on the vibrational frequencies. The numerical accuracy on the latter, as due to the pseudopotential approximation and other factors, is estimated to be of the order of 1%, resulting in an additional 5° of uncertainty in the calculated critical temperature.

The quality of the agreement between theory and experiment achieved for the $\alpha \leftrightarrow \beta$ transition in tin is such as to give confidence in the predictive power of free-energy calculations based on the harmonic approximation and vibrational frequencies calculated from first principles, and it indicates that this is the method of choice in all those cases where the relevant phenomena occur at temperatures well below the melting point.

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