Brief Reports

Calculations for the transverse N-point phonons in bcc Zr, Nb, and Mo

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The frequencies of the transverse N-point phonons in Nb and Mo have been calculated using the first-principles frozen-phonon method. The ordering of the modes is reversed in these metals in agreement with experiment. Similar calculations for the L and T_2 N-point phonons in the high-temperature bcc phase of Zr agree with recent measurements, while the results for the T_1 phonon of Zr indicate an instability toward the formation of the hcp phase.

I. INTRODUCTION

The transverse T_1 phonon branches along the [110] direction of the high-temperature bcc phases of La and Zr have recently been measured.[1] These branches have a very low frequency, reaching at the zone-boundary N point only 1.0 THz for Zr and 0.4 THz for La. At the zone center this branch is associated with the $(c_{11} - c_{12})/2$ elastic constant, and it was the small value of this elastic constant that led Zener[2] more than 30 years ago to suggest that the whole T_1 branch was low and was the source of the large vibrational entropy needed to stabilize the bcc phase at high temperatures. The T_1 mode at the zone-boundary N point is particularly interesting since the displacements for this mode take the bcc lattice in the direction of the hcp phase (with only an additional small shear required to complete the transformation).[3] Both La and Zr do in fact have low-temperature hexagonal close-packed phases. This particular mode in bcc La and Zr has also been observed to have a relatively high intensity from incoherent elastic scattering, and is expected to have a large phonon population at ~ 1200 K (e.g., $k_B T / \hbar \omega \sim 60$ for the T_1 branch of La), both of which suggest that anharmonic effects may play a role in stabilizing the bcc phase and causing the phase transition. The transverse modes at the N point are also unusual in Nb and Mo, the bcc metals following Zr in the periodic table. For Nb, the T_1 and T_2 frequencies are 3.9 and 5.1 THz, respectively, while for Mo this ordering is reversed with the T_2 frequency at 4.6 THz and the T_1 at 5.7 THz.

In this Brief Report, we apply the first-principles frozen-phonon method to study the N-point vibrational modes in Mo, Nb, and bcc Zr. We have previously studied, with some success, the H point and the $q = L(\frac{2}{3}, \frac{2}{3}, \frac{2}{3})2\pi/a$ modes in these metals using the same methods.[4] The procedure is to calculate the total energy of the distorted crystal with atomic displacements corresponding to a particular phonon. The total energy for different magnitudes of the lattice distortion is precisely evaluated using modern self-consistent band-theoretical techniques (in this case a first-principles

pseudopotential method with a mixed basis of Gaussian and plane-wave functions[5]). The only approximations entering the calculations are the standard exchange-correlation potential from local density functional theory,[6] the frozen-core approximation, and the Born-Oppenheimer approximation,[7] which provides the justification for "freezing" the phonon. From the total energy versus distortion curves, the harmonic phonon frequency can be obtained, along with information about anharmonicity and lattice stability.[4]

II. CALCULATIONS AND RESULTS

Before performing extensive calculations on distorted lattices to obtained phonon frequencies, we tested the programs, the adequacy of the basis, and the potential for each element, by first evaluating the total energy for several different bcc unit-cell volumes. These calculations yield the equilibrium lattice constant, bulk modulus, and cohesive energy of the crystal. The results for Nb and Mo have been reported previously[8] and we include those in Table I along with new results for bcc and hcp Zr, which show excellent agreement with experiment for the hcp phase and reasonable agreement for the high-temperature bcc phase (note that thermal expansion effects were not included in the theoretical treatment). The calculational procedures used for Zr were the same as those used for Nb and Mo,[8] except that there were two sets of Gaussian functions. We used one set to aid convergence of the $4d$ orbitals, and another for the rather extended $4p$ core orbitals, which in these calculations were treated as valence states. With the $4p$ orbitals as valence states, the equilibrium lattice constant was expanded by 2% over that obtained when the $4p$ orbitals were treated as core states. For the zone-boundary phonon calculations, where local changes in volume during distortion are less important, the $4p$ orbitals were treated as core states and the phonon frequencies were evaluated at the smaller equilibrium volume. This results in a small shift ($< 5\%$) in the calculated frequencies.

TABLE I. Comparison of calculated and measured values for the static bulk properties of Mo, Nb, and Zr.

	Lattice constant (Å)		Bulk modulus (Mbars)	Cohesive energy (eV/atom)
Mo				
Calculated	3.14[a]		2.85	6.64
Experiment	3.14[b]		2.62[c]	6.82[d]
Nb				
Calculated	3.26		1.82	7.55
Experiment	3.29[b]		1.735[e]	7.57[d]
bcc Zr				
Calculated	3.54[f]		1.05	6.93
Experiment	3.61[f]		. . .	. . .
hcp Zr	a	c		
Calculated	3.20	5.13	1.01	6.98
Experiment	3.23[g]	5.14[g]	0.95[h]	6.25[d]

[a]Reference 8.   [d]Reference 11.   [g]Reference 14.
[b]Reference 9.   [e]Reference 12.   [h]Reference 15.
[c]Reference 10.   [f]Reference 13.

The good results for the calculated bulk properties with the undistorted lattice allowed us to proceed with the phonon calculations with some confidence. With distortions of the crystal corresponding to the N-point phonon displacements, the original cubic symmetry of the bcc lattice is reduced to D_{2h} (8 group operations), and the real-space unit cell is doubled. For some of the calculations, the energy for the distortion converged slowly with respect to the number of k points sampled, and as many as 612 k points in the irreducible $\frac{1}{8}$th Brillouin zone were employed. This difficulty in converging some of the phonons at the N point is probably related to the observation made by Varma and Weber,[16] who found that strong interband electron-phonon matrix elements for these modes occur in a rather small region in the Brillouin zone. A more complete account of the calculational details will be published in a longer paper (for details of the method see Ref. 4).

The calculated total energy versus displacement curves for the T_1 (polarization, $\hat{e}_{\parallel}\langle 1\bar{1}0\rangle$) and T_2 ($\hat{e}_{\parallel}\langle 001\rangle$) modes are shown in Fig. 1 for Nb and Mo. For small displacements, the quadratic part of the curves may be used to obtain (via $E = \frac{1}{2}m\omega^2\delta^2$) the harmonic frequencies in Table II. The calculated frequencies are in reasonably good agreement with experiment, and display the same reversal of the T_1 and T_2 modes found experimentally. This reversal was previously shown by Varma and Weber[16] to arise from de-
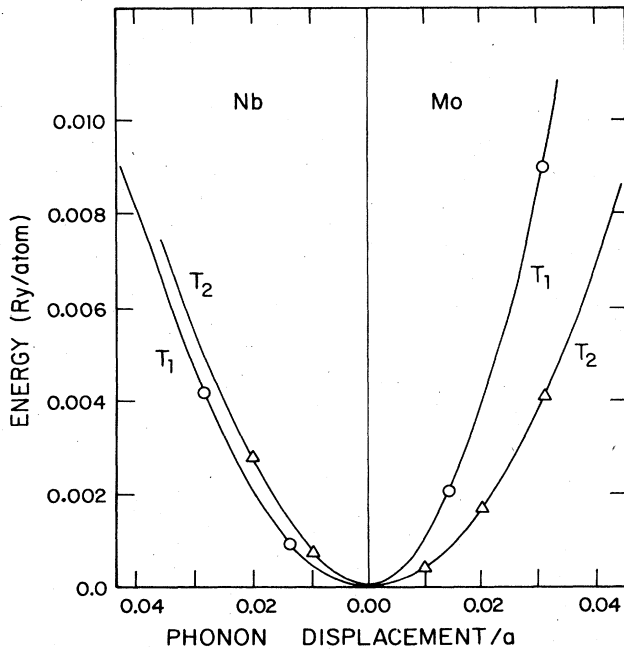

FIG. 1. The total energy vs displacement for lattice distortions corresponding to the two transverse-phonon modes at the N point. Because of symmetry, the curves are symmetric about zero displacement, so only positive displacements are shown for Mo, and negative for Nb.

TABLE II. Comparison of the calculated and measured values for the frequencies of the N point, $(1, 1, 0)\pi/a$, transverse vibrational modes in Mo, Nb, and the high-temperature bcc phase of Zr. The theoretical values are converged to ± 0.1 Thz.

	T_1, ($\hat{e}_{\parallel}\langle 1\bar{1}0\rangle$) (THz)	T_2, ($\hat{e}_{\parallel}\langle 001\rangle$) (THz)
Mo		
Calculated	5.8	4.0
Experiment	5.73 ±0.06[a]	4.56 ±0.06[a]
Nb		
Calculated	4.3	5.1
Experiment	3.93 ±0.06[a]	5.07 ±0.10[a]
bcc Zr		
Calculated	Unstable	3.6
Experiment	1.00 ±0.05[b]	3.94 ±0.07[c]

[a]Reference 17.   [c]Reference 18.
[b]Reference 1.

FIG. 2. Similar to Fig. 1 for the bcc phase of Zr.

III. DISCUSSION

The total energy calculations showing the instability of bcc Zr for displacements corresponding to the zone-boundary T_1 mode (Fig. 2) represent a significant step in understanding the bcc-to-hcp phase transition in this class of materials.[19] In the past, the transition to the high-temperature bcc phase was frequently explained by the nearly tautologous remark that the entropy of the bcc phase was higher. Zener[2] and Friedel[20] have speculated on the source of the required excess vibrational entropy (over that of the lower temperature phase), but there has been little progress toward a detailed microscopic understanding of the phase transition. Iizumi has used neutron scattering to look for soft-mode behavior of the low-lying N-point T_1 mode in the high-temperature bcc phase of thallium, which also exhibits a hcp-to-bcc transition, but he did not detect any discernible temperature dependence of the phonon frequency, or any conspicuous change of the elastic scattering.[21] Based on the calculations presented above, and the available experimental data, we may speculate a bit further than Iizumi as to the nature of the transition. For those metals possessing a low T_1 branch in a high-temperature bcc phase, we believe the situation is similar to the case of solid helium, where the crystal structure is unstable within the harmonic approximation, but because of large displacements and attendant anharmonic effects, the lattice is stabilized. Calculations for the vibrational modes of the bcc phase would then require some form of renormalized or self-consistent phonon theory.[22] The ingredients required to implement such theories are the anharmonic mode coupling strengths which are extractable, in principle, from frozen phonon calculations, and will be the subject of a future publication.

tails of the electronic structure. The corresponding total energy curves for bcc Zr are shown in Fig. 2. The negative curvature for the T_1 curve indicates the bcc phase (at $T = 0$ K) is unstable for displacements associated with the T_1 mode, while the phonon frequency of the T_2 mode is again in reasonable agreement with experiment. The longitudinal N-point phonon frequency for bcc Zr was also calculated (3.9 THz) and found to be in good agreement with the experimental value (4.2 THz). The large temperature (1340 K) at which the phonon frequencies were measured for bcc Zr would normally lead to a softening of the lattice and measured frequencies somewhat below the calculated values. However, the T_1 curve for Zr indicates that the situation is more complex.

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