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Anharmonic effects and vibrational spectrum of bcc Zr under pressure studied by molecular dynamics simulations

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The structural stability and the lattice dynamics of the high-pressure bcc phase in zirconium are studied by the molecular dynamics method at different volumes and a fixed temperature $T=500$ K. The dispersion curves of the vibrational spectrum obtained from the molecular dynamics simulations are compared with the phonon spectra calculated in the harmonic approximation. The frequency shifts and phonon damping obtained from the spectral density of vibrations at different volumes show that in zirconium the high-pressure bcc phase is strongly anharmonic. Therewith, not only the particular vibrational modes (N,L), but also most of the modes with wave vectors directed along the high-symmetry lines of the Brillouin zone, are anharmonic. Under pressure, the anharmonicity-induced frequency shifts can reverse sign. At high pressure the strongest anharmonic effects are observed in the vicinity of the H point and the second band of the [110] direction.

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I. INTRODUCTION

In recent decades the structural stability of metals which have a high-temperature bcc phase region in the P-T phase diagram has been the subject of much investigation. It has been found that in such metals the bcc phase stability at high temperatures is due to strong anharmonicity of the lattice vibrations,[1–6] the anharmonic effects being more pronounced near the boundary of high-temperature phase transition. Zirconium is one of the most suitable elements for theoretical study of the influence of the vibrational mode anharmonicity on structural stability of transition metals. At atmospheric pressure, β-Zr is known to become unstable at temperatures below 1136 K.[7] It has been shown by inelastic slow-neutron scattering experiments that in bcc Zr near the $\beta \rightarrow \alpha$ transition, as the temperature goes down a considerable decrease of the vibration frequency (softening) of the transverse T_1 mode is observed at the N point of the Brillouin zone (BZ) with wave vector $\mathbf{k}=1/2$ [110] (N_{T1} phonon). Such a nonstandard temperature dependence of the vibration frequency is accounted for by strong anharmonicity of this mode. Theoretically, it was first demonstrated by Chen[1] who has calculated the change of the total energy of crystal in the ground state with the atomic displacements corresponding to the N_{T1} mode (the frozen-phonon model). The effective potential for the N_{T1} phonon obtained by Chen had a strongly anharmonic double-well shape with a maximum of energy at zero displacements corresponding to the perfect bcc lattice. Such a shape of the effective potential leads to the following: in the harmonic approximation the square of the phonon frequency proportional to the second derivative of the energy with respect to the displacement proves to be negative and, as a result, the bcc lattice is unstable. Using perturbation theory for anharmonic effects it has been shown[2] that allowance for the contributions from three- and four-phonon processes results in renormalization of the vibration frequency of the N_{T1} mode which at $T=1400$ K becomes positive and coincides with the experimental value.[8] In this case the shift of the vibration frequency to the positive-value region and hence the bcc lattice stability at high temperature are provided only by the fourth-order contributions related to the N_{T1}-phonon interaction with the other phonons of the $T1$ branch. Using the frozen-phonon model proved to be very fruitful to describe the particular strongly anharmonic vibrational modes and allowed an understanding of the peculiarities of structural transformations in Zr at both atmospheric[2] and high[5] pressures.

Unfortunately, the frozen-phonon model can be applied only to a limited number of the BZ points and does not provide the answer to the question concerning the lattice anharmonicity as a whole. In Ref. 9 the self-energies, frequency shifts of, and characteristic phonon lifetimes, as well as the inelastic scattering spectra were calculated over the whole BZ for β-Zr and β-Ti using the phenomenological Born-Mayer potential and the anharmonic one-phonon Green functions. It was shown that strong quasielastic scattering observed in the experiment near the points with vectors $\mathbf{k}=1/2$ [110] and $\mathbf{k}=2/3$ [111] (L phonon) is explained by anharmonic line broadening and a reduction of the lifetime of these low-energy phonons to a value of the order of a vibrational period. The calculation of the Green functions in Ref. 9 was restricted to the consideration of the three- and four-phonon terms only. The higher-order contributions were not taken into account. Using perturbation theory in analyzing anharmonic corrections implies that the characteristic amplitudes, d, of the thermal atomic vibrations are considerably less than the lattice period, a, i.e., $d/a \ll 1$. Nevertheless, as shown in Refs. 3 and 10, at high temperature in zirconium for some modes (e.g., for phonons with $\mathbf{k}=2/3$ [111]) the atomic displacements are comparable to the interatomic distance. In this case a breakdown of the phonon pattern may occur manifesting itself, in particular, as a complicated multipeak structure of the spectral density of vibrations (SDV). In Ref. 10 we have shown that even the presence of only one strongly anharmonic mode gives rise to the induced anharmonicity in other vibrational modes which are almost harmonic in the absence of interaction. To describe such vibrations using the Green functions theory, in the process of summing up, one should consider the terms of higher orders than the third and the fourth ones. However, even for simple model interatomic potentials this is very difficult to realize. One can state that, on the whole, the dynamics of strongly anharmonic crystals of Zr, Ti, Hf remains still unknown.

Additional information on the anharmonicity influence upon crystal stability may be obtained by analyzing the vibrational spectra under pressure. The theoretical study of the pressure dependence of the strongly anharmonic N_{T1} and L vibrational modes carried out in Refs. 5 and 6 have shown that the effective potential calculated in the frozen-phonon model considerably changes under pressure and may become almost harmonic upon strong compression. Unfortunately, at present, both experimental and theoretical investigations of this kind are lacking excepting the calculations at the Γ, L, and N points of the BZ.

In principle, an answer to the question about the pressure effect on the vibrational spectra of β-Zr may be provided by molecular dynamics (MD) calculations at various pressures. At zero pressure similar calculations have been carried out for β- and α-Zr using the model pair potentials[11] and many-body interatomic potentials.[4,12,13] According to the P-T phase diagram,[7] with increasing pressure the temperature stability boundary of β-Zr goes down, and at 30 GPa bcc Zr remains stable even at room temperature.[16,17] No systematic experimental investigations of the stability boundary of the Zr bcc phase have been performed at high pressures and various temperatures. So, it is of particular interest to define the stability boundary of the bcc phase based on MD calculations at different pressures and a fixed temperature. In addition to the standard investigation of the structural stability (see, e.g., Refs. 4 and 11–13) the MD calculations can be used in studying the anharmonic effects near the phase transition. A method for obtaining the phonon dispersion curves from the molecular dynamics simulation has been proposed in Ref. 15. Comparing the results of the MD calculation with those obtained in the harmonic approximation (HA) one can find the frequency shifts caused by anharmonic effects. It should be noted that in the MD calculation the interactions of all lattice atoms are taken into account, which allows one to avoid the problems connected with the d/a parameter value and the order of the terms considered when summing up in anharmonic perturbation theory. Thus, the method of obtaining the vibrational spectrum dispersion from the MD simulation may provide information about the degree of lattice anharmonicity over the whole BZ even in the case of strong anharmonicity and atomic displacements of the order of $d/a \approx 1$.

In this paper we present the results of MD calculations carried out at a fixed temperature equal to 500 K and various volumes ranging from $0.87V_0$ to $0.73V_0$ ($V_0 = 23.5$ Å^3 is the β-Zr equilibrium volume at atmospheric pressure and $T = 1136$ K). We have also considered the changes in the dispersion curves of the vibrational spectra, calculated the frequency shifts connected with anharmonic effects, and determined the phonon lifetimes along the high-symmetry directions of the BZ in bcc Zr.

II. CALCULATIONAL METHODS

A. Molecular dynamics

In our simulation we have built a structurally ideal bcc crystallite consisting of $24 \times 24 \times 24$ unit cells (27 648 atoms). In all calculations, cyclic boundary conditions were used along the x, y, z directions. In the process of simulation with a thermostat described in Ref. 14 after reaching $T = 500$ K, the system was held at this temperature freely evolving to an equilibrium state. Equilibrium was considered to be attained if the velocity-distribution function did not vary with time and the main system parameters (the kinetic, potential, and total energies; the minimum interatomic distance, etc.) fluctuated, due to the finite size of the system, near average values that remained unchanged for a time of the order of 10^{-12} s. The time step was $\delta t = 1 \times 10^{-15}$ s in all calculations. The coordinates of all the atoms of the system were recorded every 10 time steps for further averaging. The interatomic interaction was described by an earlier selected pair potential[18] constructed within the Animalu pseudopotential model for transition metals.[19] To fit the pseudopotential an experimental phonon spectrum of the Zr hcp phase[20] was used. In Ref. 18 with the help of this pair potential using the molecular dynamics method we succeeded in describing the hcp-Zr structural stability within a wide temperature and pressure range, obtaining the transition from the α to the β phase, and the reverse transition, as well as constructing the boundaries of the phase transitions in the P-T diagram. Besides, the phonon spectra of the bcc and hcp Zr were calculated by the dynamical matrix diagonalization, which was in good agreement with the experimental results on inelastic neutron scattering.[8,20]

B. Calculation of dispersion curves in monoatomic lattice based on MD data

One of the most attractive peculiarities of molecular dynamics is the possibility for easy determination of the phonon dispersion curves. For monoatomic metals with bcc lattice the time evolution of the atomic displacement in the normal coordinates can be determined in the following way:[15]

$$\alpha_{\mathbf{k}}(t) = \sum_i [\mathbf{r}_i(t) - \mathbf{l}_i]\mathbf{e}_{\mathbf{k}} \cos(\mathbf{k} \cdot \mathbf{l}_i), \tag{1}$$

where $\mathbf{l_i}$ are the equilibrium positions of the crystallite atoms obtained by averaging the coordinates of each ith atom over the considered time interval; $\mathbf{r_i}$ are the coordinates of the ith atom at the current moment of time taken from the MD simulation at a given temperature and pressure. The vectors of polarization, $\mathbf{e_k}$, for the selected mode with wave vector $\mathbf{k}$ were calculated in the HA simultaneously with the phonon spectrum. The required lattice parameter was taken from the corresponding MD simulation performed at a given temperature and pressure.

Since in the MD simulation the crystallite has a finite size, the wave vector may take only certain discrete values,

$$\mathbf{k} = \left(\frac{2\pi n_a}{a}, \frac{2\pi n_b}{b}, \frac{2\pi n_c}{c}\right), \tag{2}$$

where n_a, n_b, n_c are integers ranging from 1 to a value equal to the number of unit cells in the crystallite along the respective a, b, c directions (in our case, from 1 to 24). In the present paper all calculations were carried out for four high-symmetry directions of the BZ of the bcc structure with wave vectors $\mathbf{k_1}=[\xi\xi 2\xi]$, $\mathbf{k_2}=[\xi\xi 0]$, $\mathbf{k_3}=[00\xi]$, $\mathbf{k_4}=[\xi\xi\xi]$.

The spectral density of vibrations for the selected wave vector was determined by the fast Fourier transform of the function $\alpha_{\mathbf{k}}(t)$. The averaging of the coordinates was carried out over a time interval equal to 40 ps.

In the case of harmonic vibrations the Fourier transform yields the δ function at a definite frequency $\omega_{\mathbf{k}}$. As the temperature increases, the energy of a particular mode is not conserved because of anharmonic interaction, and can be transferred to other vibrational modes. This leads to the broadening of the SDV peaks, and in the case of strong anharmonicity to the appearance of a fine structure or even of additional peaks in the SDV curve. Besides, anharmonicity makes itself evident in a shift of the peaks positions in frequency. Additional peaks or the fine structure in the SDV curve resulting from the anharmonic interactions of the modes make it difficult to uniquely determine the phonon energy. In our calculations the frequency at which the SDV of a given mode with vector **k** is maximum was chosen as the frequency of the anharmonic phonon.

Thus, the method presented can be used for theoretical calculations of the dispersion curves of vibrational spectra at various temperatures and pressures. The advantage of this method is that it allows studying not only harmonic but also strongly anharmonic vibrations which occur at high temperature and pressure or near the boundary of the phase transition when the atomic displacements from the equilibrium position are quite considerable.

III. RESULTS AND DISCUSSION

In our MD simulations with the above-mentioned interatomic potential and crystallite size it was found that at $T=500$ K the Zr bcc lattice becomes unstable for $V>0.87V_0$. This result agrees with the phase diagram calculated in Ref. 6 from which it follows that at $T=500$ K bcc Zr is unstable at pressures lower than 18 GPa. According to the equation of state,[6,17] the pressure of 18 GPa corresponds to a volume of about $0.86V_0$. In what follows, we discuss the vibrational properties of bcc Zr obtained from the MD simulation data at $T=500$ K and V ranging from $0.87V_0$ to $0.73V_0$.

As expected, when the volume goes down the vibration frequency of each branch of the phonon spectrum increases, the largest changes in the spectrum occurring at the high-symmetry points N,H,P with maximum wave vectors localized at the BZ boundary as well as at the L point with vector $\mathbf{k}=2/3$ [111]. For example, at the H point the vibration frequency increases by approximately 25% with decreasing volume from $0.87V_0$ to $0.73V_0$.

Figure 1(a) shows the volume dependence of the vibration frequency at the H,P,L points for $T=500$ K. In the harmonic approximation at the H and P points the three vibrational branches are degenerate, while at the L point only the second and the third transverse vibrational branches are degenerate [they are denoted L-2,3 in Fig. 1(a)]. Hereafter the vibrational spectrum branches (or bands) are numbered in order of increasing frequency. It should be noted that contrary to the harmonic approximation, in the MD calculation there occurs complete splitting of the degenerate vibrational states due to anharmonic effects. However, this splitting is not plotted because of it being very small. Its maximum value (~0.2 meV) is reached at $V=0.87V_0$ at the stability boundary of the bcc lattice.

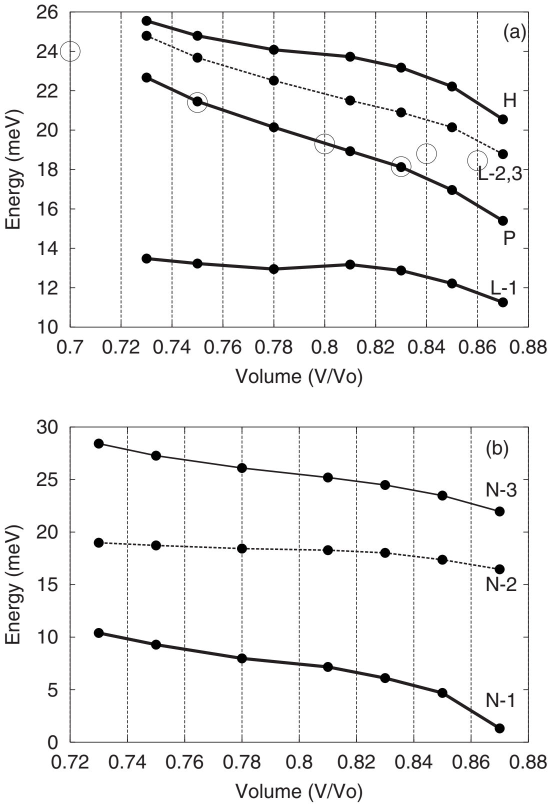

FIG. 1. The volume dependence of the frequency at high-symmetry points of the Brillouin zone in bcc Zr at $T=500$ K. Empty circles denote the results of an *ab initio* calculation for the L-2,3 mode from Ref. 6.

In the same figure are presented the results of our *ab initio* calculation of the vibrational frequency of the transverse L mode as a function of volume at $T=500$ K. As seen, the MD frequency is somewhat greater than that obtained in Ref. 6. However, the pressure dependence of this mode is similar in both calculations. The jump in frequency at $V\approx 0.84V_0$ due to a change in the character of the L mode vibrations, discussed in detail in Ref. 6, manifests itself as a slight bend in the MD calculation.

For convenience, the data calculated for the N point ($\mathbf{k}=1/2$ [110]) are given singly in Fig. 1(b). For this point the most considerable frequency changes are observed in the first band. Namely, at $V=0.87V_0$ the transverse vibrations frequency of the N_{T1} mode is practically reduced to zero. As is known, such a softening of vibrations results in structural instability, which agrees well with the bcc lattice instability obtained from the MD simulation at $V>0.87V_0$. The role of the transverse vibrational N_{T1} mode in the martensite $\beta\rightarrow\alpha$ phase transition at atmospheric pressure has been thoroughly studied in a number of works by both *ab initio* calculations[1,2,5] and the molecular dynamics method.[4] It is currently believed that it is precisely this mode that is re-

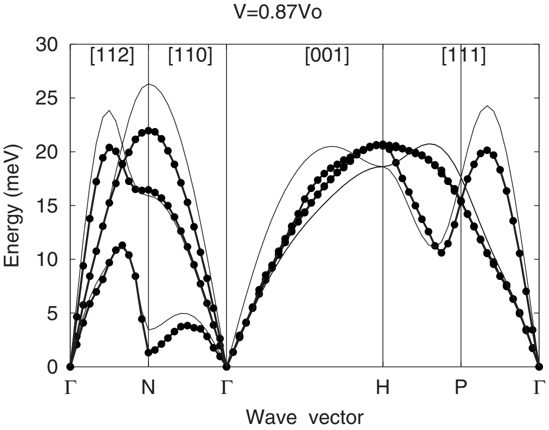

FIG. 2. Phonon dispersion curves of bcc Zr calculated at $V=0.87V_0$ and $T=500$ K. The heavy lines with circles denote the molecular dynamics calculation as described in the text. The thin solid lines represent the calculation in the harmonic approximation.

sponsible for this transition in zirconium. Our calculation has shown that also in the case of high pressures the vibrational N_{T1} mode is of considerable importance in structural instability of the bcc Zr.

A "dip" in the longitudinal vibrations frequency along the [111] direction characteristic of bcc Zr is observed at each volume under study. Figure 1(a) shows that the vibration frequency at the L-1 point with wave vector $\mathbf{k}=2/3$ [111] changes only slightly in the range $0.73V_0<V<0.81V_0$ and decreases at $V>0.81V_0$. Such a behavior of the volume dependence of the frequency should point to a change in the vibration character at $V\approx 0.8V_0$. This conclusion agrees well with the results of an *ab initio* study[6] of the changes in the dynamics of this vibrational mode under pressure. The calculations in Ref. 6 have been carried out using the frozen-phonon model. In particular, it has been shown that as the pressure increases the effective potential of the longitudinal L mode changes its shape from the three-well one at atmospheric pressure to a double-well shape at $V<0.8V_0$. As a result, with decreasing volume the character of atomic motion in the lattice and the form of the SDV substantially change.

Note that the frequency $\omega_L=11$ meV obtained for this mode at $V=0.87V_0$ is nearly 2 times as large as both the experimental value ($\omega_L^{\text{exp}}\approx 6$ meV) determined at atmospheric pressure and $T=1024$ K (Ref. 8) and that calculated in Ref. 6. As known, to this vibrational mode correspond the atomic chains displacements along the [111] direction. From *ab initio* calculations[21] it follows that low-frequency vibrations are due to the weak interaction between these chains which, in turn, results from strong anisotropy of the valence d-electrons density distribution. For this reason, the use of the spherically symmetric pair potential in MD simulation is a relatively rough approximation, which is reflected in a significantly overestimated value of vibrational frequency at the L point ($\mathbf{k}=2/3$ [111]) in our calculation.

The bcc-Zr vibrational spectrum determined at $0.87V_0$ by two different methods is presented in Fig. 2. The results of the MD calculation as described in the preceding section are denoted by heavy lines with circles. The thin solid lines show the results obtained in the harmonic approximation. The HA phonon spectrum was determined by diagonalization of the dynamical matrix calculated in the pair potential approximation. It should be emphasized that both the MD and HA calculations were carried out for the same volume of the unit cell using the same pair potential. Thus, all distinctions between the MD and HA dispersion curves in Fig. 2 are due to the anharmonic effects at $T=500$ K.

As seen from the figure, on the whole, the MD results agree rather well with those obtained using the HA. Both methods yield practically the same vibration frequency for the first and the second spectral bands along the Γ-N [112] direction, for the second band of the N-Γ [110] direction and for long-wave vibrations (around the Γ point). The most significant discrepancies between the MD and HA spectra are observed for the longitudinal vibrations in the vicinity of the points $\mathbf{k}=1/2$ [110] (N) and $\mathbf{k}=2/3$ [111] (L) longitudinal vibrations along the whole [001] (Γ-H) direction and transverse vibrations around $\mathbf{k}=1/2$ [112] (the third band of the Γ-N direction). Note that for all listed regions except for the H point the MD vibration frequency is smaller than the HA one.

The softening of the transverse N_{T1} mode is observed in both MD and HA calculations. Contrary to the results obtained in Ref. 2 at zero pressure, in our calculation the vibration frequency of this mode at $V=0.87V_0$ is positive in both cases. This implies that even in the HA at this volume bcc Zr remains stable with respect to the atomic displacements corresponding to the transverse N_{T1} mode. In Ref. 2 with allowance for the anharmonic corrections, as the temperature goes up, the square of the N_{T1} vibration frequency increases and becomes positive at $T=1400$ K. For $V=0.87V_0$ our MD calculation in which both the intrinsic anharmonicity of the N_{T1} mode and its interaction with the other modes are taken into account, yields a smaller vibration frequency for this mode than the HA calculation. Thus, in the MD calculation the bcc lattice proves to be less stable with respect to such atomic displacements than in the harmonic approximation.

Figure 3 presents the anharmonic corrections, i.e., the frequency shifts as a function of the wave vector along the main symmetry directions of the BZ of bcc Zr calculated at different volumes and $T=500$ K. The corrections were determined as the difference of the MD and HA frequencies obtained for all three vibrational branches, $\Delta\omega=\omega_{\text{MD}}(500\text{ K})-\omega_{\text{HA}}(0\text{ K})$.

From Fig. 3 it can be seen that at $V=0.87V_0$ the frequency shift due to anharmonicity is negative for most of the vibrational modes except for the first band along the whole Γ-H [001] direction and in the vicinity of the H point. The frequency shift for the third spectrum band, except the H point, is negative and does not exceed 4.2 meV in magnitude. For the first and the second band $\Delta\omega$ is shifted to the positive-value region when the crystal is compressed to $V=0.81V_0$. The frequency renormalization in the vicinity of the H point increases more than 2 times. At this volume the frequency shifts are almost completely positive for the first and the second band except for the P point, at which for all three bands $\Delta\omega$ is negative, even if small (about 0.5 meV) in magnitude. At $V=0.78V_0$ the anharmonic corrections for the first and the second spectrum bands are completely positive, with a maximum of ~7.5 meV. Only the frequency shifts for the

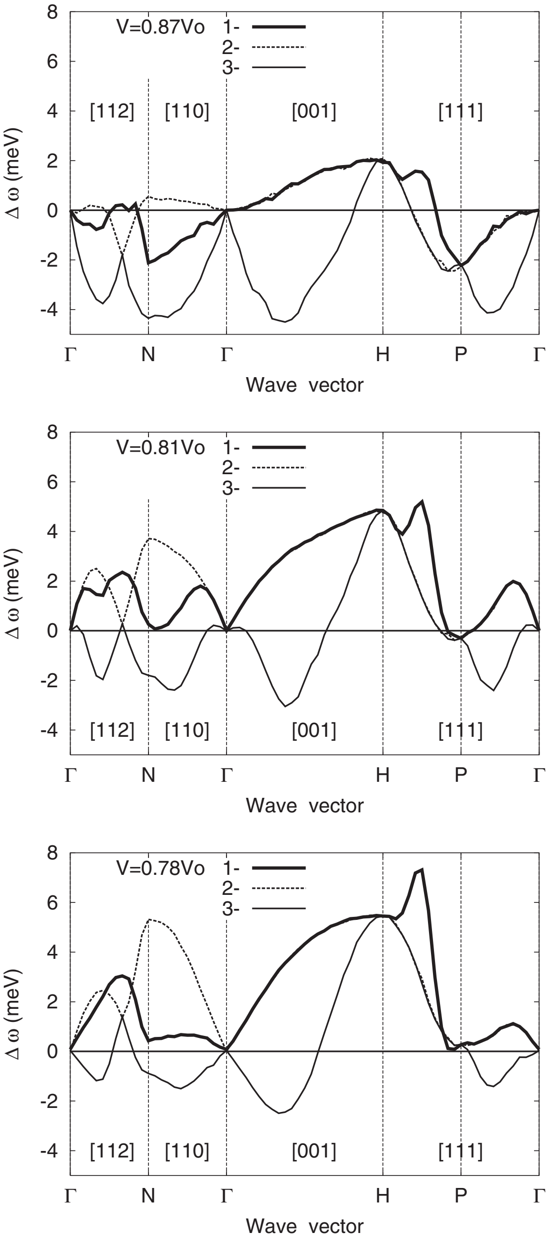

FIG. 3. Frequency shifts as a function of wave vector at $T=500$ K and various volumes in bcc Zr.

third band remain negative. From the obtained data it can be concluded that at high pressure the character of the lattice dynamics of bcc Zr considerably changes. Namely, the N_{T1} phonon anharmonicity decreases, and the anharmonic corrections for the second band of the N-Γ [111] direction as well as for vectors $\mathbf{k}$ localized in the vicinity of the H point of the BZ become substantial.

Figure 4 shows the frequency shifts as a function of volume at the high-symmetry points N,H,P,L point of the BZ. The individual frequency shifts for the three bands are shown for the N point in Fig. 4(a) and for the points H,L,P in Fig. 4(b). An analysis of the figures shows that as the lattice parameter decreases the difference of the vibration frequencies at these points nonmonotonically changes, all the curves have a more or less pronounced bend which is especially marked at the N point. At volumes ranging from $0.81V_0$ to $0.75V_0$ the frequency shift for the first band remains practically unchanged and then increases again. Besides, for the N_{T1} mode the difference of the MD and HA frequencies decreases in magnitude and amounts to zero at $V=0.81V_0$. On further crystal compression the anharmonic corrections become positive and the MD vibration frequency for the N_{T1} mode exceeds that calculated in the harmonic approximation. Thus, the anharmonic corrections for "soft" phonons reverse sign at high pressures.

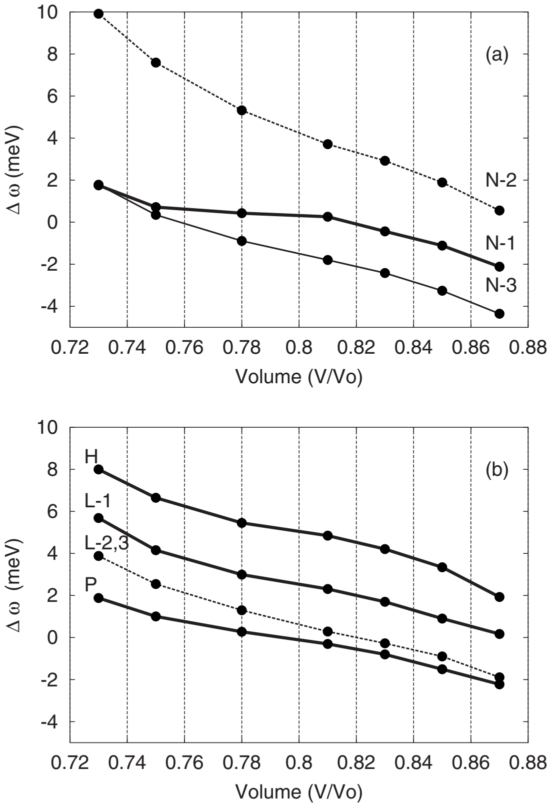

FIG. 4. Frequency shift as a function of volume at different points of the Brillouin zone in bcc Zr at $T=500$ K.

Figure 5 presents the phonon damping γ as a function of the wave vector in the [110] direction from the N to the Γ point calculated for two different volumes of the bcc-Zr unit cell and $T=500$ K. The phonon damping was calculated as the half-width of the previously smoothed SDV for each value of the wave vector and the three spectrum branches. It can be seen from the figures that at $V=0.87V_0$ the "soft" phonons are characterized by a much larger damping than at $V=0.75V_0$. The phonon damping turned out to be unexpectedly large for the first and the third spectrum band along the N-Γ direction with wave vectors from 0 to 1/4 [110]. This is clearly seen on the plot for $V=0.87V_0$ near the structural instability of the high-pressure bcc phase of zirconium.

Figure 6 shows the volume dependence of the phonon damping at the points N,H,L,P of the BZ at $T=500$ K. All the values are calculated as the half-width of the smoothed SDV for each point and averaged over two independent MD simulations. As seen from the plots, with decreasing volume from $0.87V_0$ to $0.83V_0$ the phonon damping also diminishes,

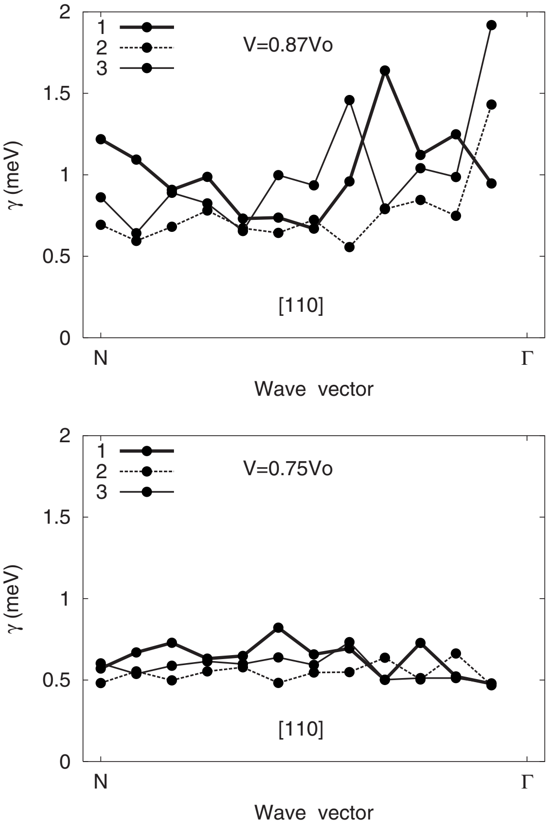

FIG. 5. Phonon damping as a function of wave vector along the [110] direction of the Brillouin zone in bcc Zr at $T=500$ K and various volumes.

and then most of the dependences have a peak in the volume range from $0.81V_0$ to $0.75V_0$. At $V=0.73V_0$ a slight increase in the phonon damping is observed at some points. The results obtained indicate that at $V=0.87V_0$ the vibrations at all the points considered are characterized by the largest anharmonic effects. On further compression their values get almost halved. These results are in excellent agreement with those of Ref. 5, where the change in the effective potential of the N_{T1} mode was calculated in the frozen-phonon model within the electron density functional theory by the full-potential linearized muffin-tin orbital method.[22] In Ref. 5 it was shown that with decreasing volume the effective potential from a strongly anharmonic double-well one at $V=V_0$ becomes almost harmonic at $V=0.7V_0$.

Thus, the present calculation shows that as the stability boundary of bcc Zr is approached, the lattice anharmonicity increases throughout the BZ, and not only for the wave vectors $k=1/2$ [110] (N phonon) and $k=2/3$ [111] (L phonon) which are usually related to the instability of bcc Zr at low temperatures. At pressures or temperatures far from the stability boundary of the bcc lattice the vibrations practically over the whole BZ (including the above mentioned N and L modes being strongly anharmonic under normal conditions) become well defined with a large lifetime, though the anharmonic frequency shifts increase.

IV. CONCLUSION

The study of the lattice dynamics and structural stability of the high-pressure phase of bcc Zr carried out at different

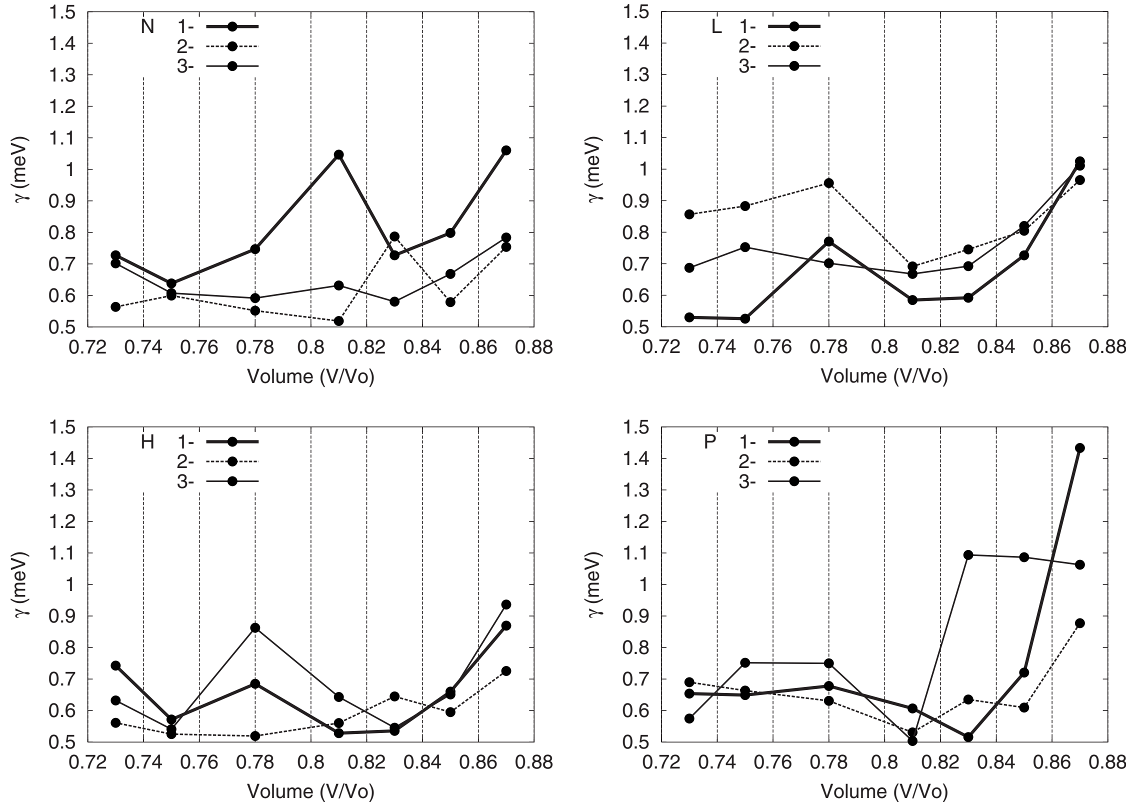

FIG. 6. Phonon damping as a function of volume at different points of the Brillouin zone in bcc Zr at $T=500$ K.

crystallite volumes and a fixed temperature $T=500$ K using MD simulation has shown that the bcc structure is unstable at volumes larger than $0.87V_0$. This value corresponds to a pressure of ~ 18 GPa, which agrees well with the calculated value in the Zr phase diagram.[6] As might be expected, with decreasing volume all frequencies of the vibrational spectrum increase. Comparing the dispersion curves obtained from the atomic vibrations in MD simulation and those calculated in the harmonic approximation (by diagonalization of the dynamical matrix), the high-pressure phase in zirconium was found to be strongly anharmonic. Note, that not only the N and L vibrational modes but also most of the modes with wave vectors directed along the high-symmetry lines of the BZ are anharmonic. Anharmonicity manifests itself in both the vibration frequencies renormalization and the decrease of the phonon lifetimes obtained from the spectral density of vibrations of each mode. Near the structural transition boundary at $T=500$ K, as well as in the high-temperature β phase at atmospheric pressure, the softening of the strongly anharmonic N_{T1} phonon is of great importance for the structural instability. Under pressure, as the volume goes down to $V=0.73V_0$, the anharmonic corrections for this phonon decrease almost by one-half. At high pressure anharmonicity makes itself most evident around the H point and in the second band along the $[110]$ direction. It should be noted that on the whole, bcc zirconium remains strongly anharmonic in the entire volume range considered. Our calculations have shown that under pressure the frequency shifts may reverse sign due to anharmonicity. The anharmonic effects are particularly noticeable for the "soft" phonon modes.

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