Phonon-Phonon Coupling and the Stability of the High-Temperature bcc Phase of Zr

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Phonon-phonon coupling strengths have been derived from first-principles total-energy calculations for bcc Zr. It is shown that the instability leading to the bcc-hcp first-order phase transition in Zr is overcome at high temperatures by the strong interactions between the T_1 N-point phonon and other low-lying (110) T_1 vibrational modes.

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There has recently been renewed interest in the stability of phases separated by a first-order temperature-dependent phase transition. Insights have been obtained by the use of simple statistical models and by computer simulations[1,2]; however, for specific materials a more detailed microscopic picture is generally lacking and needed. We show for an important class of transitions that such a microscopic picture can be obtained through modern first-principles electronic-structure calculations.

Increases in computing speed have made feasible the first-principles calculation of many material-dependent properties—including vibrational frequencies, bulk moduli, cohesive energies, and phase-transition pressures. These calculational methods are based on the very precise evaluation of the total-energy changes associated with atomic displacements in crystals. Unlike traditional perturbative methods, these calculations are not restricted to small distortions of the crystal. This enables the accurate determination of anharmonic interactions as well as coordinate paths and barrier heights for phase transitions. Until recently this anharmonic information has not been analyzed, with the notable exception of the calculation of the optical-mode frequency shift caused by the two-phonon process in diamond.[3] In this paper we use the anharmonic terms derived from accurate total-energy calculations to obtain phonon-phonon coupling strengths for the high-temperature bcc phase of Zr. The temperature dependence of the lattice vibrational modes is determined, and the interactions responsible for the high-temperature stability of the bcc phase are identified.

We have chosen to study the first-order hcp-bcc transition of Zr for several reasons. First, the transition at $T=1136$ K is martensitic, which means the atomic positions of the parent and the resultant crystal structure are highly correlated, thus limiting the configuration coordinates which must be varied.[4] (On the basis of the observed correlations in crystal orientations, Burgers proposed that the transition from bcc to hcp occurs through the displacements of the zone-boundary T_1 N-point phonon together with a long-wavelength shear.[5,6]) Second, the phonon dispersion curves as a function of temperature for both the hcp and bcc phases have been obtained by neutron scattering experiments.[7] These experiments for the bcc phase showed that the frequencies for the entire [110] T_1 phonon branch are indeed very low. In conjunction with these experimental measurements, first-principles calculations of the harmonic frequency for the T_1 N-point phonon were made.[8] These calculations yielded an imaginary frequency which indicates that *within the harmonic approximation this mode for Zr is unstable.* In contrast, similar calculations for the N-point phonons of bcc Nb and Mo, which are stable at low temperatures, yielded frequencies in good agreement with experimental values.[8] Thus, to understand the stability of the high-temperature bcc phase of Zr and in particular the measured frequency of 1 THz for the T_1 N-point phonon, it is of vital importance to include anharmonic interactions. The situation is similar to that of He for which the bcc structure is stabilized by the anharmonic forces even at zero temperature.[9]

The total-energy calculations were performed by use of an established first-principles pseudopotential method which, along with calculational procedures, has been described in detail elsewhere.[10] The only approximations involve the treatment of the exchange-correlation energy using the local-density-functional formalism,[11] the frozen-core approximation, and the Born-Oppenheimer approximation. For the analysis of a particular phonon the total energy is evaluated as a function of atomic displacements with the atoms moving in the directions corresponding to the phonon polarization vector. These so-called "frozen-phonon" calculations have been shown to be accurate for the determination of phonon frequencies in transition metals.[12] The results of such calculations for the T_1 mode of Zr are shown in Fig. 1. The inset

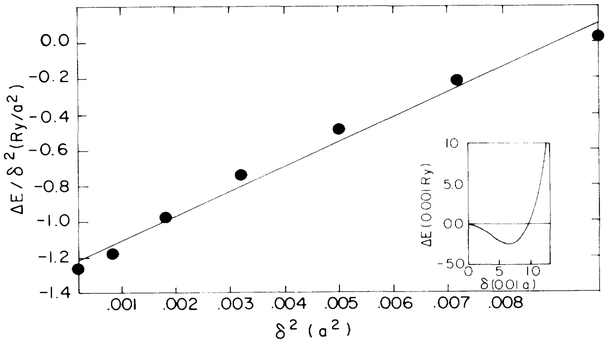

FIG. 1. $\Delta E/\delta^2$ vs δ^2 for the bcc N-point T_1 mode. The slope of the line gives the fourth-order anharmonic coefficient for the energy vs displacement expansion. A displacement corresponding to $\delta^2 \simeq 0.014$ and a long-wavelength shear are required to transform the bcc to the hcp structure.

TABLE I. Fourth-order expansion coefficients for the three N-point and the H-point phonons along with the longitudinal $(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonon, labeled ω. The top line gives the results from first-principles calculations, while the second line gives the values obtained from the two-parameter fitted function as described in the text. The units are in Ry/(Å^4 atom).

	N-T_1	N-T_2	N-L	H	ω
First principles	0.57	−0.21	1.39	−0.66	−0.21
Fit	0.37	−0.29	1.73	−0.72	−0.17

shows that the energy versus displacement curve has a minimum at finite displacements and indicates the instability toward the hcp phase. Expanding the energy in a power series in the displacement we can write $\Delta E = a\delta^2 + b\delta^3 + c\delta^4 + \dots$. The negative harmonic coefficient, a, and the positive fourth-order coefficient, c, are conveniently displayed in the $\Delta E/\delta^2$ vs δ^2 plot of Fig. 1 ($b=0$ by symmetry for the T_1 mode). Similar analyses were made for the T_2 and L phonons at the N point, the H-point phonon, and the longitudinal $(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonon (the ω-phase mode).

To determine the temperature dependence of the phonon frequencies we make use of the extensive perturbation formalism developed for the treatment of anharmonic effects in crystals.[13] The total crystalline potential energy can be expanded through fourth order in a power series in the displacement from equilibrium. The harmonic approximation consists of retaining the second-order terms and solving the quadratic Hamiltonian for the normal modes of vibration. The third- and fourth-order expansion coefficients are then rewritten in terms of these normal-mode coordinates so that the anharmonic effects are treated as interactions among the elementary excitations (phonons). Our strategy is then to first obtain the unrenormalized harmonic frequency by means of the first-principles frozen-phonon calculations. Calculations were made at lattice constants corresponding to $T=0$ and 1400 K. The renormalized frequency and phonon lifetime can then be obtained from the calculated anharmonic potential by use of the standard formulas.[14] In these formulas the temperature enters through the phonon occupation factors.

In order to evaluate the third- and fourth-order coupling coefficients for all phonon interactions the *anharmonic* part of the calculated interatomic interactions was fitted with a short-ranged two-parameter potential of the form C/R^N. The parameters C and N were determined from a least-squares fit to the fourth-order expansion coefficients from frozen-phonon calculations for five low-lying phonons. Table I lists the coefficients and the corresponding values from the fit function. The good quality of the fit indicates that this functional form is adequate for Zr; however, similar calculations for Mo required a more complicated potential form to obtain a fit of similar quality.

The required Brillouin-zone summations were performed by our dividing the zone into small cubes with the phonon coupling strengths assumed constant within each cube. The frequencies appearing in the typical second-order perturbation theory formulas were assumed to vary linearly within each cube and the integration involving the energy denominators was performed analytically.[15] To test convergence the number of cubes along Γ to H was varied between ten and thirty. The large fourth-order term was fully converged even with ten divisions, while the smaller third-order term required more than twenty divisions. For computational expediency the majority of the calculations were performed with ten divisions and the uncertainty of the third-order results is ±20%.

The second-, third-, and fourth-order contributions to the squared frequency at 1400 K for the T_1, T_2, and longitudinal N-point phonons are given in Table II. For the T_1 mode the second- and third-order contributions are negative, while the fourth-order contribution is larger and positive. The resulting frequency of 1 THz is in good agreement with experiment; however, this may be somewhat fortuitous since the theoretical uncertainty is on the order of 25%. The important point is the renor-

TABLE II. The calculated contributions at $T=1400$ K to the square of the N-point T_1 phonon frequency; ν_2 is the imaginary harmonic frequency, and ν_3 and ν_4 are the third- and fourth-order corrections. The corresponding values for the N-point T_2 and longitudinal (L) modes are also given. The experimental frequencies are from Ref. 7.

	ν_2^2	ν_3^2	ν_4^2	$\nu^2=\sum \nu_n^2$	ν (THz)	ν_{exp} (THz)
T_1	−3.7	−2.1	6.8	1.0	1.0	1.00 ± 0.05
T_2	12.7	−0.8	3.2	15.1	3.9	3.88 ± 0.15
L	9.9	−1.5	17.5	25.9	5.1	4.28 ± 0.40

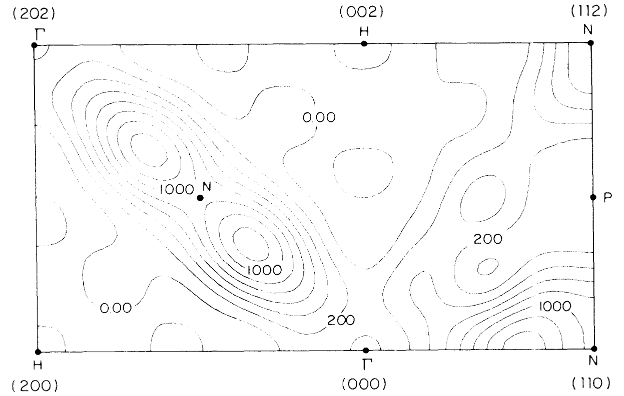

FIG. 2. Contour plot of the fourth-order contributions of branch 1 to the frequency shift for the T_1 N-point phonon. The contours are shown for the high-symmetry planes. The dominant contributions along the (110) direction arise from strong anharmonic coupling and high thermal occupation. (Contours at intervals of 200 in arbitrary units.)

malization of the T_1 mode to finite frequency, a result which is insensitive to the calculational details. The fourth-order contributions responsible for the frequency shift of the T_1 mode arise predominantly from interactions with other phonons in the T_1 branch. This is evident in Fig. 2 where the k-dependent fourth-order contributions are shown. A similar analysis shows that third-order contributions are large in the vicinity of the Γ point.

Frequencies were also evaluated for a number of other phonon modes. In general, the calculated frequency corrections are dominated by the positive fourth-order contributions and are in the direction to bring the harmonic frequencies (from the frozen-phonon calculations) into agreement with the high-temperature experimental values; however, the renormalized frequencies in some cases overshoot by as much as 20%. We believe that this may be partly due to limitations in applying perturbation theory at such high temperatures, and possibly also due to the simple central-potential approximation.

Having established that at high temperatures the bcc structure is a stable phase from the viewpoint of the finite frequency of the N-point T_1 phonon, it is instructive to consider how this stability can be understood in terms of the free energy. At high temperatures the bcc phase is stable because of its large entropy relative to other lattice configurations. For Zr the lattice vibrational entropy accounts for ~60% of the difference between the bcc and hcp phases (the other ~40% is from electronic contributions). We can calculate the change (decrease) of lattice entropy when the bcc structure is distorted toward the hcp phase by a small displacement corresponding to the T_1 N-point mode. We use the anharmonic coupling constants to evaluate the changes in all the phonon frequencies as the bcc crystal is distorted. The phonons whose frequencies are most affected by the T_1 distortion of the bcc crystal are those with strong positive fourth-order anharmonic coupling constants (see Fig. 2). The strong fourth-order coupling of the T_1 mode with other phonons raises the frequencies of these modes, leading to a decrease in the entropy. This implies that at high enough temperatures the bcc phase will be stable relative to the T_1 displacements. A similar analysis for a distortion of the bcc structure corresponding to the ω-phase displacements again shows that a strong coupling to the T_1 branch is responsible for the stability of the bcc phase at high temperatures. It is interesting that Zener long ago proposed that the extra entropy needed to stabilize the bcc phase comes from soft shear modes in the bcc structure.[16] Our investigations have confirmed this picture and singled out the T_1 branch as being most important because the phonons of this branch are low in energy and have large anharmonic coupling.

The analysis given above leads to the following microscopic picture of the first-order bcc-to-hcp phase transition. For the internal energy, there is a trough in coordinate space leading from the bcc down to the ground-state hcp structure.[17] The relevant coordinates are the displacements corresponding to the T_1 N-point phonon (internal shear) and a uniform or long-wavelength shear. At temperatures just above the transition the bcc structure is stable and has the lowest free energy. At these temperatures the hcp structure corresponds in the free-energy surface to a local minimum separated from the bcc minimum along the transition path by a low barrier. As the temperature is decreased there is a small softening of the bcc T_1 branch which lowers the free energy along the transition path and allows the hcp minimum to fall below the bcc free energy. This is consistent with the Landau theory for a weakly first-order transition and a study of the transition based on a Landau expansion of the free energy has been made with the T_1 displacements and the coupled uniform shear as coordinates.[18] There is currently much interest in precursor effects for such transitions and our calculations indicate that at the N point, in addition to a frequency decrease of roughly 2×10^{-3} THz/K for the T_1 mode, a quasielastic contribution is also present in the neutron scattering cross section. A theoretical study of the temperature and wave-vector dependence of the quasielastic linewidths is now underway. Comparison with experiment is made difficult by the extra contributions from impurities and other defects, but strong quasielastic scattering was observed under the T_1 branch in bcc Zr.[7] A more thorough experimental study of the quasielastic scattering would now seem worthwhile.

In summary, we have used first-principles total-energy calculations to derive phonon-phonon coupling strengths and have established the interactions responsible for stabilization of the high-temperature bcc phase of Zr. These calculations provide a concrete basis for understanding the weakly first-order bcc-to-hcp transformation and open the door for a detailed theoretical analysis of precursor effects in a class of materials that is experimentally interesting.

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