Vibrational behavior of metal nanowires under tensile stress

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We investigated the vibrational density of states (VDOS) of a thin Cu nanowire with ⟨100⟩ axial orientation and considered the effect of axial strain. The VDOS were calculated using a real-space Green's function approach with the force-constant matrices extracted from the interaction potential based on the embedded atom method. The VDOS of a strain-free nanowire showed quite distinctive characteristics compared to that of a bulk atom, the most striking feature of which was the existence of high-frequency modes above the top of the bulk phonon spectrum. We further predicted that the low-frequency characteristics of the VDOS would reveal quasi-one-dimensional behavior only when the wire was extremely thin. Through decomposition of VDOS into local atoms, we also exhibited that while the anomalous increase in the low-frequency density of states was mainly due to the corner atoms, the enhancement in high-frequency modes was primarily moderated by core atoms. Additionally, we found that the high-frequency band above the top of the bulk phonon spectrum shifted to higher frequencies, whereas the characteristics at low frequencies remained almost the same upon stretching the nanowire along the axial direction.

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Nanostructured materials are excellent examples for investigating finite size effects on the physical properties of a system of interest. One such effect is the novel characteristics observed in the vibrational behavior of these materials in comparison with the corresponding bulk and surface systems. The driving factors for such modifications in the vibrational density of states (VDOS) may be varying characteristics in the force fields experienced by individual atoms, and thus a distinct vibrational contribution for every atom, or dimensional confinement effects on the phonons of the system. Key questions concerning the thermal conductivity, electron transport, and thermal stability of nanostructured materials are clearly related to modifications in VDOS induced by the finite size effects that are very often manifested in novel characteristics of the system, such as an increase of low-frequency modes, higher vibrational amplitudes of the atoms, and thus excess vibrational entropy. For example, the voltage-dependent conduction of metallic, monoatomic wires is found to be associated with inelastic scattering of electrons with phonons.[1] Recently, it was suggested that the formation of $CeH_{2.84}$ nanoplates by fracture is due to the excess vibrational entropy introduced by instantaneous phonon confinement as the crack propagates.[2] Furthermore, both experimental and theoretical studies on metallic nanocrystals have revealed an enhancement of the phonon density of states (DOS) at both low and high frequencies.[3–7] Thus, studies of vibrational dynamics are essential to have a complete understanding of the varying characteristics and thermodynamic stability of nanocrystals.

For nanocrystalline materials—the inherent hosts of grain boundaries—the enhancement in the low- and high-frequency modes is attributed to the grain boundaries, where the force fields experienced by the local atoms are expected to be quite different from those in regular or denser domains of the crystal.[6] Even more interestingly, molecular dynamic simulations on helical, ultrathin gold nanowires under stretching reveal that while the low-frequency modes in the phonon density of states shift to lower frequencies upon stretching, the

high-frequency modes display almost no significant change.[8] Clearly, the arrangements of atoms within the nanocrystal, and thus the local force fields, have a crucial role in determining the varying characteristics of VDOS. In this Brief Report, through reliable calculations we have examined the VDOS of a rectangular, thin Cu nanowire and have found that the finite size effects on the vibrational characteristics are significant and that the varying behaviors of the atoms can be traced to the partial or local contribution of the atoms of the cross-sectional plane.

Here, we are interested in a rectangular Cu nanowire with ⟨100⟩ axial orientation that can be fabricated by cutting the (100) slab through the (100) walls of a square. As indicated in Fig. 1, this particular type of nanowire has a square cross-sectional area and can be specified by the number of atoms along the diagonals, namely 5×5. In our calculations, the interaction between the atoms is defined using a well-tested, semiempirical interaction potential based on the embedded atom method (EAM).[9] These potentials have so far proven to be reliable for examining the energetics, structure, and dynamics of low-coordinated surfaces and nanostructured materials.[10–12] We have taken the x and y axes to lie in the cross-sectional plane and z to be along the axial direction of the wire. In the simulations, periodic boundary conditions were applied along the axial direction to simulate an infinitely long nanowire, while no such constraint was imposed along the directions parallel to the cross-sectional plane.

To accurately determine the vibrational density of states, we used a real-space Green's function technique that is particularly suited for systems with defects, disorder, and reduced symmetry, since it does not require the system to be periodic.[13] The only prerequisite to this method is that the interaction potential between the atoms in the system be of finite range. The normalized vibrational density of states associated with locality l is then given by

$$n_l(\omega) = 2\omega g_l(\omega^2), \tag{1}$$
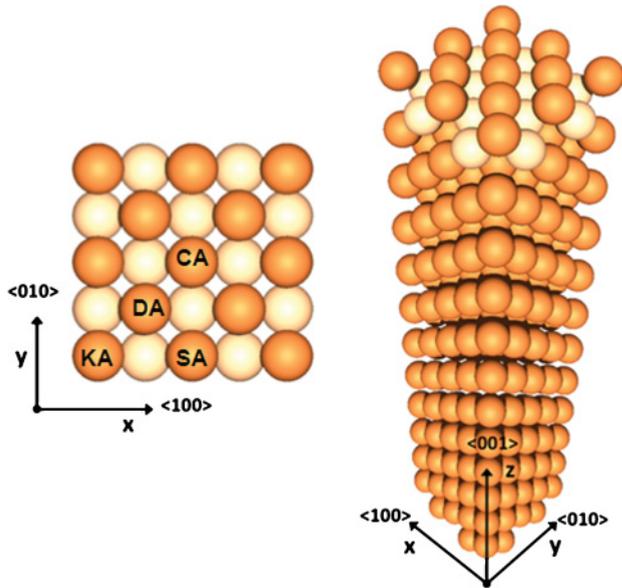
FIG. 1. (Color online) Cross-sectional (on the left) and perspective (on the right) views of the ⟨100⟩ axially oriented nanowire with 5×5 atoms along the diagonals. The darker and lighter yellow spheres show the atoms in A- and B-type stacking of a Cu(100) crystal. Here, KA, DA, CA, and SA, respectively, stand for the corner, diagonal, center, and side atoms of the cross-sectional plane.

where the function $g_l(\omega^2)$ satisfies the equation

$$g_l(\omega^2) = -\frac{1}{3N_l\pi} \lim_{\epsilon \to 0}(\text{Im}\{\text{Tr}[G_{ll}(\omega^2 + i\epsilon)]\}). \quad (2)$$

In the above equation, G_{ll} is the Green's function matrix corresponding to locality l, and N_l is the number of atoms in this locality. Then, summing over all atoms in the system gives the total VDOS corresponding to the system. Full details for calculating the Green's function corresponding to the local region of interest are described in Ref. 13.

Very briefly, the atoms in our model system are initially arranged in their perfect lattice positions in the truncated nanowire and allowed to interact via EAM potentials. Next, the standard conjugate gradient method is used to fully minimize the total energy of the system to eliminate the nonzero initial stress. Once the equilibrated structure is attained, a series of strains ranging from 0% to 5%, with increments of 0.5%, is applied. The force-constant matrix corresponding to each strained and subsequently equilibrated structure is then constructed using the analytical expressions for the partial second derivatives of the EAM potentials. Finally, we calculate the local vibrational density of states (LDOS) corresponding to any local atom of interest in each strained nanowire.

In Fig. 2(a), we have plotted the total VDOS of the 5×5 type Cu nanowire, together with that of a bulk atom. As can be seen in the figure, there are two distinctive characteristics as compared to the VDOS of a bulk atom: a strong shift toward low-frequency modes, which is expected, and the existence of high-frequency modes above the top of the bulk phonon spectrum. Indeed, the presence of such high-frequency modes for nanostructured materials has been confirmed both experimentally and theoretically.[3–7] However, in the inelastic
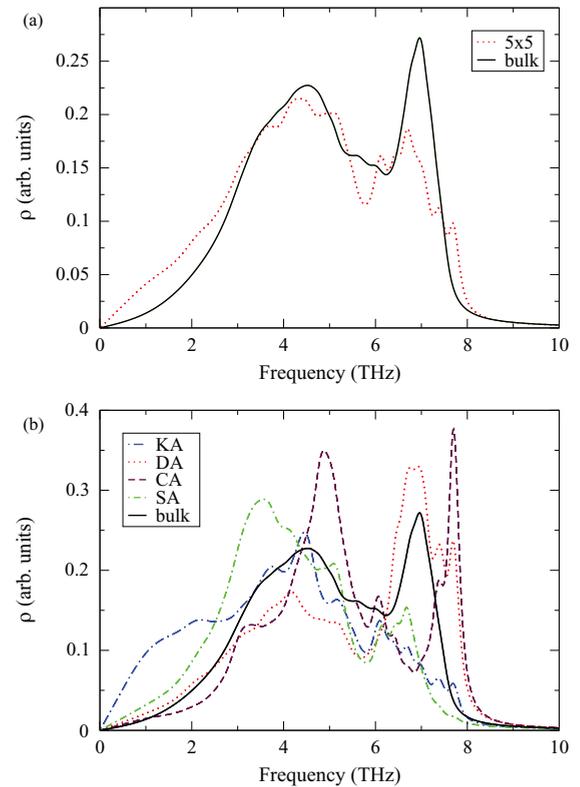
FIG. 2. (Color online) (a) The total vibrational density of states of a 5×5 type Cu nanowire (dotted line). The solid line corresponds to the density of states of a Cu bulk atom. (b) The local VDOS for a corner atom (KA; darker dash-dotted line), diagonal atom (DA; dotted line), center atom (CA; dashed line), side atom (SA; lighter dash-dotted line), and bulk atom (solid line).

neutron scattering experiment on Ni nanocrytalline samples[5] and resonant inelastic nuclear γ-ray scattering measurements[3] on nanocrystalline Fe, these high-frequency modes were attributed to hydrogen and oxygen contamination, respectively. Furthermore, in molecular dynamic simulations on nanocrystalline Cu and Ni samples, Derlet and co-workers identified these modes as an anharmonic contribution coming from the finite temperature.[6] In contrast, from our results we concluded that the existence of high-frequency modes may be an inherent characteristic of low-dimensional systems and may not be due to contamination or temperature-driven anharmonic effects as we carried out the calculations for the ground-state configuration ($T = 0$ K) of a pure Cu nanowire. However, we recognize that with temperature, anharmonic effects may become important and may even induce higher-frequency modes. Also, the low-frequency behavior of the VDOS of the wire was found to be linear with frequency, instead of the conventional quadratic dependence of bulk atoms, affirming the reduced dimensionality of the system. On the other hand, for such thin nanowires, one might treat the system as a quasi-one-dimensional (Q1D) wire and expect to observe the Q1D vibrational characteristic of frequency-independent VDOS at low frequencies. Nevertheless, even the LDOS corresponding to the center atom (CA) in a 5×5 type nanowire, a chain of which would practically form a Q1D
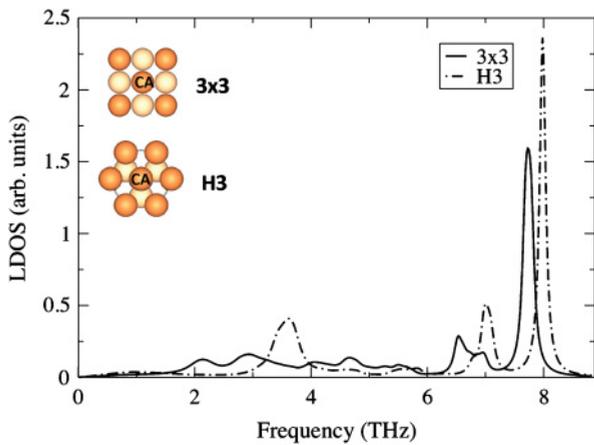
FIG. 3. (Color online) The local vibrational density of states of a center atom on 3×3 and H3 type Cu nanowires. On the left are top views of the cross-sectional area of both types. Here, 3×3 is representative of a $\langle 100 \rangle$ axially oriented wire, whereas H3 is an example of a $\langle 111 \rangle$ axially oriented wire. In H3, H stands for hexagonal shape of the cross-sectional area, and 3 represents the number of atoms along the diagonals.

system, does not display such behavior [see Fig. 2(b)]. To further address this issue, we performed similar calculations on two geometrically different nanowires with smaller cross-sectional area: One is representative of a square cross-sectional area with three atoms along the diagonals (namely, 3×3), and the other is an example of hexagonal cross-sectional area with $\langle 111 \rangle$ axial orientation. In Fig. 3, we have plotted the LDOS of a CA in both types of nanowires, together with top views of the associated cross-sectional areas. Although the LDOS for 5×5 type nanowire does not exhibit the Q1D vibrational characteristic, for 3×3 and H3 type nanowires, the LDOS of the CA clearly shows the expected low-frequency behavior—frequency-independent VDOS—at low frequencies (see Fig. 3).

In order to identify the major contributors to the predicted enhancement of the low- and high-frequency modes of the total VDOS, we have calculated the LDOS of each atom on the cross-sectional plane of the wire and presented them in Fig. 2(b). As is clear from the figure, the primary contributors to the high-frequency tail of the VDOS are the CA and the diagonal atoms (DAs), whereas the strong enhancement of the low-frequency modes is mainly due to the corner atoms (KAs). As pointed out in many studies, broken symmetries very often manifest themselves in novel characteristics such as localized modes around the edges or surfaces. Indeed, in a theoretical study, Nishiguchi *et al.* investigated the acoustic phonon modes for square and rectangular quantum wires of GaAs using the xyz algorithm and confirmed the presence of acoustic modes localized at the corners of the wire.[14] The fact that the enhanced low-frequency modes are mostly participated in by the KAs in our model system seems to echo the existence of edge-localized modes. However, detailed calculations for obtaining phonon dispersion curves together with the displacement vectors, which are beyond the scope of this work, will be needed to confirm the existence of such localized modes on these particular Cu nanowires. Furthermore, we previously calculated the LDOS of a CA

in a strain-free, 5×5 type Cu nanowire along the x and z directions and concluded that the high-frequency modes above the bulk band are due mostly to the vibrations along the directions parallel to the cross-sectional plane.[15] The characteristics of these high-frequency modes might be similar to the breathing modes—the lowest-order pure-compressional modes—observed in nanotubes, because the modes are within the longitudinal part of the phonon spectrum, with the vibrations along the radial direction.

The predicted characteristics in LDOS can be well understood in the context of changes in the bond lengths between the neighboring atoms as well as in the context of coordination number. From the surface-energy point of view, the ground-state atomic configuration of the nanowires with high surface-to-volume ratio is governed by the tendency of surfaces to reduce their surface energies, which, in turn, leads to unique relaxation patterns for the atoms and thus varying characteristics in bond lengths.[12] For the 5×5 type nanowire, the bond length between the CA—which resembles a bulk atom in terms of coordination number (12, as compared to 5 for a corner atom)—and its first nearest neighbor (a DA) along the diagonal of the cross-sectional plane is shortened by 2%, whereas that of a DA and a KA is shortened by 5.5% relative to the bond length in bulk atoms. Generally, the smaller the separation between the atoms, the stronger the force of interactions, and vice versa. With the decreases in their bond lengths with neighboring atoms, the CA and the DA would experience stronger force fields, and hence would participate in high-frequency modes. Furthermore, in contrast to atoms in the bulk and those on flat surfaces, atoms on nanowires have varying local atomic environments, due to an additional lack of neighboring atoms. For example, the lattice sites at the corner of the wire are the least-coordinated ones, with a coordination of 5, as compared to the other atoms in the cross-sectional plane; a side atom has a coordination of 8, and DA and CA have a coordination of 12, just like a bulk atom in an fcc crystal. Thus, the KAs on the wire are likely to experience the least force fields coming from their neighboring atoms. As a result, the vibrational frequencies of a KA are expected to be shifted toward the lower frequencies, as compared to the DOSs of higher-coordinated atoms such as bulk, center, and diagonal
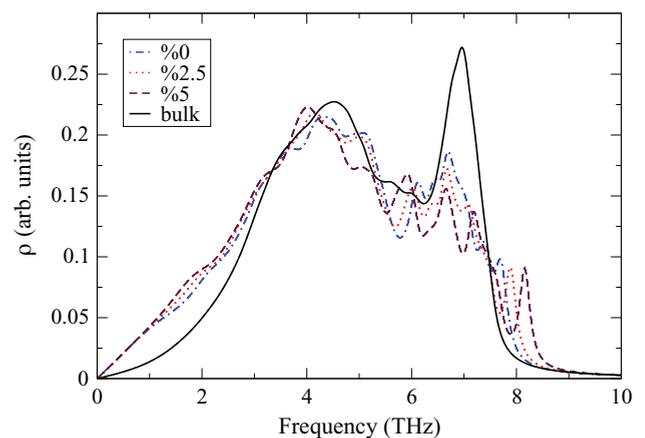
FIG. 4. (Color online) The total vibrational density of states of a strained nanowire (broken lines), together with the density of states of a bulk atom.
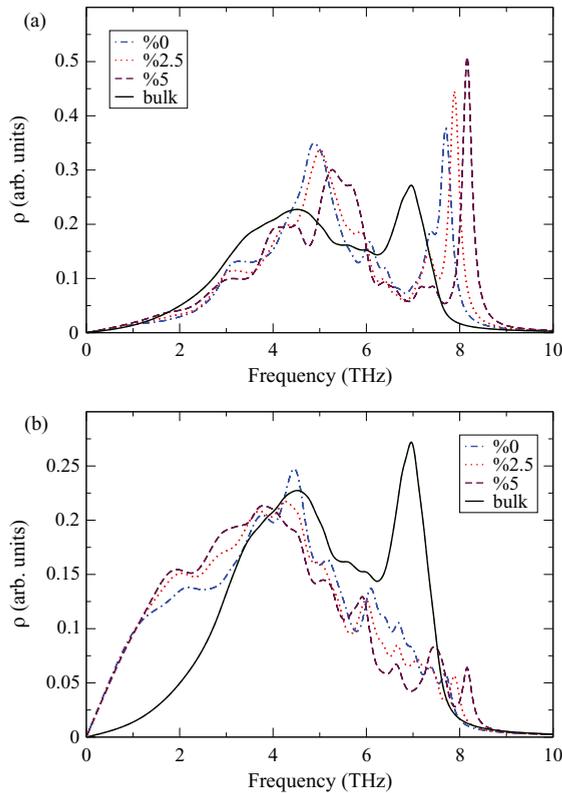
FIG. 5. (Color online) The local vibrational density of states (LDOS) for (a) a center atom and (b) a corner atom. The nanowire is exposed to a strain, ranging from 0% and 5%, and the corresponding LDOSs are plotted. The solid lines are the VDOS of a bulk atom.

atoms. Indeed, the marked enhancement in the low-frequency modes of the LDOS for KAs is a clear reflection of the reduced force fields of these low-coordinated atoms [see Fig. 2(b)]. On the other hand, the high-frequency modes observed in the tail of the LDOS of a KA are presumably due to the atomic vibrations of KAs that are coupled with the high-frequency modes of DAs in that particular part of the phonon spectrum.

Finally, we let the nanowire be exposed to an incremental axial strain with an increment of 0.5% and then calculated the total VDOS corresponding to each strained wire. The respective VDOSs, together with the DOS of a bulk atom, are plotted in Fig. 4. In contrast to what has been reported for helical, ultrathin Au nanowires, the characteristics of low-frequency modes in the total VDOS remain almost the same upon stretching the nanowire, whereas the high-frequency

modes, which are above the top of the bulk phonon spectrum, shift to even higher frequencies. We believe that these substantially different vibrational responses of a rectangular Cu nanowire and a helical Au nanowire may result from their structural differences, since the atomic arrangements within the cross-sectional plane of a rectangular nanowire comprise compact flat planes of the crystal, whereas those of a helical nanowire lack this spatial symmetry.

For nanowires, the vibrational response of each atom to the applied strain is expected to be considerably different for symmetry reasons. In Fig. 5, we have plotted the local VDOSs of a CA and a KA for a comparison. As can be seen in the figure, with increasing tensile strain along the axial direction, the KA starts participating in modes with frequencies above the top of the bulk band, whereas the vibrational response at low frequencies stays the same. We also find that the shift toward the higher-frequency modes in total VDOS is determined mainly by CA.

In conclusion, we have explored the vibrational properties of a rectangular Cu nanowire and examined the effect of axial strain on the vibrational behavior of the wire. Taking the specific example of a 5×5, pure Cu nanowire at its 0K ground-state configuration, we showed that the existence of high-frequency modes above the top of the bulk phonon spectrum is a reflection of the reduced dimensionality of the system rather than being an end effect of contamination or temperature. Through the projection of the total VDOS on local atoms of the wire, we identified the leading contributors to the enhancement of the modes at low and high frequencies: While the anomalous low-frequency modes were primarily moderated by the lower-coordinated atoms (corner atoms), the aberrant high-frequency modes were dominated largely by the higher-coordinated atoms (center atoms). In contrast to the case of helical nanowires, the existing aberrant high-frequency modes shifted to higher frequencies upon stretching the nanowire. However, the vibrational behavior at low frequencies remained almost the same with increasing axial strain. In addition, our preliminary calculations indicated that the Q1D vibrational characteristic of the frequency-independent VDOS may not be observed unless the wire is extremely thin.

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