Vibrational Frequencies and Structural Properties of Transition Metals via Total-Energy Calculations

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The vibrational frequencies of selected normal modes can be obtained entirely from first principles with use of frozen phonon calculations which involve the precise evaluation of crystal total energy as a function of lattice displacement. The calculations allow a detailed analysis of the microscopic mechanisms causing phonon anomalies and soft-mode phase transitions. Successful calculations for Zr, Nb, and Mo have been made with use of both tight-binding and pseudopotential methods.

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The lattice dynamics of transition metals and transition-metal compounds with their abundance of phonon anomalies and lattice instabilities have been the subject of extensive experimental and theoretical studies.[1] Recently Varma and Weber,[2] using a perturbative approach involving an empirical nonorthogonal tight-binding description of the electronic states and electron-phonon matrix elements,[3] have been quite successful in correlating anomalies in the phonon spectra of Nb, Mo, and Nb-Mo alloys with features of the band structure near the Fermi energy. Previous to this, general theories based on dielectric response were proposed and led to simplified models emphasizing charge fluctuations.[4] In this paper we demonstrate an alternative and complementary method to obtain phonon frequencies which not only allows a first-principles determination of the few empirical parameters entering the Varma-Weber method but also permits testing of charge-fluctuation models by providing details of the charge-density response. The method involves the calculation of the total energy of the crystal as a function of lattice displacements for a particular wave vector. From the calculated potential well the phonon frequency as well as detailed information on the phonon anharmonicity and possible lattice instability may be obtained. Recent applications of this method to semiconductors have been very successful in evaluating phonon frequencies,[5-9] elastic constants,[5,7,8] anharmonic terms,[7-8] Grüneisen parameters,[5] and temperatures and pressures for phase transformations.[5,10] The method has also been extended to evaluate interplanar force constants from which entire dispersion curves along a particular direction may be obtained.[9] In this Letter we demonstrate the applicability of the method for studying transition metals. We have performed these so-called "frozen-phonon" calculations for the longitudinal $(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonon of Nb, Mo and the high-temperature bcc phase of Zr, as well as the H-point phonon in Nb and Mo. There are remarkable differences in the dispersion curves of these metals (see Fig. 1)[11-13] which the calculations are able to reproduce accurately.

The $(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonon calculations were made using the *ab initio* pseudopotential method.[5,14,15] The wave functions were expanded by means of an efficient mixed-basis approach.[16] For the phonon at H we used initially a first-principles tight-binding method[8,17] but later switched to the more efficient pseudopotential method. The Hedin-Lundqvist form[18] was used for the exchange-correlation energy and potentials. Before attempting any calculations for the displaced lattice, we have calculated various structural properties for the bulk using both methods. The results obtained are in excellent agreement with measured values (see Table I).

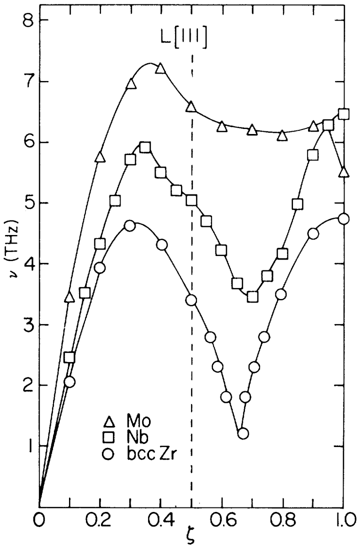

FIG. 1. Phonon dispersion curves for the longitudinal (111) branch measured by inelastic neutron experiments on Nb (Ref. 11), Mo (Ref. 12), and the high-temperature (1400-K) bcc phase of Zr (Ref. 13).

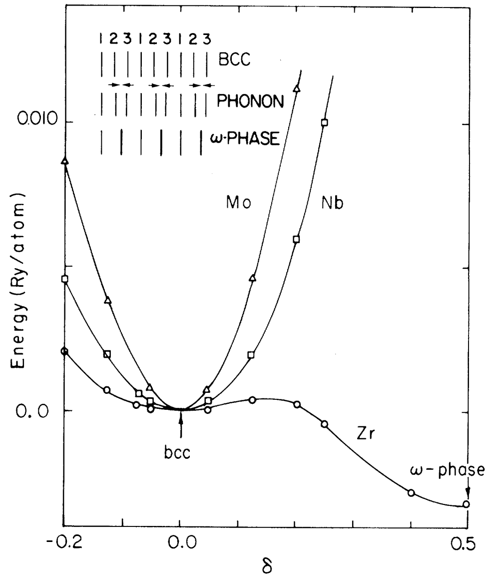

FIG. 2. The calculated energy vs displacement curves for the $L(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ mode in Nb, Mo, and bcc Zr. Inset: the displacements of the (111) planes. Plane 1 is fixed, plane 2 is displaced by $\delta(a/6,a/6,a/6)$, and plane 3 by $-\delta(a/6,a/6,a/6)$.

In dealing with lattice distortions in metals it is necessary to consider changes in the Fermi surface and band occupancies. For the tight-binding method, the band structure near the Fermi level is fitted with empirical tight-binding parameters and the weight of a state near the Fermi level is determined by the occupied portion of the reciprocal space volume it represents. With this scheme, 32 first-principles points in the frozen-phonon Brillouin zone gave good agreement between the calculated and the measured phonon frequencies. The pseudopotential method allows more points to be sampled economically and a Gaussian smearing of state energies proved a convenient means of weighting points. The width of the smearing Gaussian is chosen to be roughly equal to the dispersion of the state energies between grid points near the Fermi level. Convergence for both weighting schemes was tested by varying the number of k points. Grids of up to 124 points for the $(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonon and 196 points for the H phonon have been tested. At the same level of convergence both the tight-binding and pseudopotential methods were in agreement.

Our motivation for studying the $L(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ and the H phonon in Nb and Mo is the marked differ-

TABLE I. Comparison of calculated and measured values (Refs. 11–13 and 19) for (i) the properties and (ii) the frequencies of the $L(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonons, and (iii) the frequencies of the H phonon in Nb and Mo.

		Nb			Mo		
		Expt.	Pseudo-potential	Calc. Tight binding	Expt.	Pseudo-potential	Calc. Tight binding
Lattice constant (Å)		3.30	3.26	3.34	3.15	3.14	3.17
Bulk modulus (Mbar)		1.702	1.79	1.62	2.725	2.82	2.57
Cohesive energy (eV/atom)		7.57	7.55	6.63	6.82	6.64	6.28
Phonon frequency (THz)	$L(2/3, 2/3, 2/3)$	3.57 ± 0.06	3.6		6.15 ± 0.08	6.0	
	H point	6.49 ± 0.10	6.4	6.6[a]	5.5 ± 0.08	5.1	5.7[a]

[a] These results are from calculations that have not fully converged.

ences in the phonon spectra of the two metals at these wave vectors. For Nb the longitudinal (111) phonon branch exhibits a dip at the $(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ position whereas the same branch in Mo is flat near $(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ but shows a dip at the zone boundary. We first discuss the results for the $L(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonon for which the distorted bcc crystal can be described by a unit cell consisting of three atoms with displacements as indicated in the inset in Fig. 2. The calculated crystal energy as a function of displacement is plotted in Fig. 2 for the $L(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonon in Nb and Mo. The frequencies derived from these curves are in excellent agreement with inelastic neutron scattering results (Table I).[11,12] Of particular interest is the result we calculated for bcc Zr,[20] also shown in Fig. 2. The calculated potential well is highly anharmonic; moreover, the minimum in energy does not occur at the undisplaced bcc position but rather it occurs when two of the (111) planes in the unit cell collapse together to form what is known as the ω-phase structure. The instability of the bcc phase towards the formation of the ω phase at low temperatures occurs in a wide variety of Ti, Zr, and Hf alloys[21] and also in pure Ti and Zr under pressure.[22] The bcc-ω transition has been studied extensively[23] because of its anomalous effects on the diffusion process and the mechanical properties of the metal. This is the first time that a potential energy curve has been calculated for this important transition. We obtained an energy difference of 0.045 eV (or 520 K) per atom between the two phases. Our results suggest that the transition is first order in nature since we find the Zr bcc lattice has very low but *nonzero* restoring forces when subjected to the distortions of the $L(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonon. Stassis, Zarestky, and Wakabayashi[13] have measured phonon dispersion curves for the bcc phase of Zr at high temperatures and their results show that there is a sharp dip in the longitudinal mode at the $(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ position (Fig. 1) as well as quasielastic scattering at Bragg positions corresponding to the ω phase.

The sharp dip at the H point in the phonon dispersion curve of Mo has been associated with features of the Fermi surface.[2] Indeed, an analysis of the distorted Mo band structure for displacements corresponding to this phonon confirms that a large band splitting occurs at the Fermi level.[3] With a displacement corresponding to ~4% of the lattice constant, the total energy changes by ~0.03 eV/atom while the band splitting is greater than 1 eV. The large volume of the Brillouin zone affected and the size of the splitting for modest displacements allow convergence of total-energy calculations with a reasonable number of k points. The calculated values for the H-point phonons of Mo and Nb are in good agreement with experiment (Table I).

In the analysis of the phonon spectra of Nb and Mo using the traditional Born–von Kármán model it is necessary to include interactions up to the eighth neighbors to obtain a good fit.[11] Wakabayashi[24] and Allen[25] have proposed alternative models in which the phonons are coupled to charge fluctuations in the crystal. They were able to fit the phonon dispersion curves in Nb very well with considerably fewer parameters. Our preliminary investigations of the charge fluctuations produced by the $L(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ phonon in Nb, Mo, and Zr indicate that the monopolar fluctuations are similar in magnitude but very different in character. For Mo there is a transfer of sp-like charge about atoms in plane 1 (Fig. 2) to d-like charge about atoms in planes 2 and 3 whereas in Zr, especially at large displacements, the transfer is directly opposite with d-like charge going over to sp-like charge in planes 2 and 3 accompanied by a decrease in the kinetic energy. In the ω phase 0.14 electron/atom is transferred from plane 1 to planes 2 and 3, an amount which should be detectable by high-resolution measurements of core-level shifts. A complete analysis of the charge-density distortions associated with the phonons is lengthy and will be published elsewhere together with comparisons with phenomenological models.

The encouraging results we have obtained demonstrate that total-energy calculations for distorted lattices offer a viable method for studying the lattice dynamics of transition metals. We are presently extending these methods (using the Hellman-Feynman theorem[14]) to calculate forces on the atoms in the presence of distortions.

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Orientational Order-Disorder Transition on a Surface

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A system of diatomic molecules with atoms interacting via Lennard-Jones potential and with the centers of mass of molecules fixed on a square lattice is studied by molecular dynamics technique. Temperature dependences of internal energy and orientational order parameter are calculated. The development of an ordered state from a disordered state is also studied. It is found that the system undergoes a continuous orientational order-disorder transition.

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In recent years, many experimental and theoretical investigations have been carried out on systems of molecules adsorbed on surfaces.[1] Because of the anisotropic nature of intermolecular forces, it is possible that these systems will exhibit distinct orientational order-disorder phenomenon and a melting transition associated with translational degrees of freedom. Theoretical proposals[2] concerning the role of topological defects in the melting of two-dimensional (2D) solids have contributed a great deal to the recent surge in experimental[1,3] and computer simulation[4-7] studies.

In this Letter we shall discuss the problem of orientational order-disorder phenomenon for diatomic molecules adsorbed on surfaces. To separate this issue from melting, it is customary to study the problem in which centers of mass of molecules are fixed on a lattice (e.g., square, hexagonal, etc.), thereby eliminating the trans-