Lattice Dynamics of an Anharmonic Crystal: Evidence for Interactions between Atomic Vibrations at High Temperatures

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In studying the lattice dynamics of a strongly anharmonic crystal, we solve a set of nonlinear Langevin equations for interacting oscillators while a multiwell potential is calculated in the displacive limit from the first principles. The model applied to the peculiar vibrations of β-Zr along [111] allows us to analyze all contributions to the spectral density and their influence on each other. We predict the effect of induced anharmonicity for quick vibrations due to their interaction with intrinsically anharmonic slow vibrations. This effect results in the broadband distribution in energy of inelastic neutron scattering known as the symmetry-forbidden phonon-branch splitting.

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The fundamental properties of simple materials under extreme temperatures and pressures, such as the Earth's core conditions, are currently generating enormous interest [1–4]. In solid state theory, static *ab initio* calculations of total energy have been in routine use for many years. But to describe accurately the finite-temperature energetics which underpin the varied phase diagrams of materials, one should know the phonon dispersion relations [5] including those which model their behavior under extreme conditions. In studying the structural stability of metals, Zr is a particularly useful testing benchmark. It is a most extensively investigated material both experimentally and theoretically (see, for example, Refs. [6,7]). Above temperatures of 1136 K, Zr undergoes a first-order martensitic transition from a hcp α phase to a bcc one, β-Zr. With increasing pressure the α-β interface has been observed at high temperatures up to the triple point ($P =$ 55 kbar, $T = 973$ K) when another hexagonal (AlB_2-type) ω phase appears. At room temperatures the ω phase can exist between 33 and 350 kbar, and then with increasing pressure Zr transforms back into the bcc structure [8,9].

The main contributing factors to the phase transformations of Zr come from the peculiarities of its lattice dynamics. For instance, the $\beta \rightarrow \alpha$ and $\beta \rightarrow \omega$ temperature-induced transitions are due to a drop in frequency [10,11] of the bcc N-point transverse (T) phonon and the longitudinal (L) phonon at $\mathbf{q}_\Lambda = \frac{2}{3}[111]$. In α-Zr, an anomalous decrease in the frequency of a zone-center ($q = 0$) optical mode has been observed [12] with increasing pressure. The phonon softening can be very strong indeed for some particular vibrational modes near structural instabilities. This has been confirmed on *ab initio* grounds [13–17] when the specific details of the electronic and crystal structures of the material lead to the strongly anharmonic shape of the potential of the nuclear motions. Such a multiwell potential naturally appears in *ab initio* calculations as the difference in energy between the perfect and distorted lattices for various amplitudes of atomic displacements made according to the symmetry of the phonon. However, the benefits from such a potential are typically hampered by the limitations of subsequent approximations that are made. For example, for the multiwell potential when the harmonic approximation is used, imaginary phonon frequencies are found.

The worst errors of a harmonic theory can be overcome by using the pseudoharmonic approximation (PHA), which treats anharmonicity in such a way that stable lattice dynamics are found [15]. Allowance for anharmonicity in this way makes it possible to stabilize the Zr bcc structure. In the PHA, the phonon modes are independent and noninteracting. Using perturbation theory for the anharmonic effects, Chen *et al.* [14] conclude that β-Zr becomes stable at high temperatures as the result of interaction between different vibrations. The so-called modified PHA [18] takes into account intrinsic anharmonicity for some particular modes while its interactions with other vibrations come via a thermostat, i.e., the vibrational modes remain quasi-independent. In the case of Zr, the N-point phonon frequency, calculated within the modified PHA [16], is almost twice as large as the measured value. The perturbation theory approach [14], which takes into account the phonon-phonon interactions, on the contrary, gives a frequency about 25% smaller than that of the experiment. Thus, the use of PHA shows poor agreement with experiment and any attempt to evaluate the phonon frequency needs to include the phonon-phonon interactions. Moreover, the PHA which is in routine use cannot explain the experimental phonon features of bcc-Zr near the melting temperature, known as the phonon-branch splitting. In this Letter, we present a theory, based on a stochastic model of lattice dynamics, which should address such a shortcoming.

To develop a more realistic description for the lattice dynamics under extreme conditions we solve a set of nonlinear Langevin equations (LE) for interacting oscillators. The potential for the oscillators is given by first-principles electronic structure calculations, although the parametrized model of anharmonic potential can be used. We think, however, that the *ab initio* background for the potential is a much better and natural estimate than any artificial construction [19]. In the past, Gornostyrev *et al.* [20] have developed a LE-based model describing the dynamics of a single mode embedded in a thermostat, within the white noise approximation which holds in the classical limit ($\hbar\omega \ll k_B T$). In fact, this is a stochastic approach to the molecular dynamics problem, and the results obtained may go beyond the limits of the conventional phonon picture. In this Letter, we develop the dynamics of interacting vibrations embedded in the bath of all other excitations. This model allows us (i) to take into account all anharmonic contributions to the spectral density for the vibrational modes investigated and (ii) to analyze their influence on each other. As an example we take the L and T vibrations of β-Zr at $\mathbf{q}_\Lambda$. The atomic positions of the bcc structure can be considered as regular chains along [111]. In Zr, these chains interact quite weakly with each other in comparison with such transition metals as Nb and Mo. This explains the instability of β-Zr with respect to the L vibrations along [111]. With an increase of pressure the interchain bonds become stronger, and this stabilizes the bcc structure. However, this can also be achieved by taking into account the interactions between vibrations.

An important part of our work is the construction of a 2D potential, $V(x, y)$, in the form of cubic and higher terms in the energy versus atomic displacement along x and y. This is made in the displacive limit of the frozen-phonon method. We use the first-principles full-potential linear muffin-tin orbitals (LMTO) technique [21] to calculate the differences in energy between the perfect and the distorted lattices. It must be noted that the ω phase arises from the β phase as the result of the merging of the atomic (111) planes with period tripling [14]. The various amplitudes of displacements were made according to the L and T vibrations in a hexagonal geometry of the ω phase. Since a restricted number of displacements were made, we have approximated $V(x, y)$ by a high-degree polynomial along the x axis and by the fourth-degree polynomial along y. We find that the use of the eight-degree polynomial along the x direction yields fairly stable solutions. The $V(x, y)$ is shown in the upper panel of Fig. 1. A global minimum of V at $x = y = 0$ corresponds to the equilibrium atomic positions of ω-Zr while the appearance of two other shallow minima at $x \approx \pm 0.2$ leads to the bcc structure obtained as the result of displacements. In the lower panels of Fig. 1, we show the V profiles for the L displacements in the absence of the T degrees of freedom and vice versa. As seen in Fig. 1, the T vibrations at $\mathbf{q}_\Lambda$ in the absence of L displacements are purely harmonic. The L profile in the absence of T displacements has a strongly anharmonic triple-well shape confirming earlier theoretical findings [14]. For large T displacements when $y > 0.04$, the L profile adopts the double-well shape with both minima corresponding to the bcc structure. With increasing temperature, the magnitude of T vibrations becomes large. This may stabilize the bcc phase. When the larger lattice parameter, a, is used, both local minima of V become shallow. Since the V minima at $x \approx \pm 0.2$ are associated with the bcc structure being stable at high pressures and temperatures then becoming more shallow means that bcc-Zr becomes less stable for larger a and the ω-β transition temperature may increase.

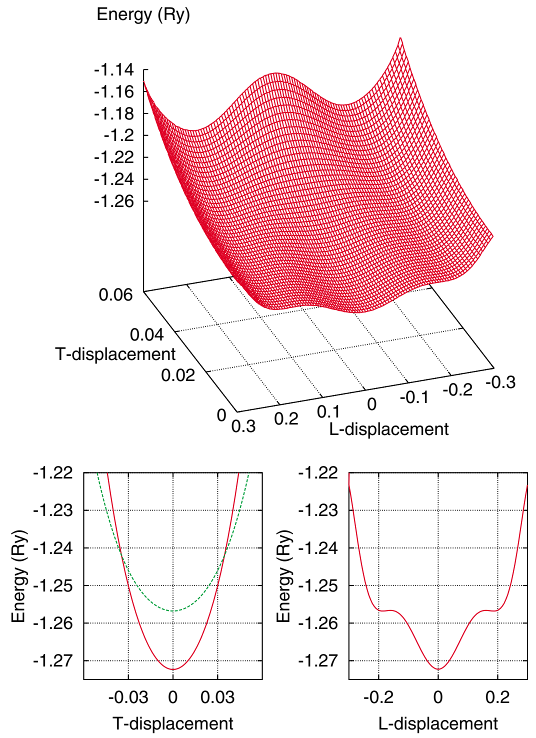

FIG. 1 (color online). Potential $V(x, y)$, calculated as the change in energy vs atomic displacements at $\mathbf{q}_\Lambda = \frac{2}{3}[111]$ (in units of $\frac{2\pi}{a}$) is shown in the upper panel. All displacements are shown in the units of lattice parameter of β-Zr. In the two lower panels, the V profiles are plotted vs the T (L) displacements with the absence of L (T). The T profiles correspond to the vibrations in the ω (continuous curve) and β (dashed curve) phases.

We describe the collective atomic vibrations as a particle oscillating in the field of the anharmonic potential shown in Fig. 1. A couple of LEs defines the dynamics of an oscillator embedded in a thermostat: $\frac{d^2x}{dt^2} + \frac{\partial V(x,y)}{\partial x} + \gamma_x \frac{dx}{dt} = F_x(t)$ and $\frac{d^2y}{dt^2} + \frac{\partial V(x,y)}{\partial y} + \gamma_y \frac{dy}{dt} = F_y(t)$. Here $x(t)$ and $y(t)$ are the dynamical variables, γ_i is the damping of small vibrations and $F_{i=x,y}$ are random forces. For the latter we use Gaussian white noise [20], i.e., $\langle F_i(t) \rangle = 0$ and $\langle F_i(t) F_j(t') \rangle = 2\Theta\gamma\delta_{ij}\delta(t - t')$, where Θ is the temperature of the thermostat. The LEs are integrated numerically by a method [22] based on the four-step Runge-Kutta scheme of third order so that the theoretical error is at worst h^3 for all cumulants of x and y. We have also investigated the values of the time step, h, and the total time of time steps, N, required. When $h = 1.5 \times 10^{-16}$ s and $N = 3 \times 10^8$, the calculated spectral density approaches its stable solution. More details on the accuracy of the LE solution can be found from the works of Greenside and Helfand [22].

In Fig. 2 we show the trajectories $x(t)$ and $y(t)$ for the L and T vibrations, respectively. For the L mode, the results can be summarized as follows. At finite temperatures one can find three types of vibrations: (i) ω-like and (ii) β-like vibrations, localized near the global and local minima seen in Fig. 2 at $t \sim 100$ and $t \sim 25$, respectively, and (iii) the excited overbarrier vibrations. With increasing temperature, the relative portion of the ω-type vibrations diminishes, whereas the β-type one increases. The latter vibrations prevail above a temperature of 600 K which defines a barrier between the structures. Finally, for $T >$ 1000 K all types of vibrations coexist. Regarding the transverse vibrations, their frequencies, as seen in Fig. 2, are much larger than those of the L vibrations. The T vibrations are always localized near equilibria which depend on the crystal structure and, hence, on the temperature dependence of the L modes. Thus, the dynamical variables have a too complicated character to classify them using conventional phonon theory.

The spectral density $g(\omega)$, calculated using a discrete Fourier transformation, is shown in Fig. 3. The case of independent vibrations is plotted in the two upper panels, Figs. 3(a) and 3(b). When the L and T vibrations are independent, the LEs are integrated using initial conditions $x(0) = y(0) = 0$ and $\dot{y}(0) = 0$, $\gamma_y = 0$ [$\dot{x}(0) = 0$, $\gamma_x = 0$] for the x (y) variables. With increasing temperature, as seen in Fig. 3(b), the T vibrations remain harmonic with frequencies close to $\omega_T^2 = \frac{1}{m}\partial^2 V(y)/\partial y^2|_{y=0}$. The temperature dependences of the L vibrations, shown in Fig. 3(a), are relatively strong when compared to that of the T modes. At room temperature the main peak of the L mode, ω_{L0}, corresponds to the vibrations near the global minimum in ω-Zr. With increasing temperature, the excited overbarrier vibrations appear near $\omega_e \simeq \omega_{L0}/2$ and ω_{L0} decreases. These findings are in qualitative agreement with previous numerical results [20]. At $T =$ 1600 K, the intensity of the $L0$ peak falls and the cubiclike e vibrations become dominant. The presence of wide L features in $g(\omega)$ may illustrate the fact that the L vibrations are strongly anharmonic. As seen in Fig. 3(a), $g(\omega = 0) > 0$, and therefore very slow L vibrations exist in the system. This has been experimentally confirmed [10].

The result of interaction between vibrations is shown in Figs. 3(c) and 3(d). The temperature dependences of the L vibrations are very similar to those of independent vibrations. This is because of their strong intrinsic anharmonicity. For the T vibrations, their anharmonicity is mostly due to their interaction with the L vibrations. The T modes have noticeably different spectral density as compared to those of independent vibrations as shown in Fig. 3(b). When a strongly anharmonic L mode occurs in the system, the interaction between vibrations may result in an induced anharmonicity for others even though V is locally harmonic for them. Some vibrational modes having atomic displacements directionally close to one another should interact more strongly. In β-Zr, the L mode may couple and induce anharmonicity into the high-frequency T vibrations with $\mathbf{q} = \frac{1}{3}(112)$. The 2 T phonons at $\mathbf{q} =$ (110) and $\frac{1}{2}(112)$ can also affect each other. Recent ex-

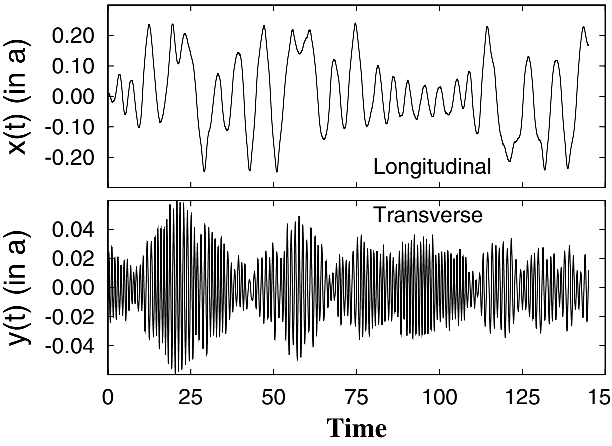

FIG. 2. Dynamics of the coupled L and T vibrational modes during the arbitrary time interval shown as the $x(t)$ and $y(t)$ variables in the upper and lower diagrams, respectively.

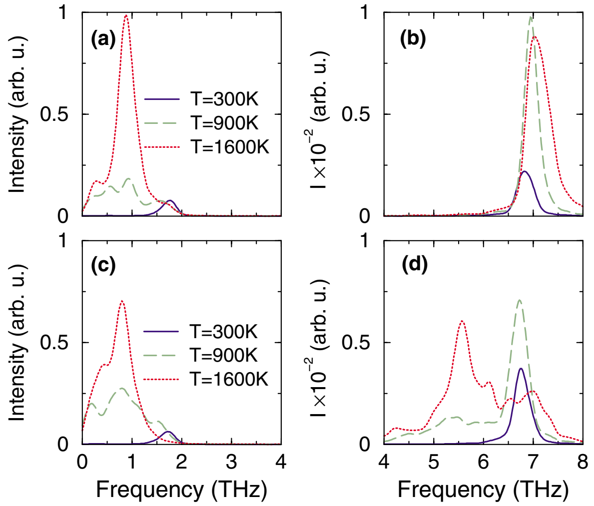

FIG. 3 (color online). Spectral density of independent L and T vibrations for $\mathbf{q}_\Lambda$ are plotted in the upper panels (a) and (b), respectively. The two lower panels, (c) and (d), show the corresponding densities, calculated as the result of interaction between vibrations.

periments have suggested [23] that the whole branch of vibrations throughout the [112] direction is anharmonic. We also predict a soft X-point T mode in the ω phase. Unfortunately, the experimental phonon data of this Zr phase are not currently available.

The effects of anharmonicity lead not only to phonon renormalization but also to an increase of phonon damping. As Figs. 3(c) and 3(d) show, the spectral density at $T > 900$ K has a wide double-peak structure. Experimentally a broadband energy distribution of inelastic neutron scattering without a clearly visible central peak has been observed for β-Zr near the melting temperature where a considerable part of $g(\omega)$ is detected above the central peak region. The two maxima of $g(\omega)$ can be naively interpreted as a splitting of the phonon branch. A qualitative explanation has already been made by the authors of Ref. [20] who conclude that the phonon-branch splitting can take place in the case of sharply asymmetric potential wells. This conforms well to the kink theory [24] of lattice dynamics where the central peak exists only in the case of symmetrical wells. In this work we emphasize the role of induced anharmonicity when its presence results in the symmetry-forbidden phonon splitting of the optical branches, the vibrations of which were thought to be "purely" harmonic. It is now clear that the splitting of the E_{2g} mode, observed recently in hcp Mg with increasing pressure [25], cannot be reproduced by the calculations [26] within the PHA. Our findings suggest it will be worthwhile to carry out the more appropriate stochastic calculations of the lattice dynamics of Mg.

When the estimates of the phase stability from the free energy calculations are inaccessible in general, one can use the displacement probability density, known to indicate the stabilization process or even to quantify the temperature above which the high temperature phase is stabilized [27]. In Fig. 4, we pick up some representative probability densities of the mean square displacements, calculated at different temperatures for the L vibrations. These are shown in Fig. 4 as the function of x, where $x = 0$ and 0.2 correspond to the ω and β phases, respectively. With increasing temperature, the probability of finding the system in the bcc structure increases, as seen in Fig. 4. We find that β-Zr becomes dynamically stable at $T \geq 1600$ K.

In summary, our stochastic model of lattice dynamics, based upon the Langevin equations and *ab initio* energetics for the potential, can well describe all experimental phonon features observed in solids at high temperatures and pressures. For Zr, the method results in the double-peak features of the spectral density, known as the symmetry-forbidden phonon-branch splitting and observed in inelastic neutron scattering. The effect of induced anharmonicity is predicted for the first time for fast vibrations due to their interaction with the intrinsically anharmonic slow vibrations. We believe that this model might be potentially fruitful in studying various materials, such as yttria-stabilized zirconia [27], relevant to thermal barrier coatings and iron-rich minerals in Earth-core conditions.

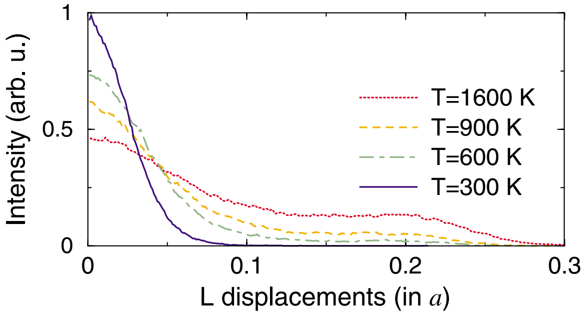

FIG. 4 (color online). Probability densities of the mean square displacements are shown vs the longitudinal displacement at different temperatures.

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