Ab initio pseudopotential calculations of infinite monatomic chains of Au, Al, Ag, Pd, Rh, and Ru

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(Received 9 December 2002; published 25 July 2003)

Ab initio pseudopotential total-energy calculations on infinite monatomic chains of Au, Al, Ag, Pd, Rh, and Ru were performed within the local-density approximation. We used the frozen phonon approximation to study the stability of these chains as a function of strain. Within a window of strains the Au, Al, Ag, Pd, and Rh linear chains are stable with respect to $q=\pi/a$ deformations. For large strains all the chains dimerize. All the chains exibit at least one zero-strain zigzag stable equilibrium configuration, and Au, Al, and Rh zigzag chains exibit two. The ideal strengths of the different chains were calculated. The stability of the chains is discussed in connection with the electronic structure.

DOI: 10.1103/PhysRevB.68.035423 PACS number(s): 61.46.+w, 73.22.−f, 62.25.+g, 63.22.+m

I. INTRODUCTION

In recent years a great deal of attention has been devoted to low-dimensional nanoscale systems. Experimentally, it is possible to synthesize single chains of gold atoms[1,2] and observe the effects of the quantization of conductance for different applied strains. The early experimental measurements reported a bond length for the Au monatomic chain of 4 Å . However, recent experimental results claim that the bond length should be 2.5 Å .[3] The latter value is in much better agreement with theoretical calculations.[4,5]

Theoretically, a great deal of research as been done both on finite and infinite chains of atoms. Calculations of finite chains have been performed for chains of Ni, Pd, Pt, Cu, Ag, and Au,[4] and Na (Ref. 6) atoms. Conductance calculations have also been performed on Au (Ref. 7–11) and Al and Na[12], and Na (Ref. 6) finite chains. Finally, the study of infinite chains of Au[5,13–15], Al,[16] Cu, Ca, and K (Ref. 13) has shown a wide variety of stable and unstable configurations. In this work we present results on the structural stability of infinte chains made of Al, Au, Ag, Pd, Rh, and Ru.

II. METHOD

We performed *ab initio* pseudopotential total-energy calculations[17] within density-functional theory and the local-density approximation using the Ceperley-Alder functional[18] for the exchange-correlation energy. The interaction of the valence electrons with the ionic cores is modeled by separable[19] norm-conserving, Troullier- Martins[20] pseudopotentials.

We simulate an isolated chain as a periodic array of parallel chains 13-Å apart. The total energy is calculated by a numerical integration over the Brillouin zone, with a k-point grid of $1\times1\times20$ ($1\times1\times40$ for aluminum chains). The forces are given by the Hellmann-Feynman theorem. The wave functions are expanded in plane waves[21] up to a cutoff of 60 Ry. With these parameters, the total-energy precision is better than 0.2 mRy/atom.

To study the stability of the chains we calculated the phonon frequencies of the chains (at $k=\pi/a$ for the linear chain and at $k=0$ for the zigzag chains) using the frozen phonon approximation. The frequencies of the phonon modes are obtained from the forces using the assumption that the modes are harmonic.

III. RESULTS

In Fig. 1 and Fig. 2 the total energies and tensions of the six studied systems are shown. All the energies are plotted relative to the energy of an isolated atom, and the energy window shown is 3-eV wide for all the plots. The tension plot is the derivative of the energy plot directly above and corresponds to the force applied on the chain to maintain it at

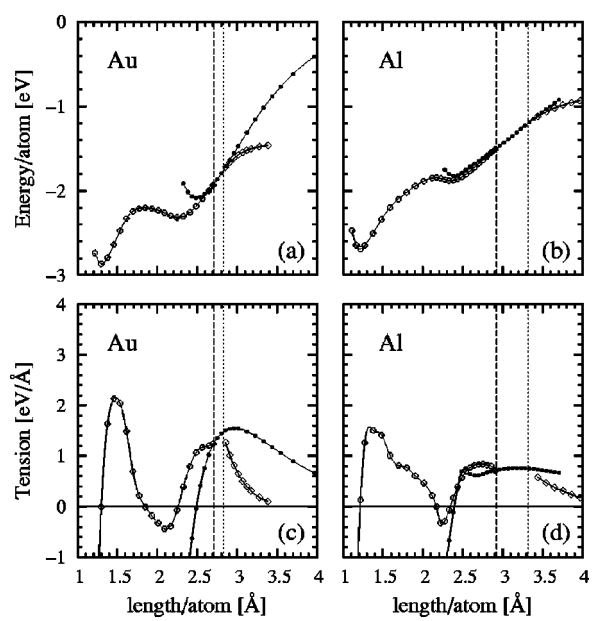

FIG. 1. Calculated total energy per atom and tension of Au and Al chains. The 0 of the energy corresponds to the energy of an isolated atom. Small solid circles correspond to a linear chain, open circles to a zigzag chain, and open diamonds to a dimer chain. The full lines are guides for the eye. The vertical dashed (dotted) line corresponds to the transition between a stable and an unstable linear chain with respect to a transverse (longitudinal) deformation.

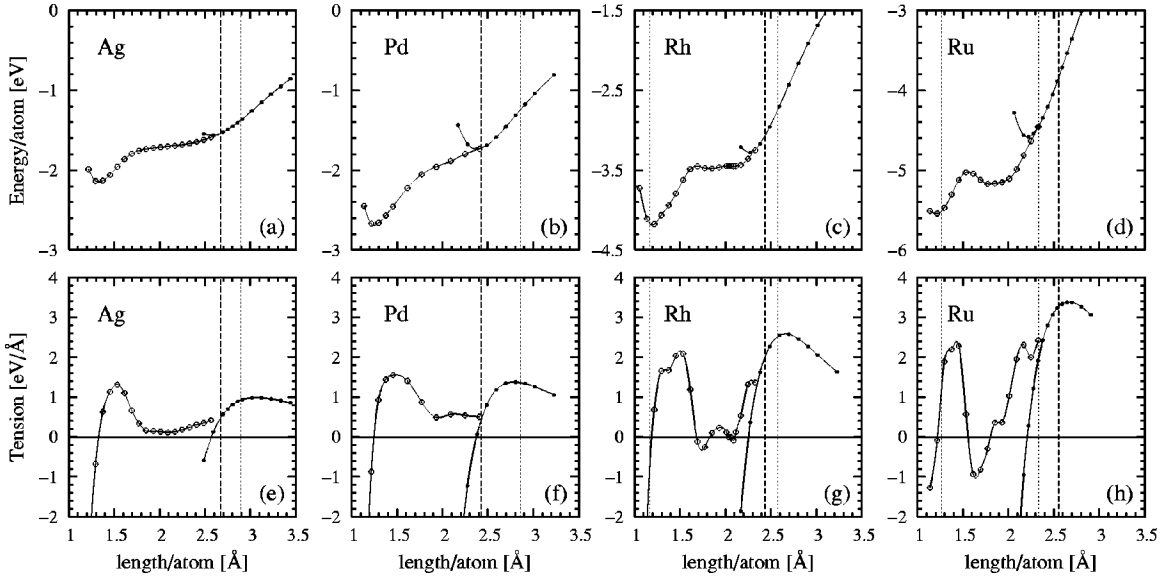

FIG. 2. Calculated total energy per atom and tension of Ag, Pd, Rh, and Ru chains. The 0 of the energy corresponds to the energy of an isolated atom. Small solid circles correspond to a linear chain, and open circles to a zigzag chain. The vertical dashed (dotted) line corresponds to the transition between a stable and an unstable linear chain with respect to a transverse (longitudinal) deformation.

that specific length. The zeros of the tension correspond to minima or maxima of the energy, and positive (negative) slopes of the tension correspond to stable (unstable) configurations relative to changes in strain or lattice constant. When a maximum of tension is reached with increasing strain, the maximum is called the ''ideal strength'' or ''theoretical strength'' and corresponds to the maximum tension that can be applied to a chain before it breaks. The chains made of Ag, Pd, Rh, and Ru exhibit a trend of increasing bonding energy (relative to an isolated atom) and ideal strength as the number of electrons decreases. From elastic theory we know that the velocity of sound of the longitudinal-acoustic mode is proportional to the square root of the slope of the tension. So, at a maximum tension the velocity of sound of the longitudinal-acoustic mode is zero, and the chain breaks due to long-wavelength pertubations. Therefore, a chain can only be stable if the slope of the tension is positive.

In Fig. 3 the frequencies of the longitudinal and transverse phonon modes at $k=\pi/a$ for the linear chain and at Γ for the zigzag chain (and the dimer chain for gold) as a function of length are shown. The points at which the the frequencies are zero correspond to the lengths at which a certain configuration becomes unstable relative to a specific phonon deformation, and a structural phase transition occurs. The vertical dashed (dotted) lines in the energy, tension, and phonon frequency plots show the length at which there is a transition between stability and instability for transverse (longitudinal) phonon modes. To establish that a specific chain configuration is stable, the frequencies of all the phonon modes must be real and the slope of the tension must be positive. To calculate the full phonon frequency dispersion a supercell calculation with many atoms per unit cell must be performed. In this work we only focus on deformations with $\lambda = 2a$ (two atoms/cell), which is the shortest wavelength for a perturbation. The limit of stability relative to long-wavelength perturbations is given, as discussed above, by the

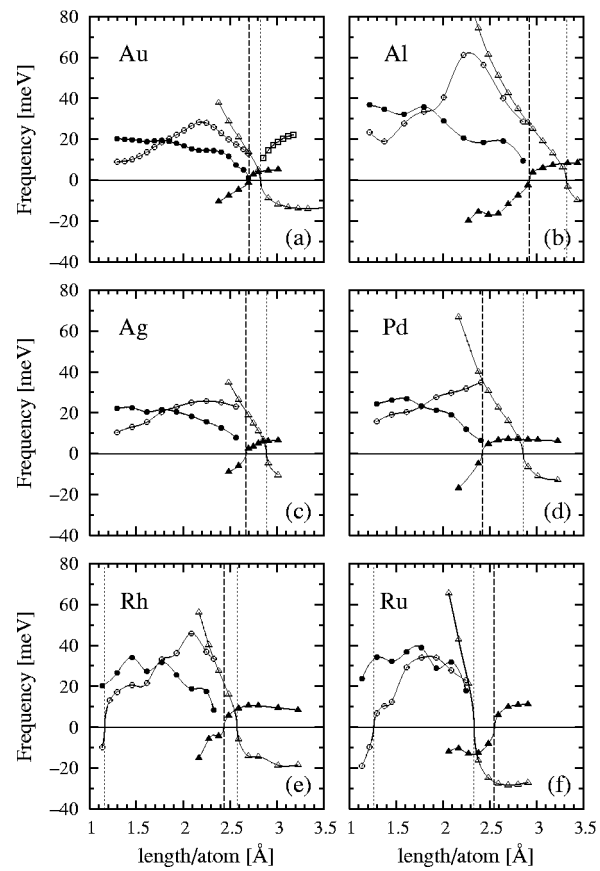

FIG. 3. Phonon frequencies as a function of the length of the chains. Negative values correspond to imaginary frequencies. Circles, triangles, and squares denote phonons for zigzag ($k=\Gamma$), linear ($k=\pi/a$), and dimer ($k=\Gamma$) chains, respectively. Dimer phonons were only calculated for gold chains. Open and solid symbols denote longitudinal and transverse modes, respectively. A vertical dashed (dotted) line corresponds to the transition between a stable and an unstable transverse (longitudinal) mode.

TABLE I. The lengths per atom for which a longitudinal (L) or transverse (T) mode has zero frequency [$q(ln)=\pi/a$ and $q(zz)=0$].

	Au	Al	Ag	Pd	Rh	Ru
c_L^{ln} (Å)	2.83	3.32	2.89	2.86	2.57	2.33
c_T^{ln} (Å)	2.71	2.93	2.67	2.42	2.44	2.55
c_L^{zz} (Å)					1.16	1.26

sign of the slope of the tension. So, although the full phonon frequency dispersion is not known, conclusions about the stability can still be drawn. From here on, we use the word "stable" in the sense of stability relative to deformations with $\lambda=2a$. Our results for infinite chains of Au and Al atoms are in good agreement with previous work (Au chains,[5,13–15] Al chains[16]).

In all the systems studied, the linear chain is unstable at zero strain. There is, however, except for the case of Ru, a region of strains for which the linear chain is stable. This region is the region on the phonon frequency plots of Fig. 3, at which both the tranverse and longitudinal linear-chain phonon frequencies are real. For low strains the transverse mode is unstable, which means that the chains have a tendency to buckle and form zigzags. For high strains the longitudinal mode is unstable and the chains dimerize. In Ru, unlike the other systems, the longitudinal mode becomes unstable at a lower strain than the strain at which the transverse mode stabilizes (see Fig. 3, Ru). This suggests that the equilibrium structure with two atoms/cell for this region should be a dimerized zigzag chain.

With increasing strain a linear chain will eventually break. As discussed previously, we can identify two reasons for the breaking: either the frequency of a $\lambda=2a$ phonon becomes imaginary (short-wavelength perturbation) or the slope of the tension becomes negative (long-wavelength longitudinal dislocations). Comparing the lengths at which the longitudinal phonon mode becomes unstable (Table I) with the lengths at which the maximum strength is reached (Table II) we conclude that the linear chains of Au, Ag, and Rh break before reaching the maximum strength — they dimerize — while Al and Pd never dimerize with stretching, breaking due to long-

TABLE II. The maximum tensions (or ideal strengths) of different zigzag (zz) and linear (ln) chains and the corresponding lengths per atom.

	Au	Al	Ag	Pd	Rh	Ru
T_{m1}^{zz} (eV/Å)	2.15	1.57	1.31	1.56	2.16	2.42
T_{m2}^{zz} (eV/Å)		0.84			0.24	2.31
T_{m3}^{zz} (eV/Å)					1.42	
T_m^{ln} (eV/Å)	1.55	0.76	0.99	1.37	2.58	3.37
c_{m1}^{zz} (Å)	1.48	1.33	1.54	1.48	1.51	1.43
c_{m2}^{zz} (Å)		2.73			1.96	2.16
c_{m3}^{zz} (Å)					2.29	
c_m^{ln} (Å)	2.96	2.52	3.06	2.79	2.66	2.66

TABLE III. The equilibrium lengths per atom and the energies per atom relative to an isolated atom for the zigzag (zz) and linear (ln) chains.

	Au	Al	Ag	Pd	Rh	Ru
c_{01}^{zz} (Å)	1.29	1.21	1.33	1.24	1.19	1.22
c_{02}^{zz} (Å)	2.26	2.34			1.83	1.80
c_{03}^{zz} (Å)					2.10	
c_0^{ln} (Å)	2.49	2.39	2.57	2.37	2.25	2.21
E_{01}^{zz} (eV)	−2.87	−2.69	−2.15	−2.69	−4.18	−5.54
E_{02}^{zz} (eV)	−2.31	−1.88			−3.49	−5.17
E_{03}^{zz} (eV)					−3.45	
E_0^{ln} [eV]	−2.08	−1.82	−1.56	−1.73	−3.27	−4.58

wavelength longitudinal dislocations. The dimerized chain is in fact not stable, because the slope of the tension is negative, as can be seen on the tension plots of Au and Al in Fig. 1.

Consider next the behavior of the zigzag chains. At roughly half the length per atom of the minimum of energy of the linear chain, the zigzag chains also have a minimum (see Table III). From Figs. 4(a) and 4(b) we conclude that the angle at this energy minimum is roughly 60° and it grows monotonically up to 180° (linear chain). Therefore, this equilibrium zigzag configuration can be interpreted as two linear chains side by side but dislocated from each other in the longitudinal direction by half the interatomic distance, with nearest neighbors forming roughly an equilateral triangle. An

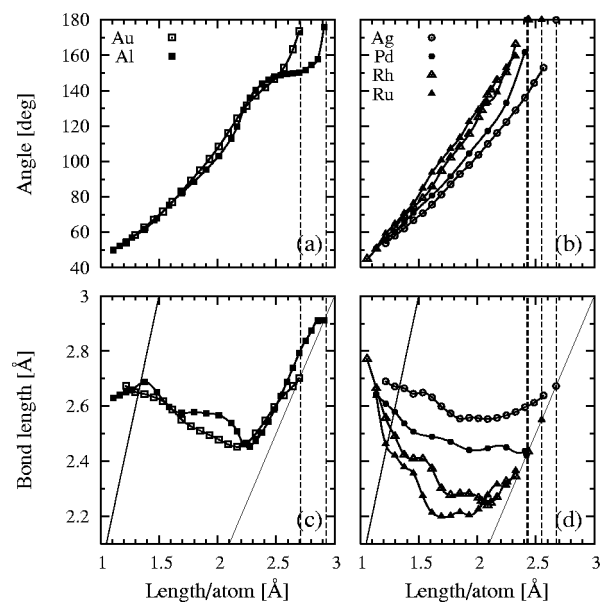

FIG. 4. Bond length and angle of zigzag chains as a function of length. The leftmost solid diagonal line in the bond-length plots stands for the distance between second neighbors while the rightmost solid line corresponds to the bond length in a linear chain. The vertical dashed lines show the length for the stabilization of the linear-chain transverse mode for (left to right) Au and Al on the left plots, and Rh, Pd, Ru, and Ag on the right plots.

exact equilateral triangle is obtained when the bond length is equal to the second-nearest-neighbor distance which in the plots of the bond lengths [Figs. 4(c) and 4(d)] corresponds to the intersection of the leftmost diagonal straight line with the numerical data. In this range of lengths the frequency of the longitudinal-optical phonon at Γ for the Rh and Ru zigzag chains becomes imaginary, indicating a phase transition. For the Ru zigzag chain this transition occurs for a length larger than the length of the minimum of energy, showing that the minimum is unstable with respect to this $q=0$ longitudinal deformation. So, the Au, Al, Ag, Pd, and Rh 60° zigzag chains are stable while the Ru 60° zigzag chain is unstable.

As we stretch the 60° zigzag chain, the angle increases monotonically while the bond length initally decreases, rising when the angle approaches 180°. It is interesting to notice that the variation in bond length with chain length [Fig. 4.(d)] is small for Ag chains and increases monotonically as the atomic number decreases. Upon stretching the zigzag chain, the tension reaches a maximum (Fig. 1 and Fig. 2), and further stretching is impossible because the chain breaks due to long-range longitudinal deformations, as we discussed before. Theoretically, we can enforce the zigzag symmetry and the length and calculate the corresponding energy, forces, and phonons. By doing that we find that Au, Al, Rh, and Ru exhibit another stable energy minimum, and, in fact, Rh might exhibit two other stable minima of energy (see Fig. 1, Fig. 2, and Table III) although the existence of this extra minimum is not certain because the energy barrier is close to the precision of our calculation. From the tension plots we see that if we stretch the second stable Au zigzag chain it smoothly changes to the stable — although strained — linear chain. The second stable Al, Rh, and Ru zigzag chains, on the other hand, break down since, once more, the tension reaches a maximum (the Rh chain breaks down under a very small tension of 0.24 eV/Å). Also, the possible third equilibrium Rh zigzag chain also breaks under tension.

In Fig. 5 the band structures of the linear and zigzag chains with minimum energy are shown. All the linear and zigzag chains are metallic, and dimerized chains are semiconducting. The zigzag band structures show similar features to the linear band structures. This is not unexpected because, as we've discussed earlier, these zigzag chains can be thought of as two parallel linear chains close together. The Al chain band structures are significantly simpler than the bands of the other five systems. This is because Al only has three valence electrons ($3s^2 3p^1$) while Au, Ag, Pd, Rh, and Ru have 11, 11, 10, 9, and 8, respectively (with *s* and *d* character). The lower band in the Al linear-chain band structure is a σ bonding band and the band that crosses the Fermi level is a π bonding band and it is doubly degenerate. For the Au, Ag, Pd, Rh, and Ru linear chains, the lowest band at Γ and the highest at $\pi/2$ are σ bonding and singly degenerate, the flattest band is δ bonding and doubly degenerate, and the remaining band is a doubly degenerate π bonding band. The bands for these transition metals chains are very similar, differing in the position of the Fermi level and the dispersion of the bands. As the number of electrons is reduced, the bands shift up, increasing the number of (one-dimensional) sheets

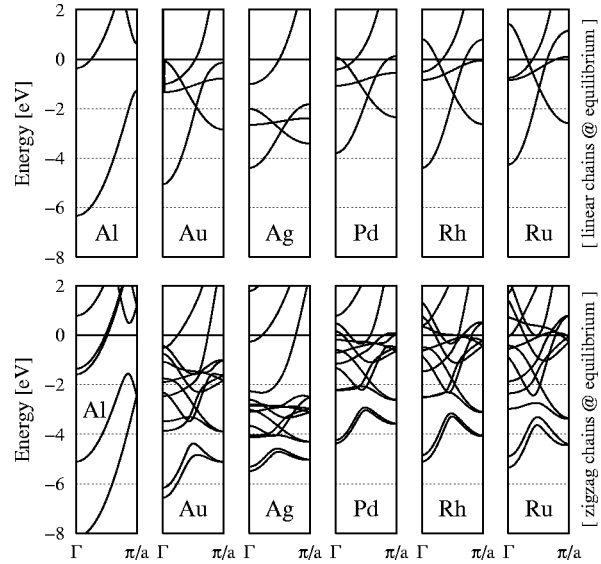

FIG. 5. Comparison between band structures of linear (top) and zigzag (bottom) chains at the equilibrium configurations. The Fermi level is at 0 eV.

of the Fermi surface. Also, because the nucleus is less attractive (as we move from Ag to Ru) the valence electron wave functions extend further away from the core and the bands dispersion increases.

IV. CONCLUSION

We have seen that monatomic chains of of Al, Au, Ag, Pd, Rh, and Ru show very interesting and varied equilibrium configurations. Zero-strain linear chains are not stable in any of the cases studied, but for Al, Au, Ag, Pd, and Rh there is range of strains for which there is a stable configuration. The linear chains break due to either long-range longitudinal deformations (Al and Pd), or short-range $\lambda=2a$ deformations (Au, Ag, and Rh). Chains of Al, Au, Ag, Pd, and Rh all exhibit stable zigzag chains — the global zigzag chain energy minimum — corresponding to two parallel linear chains, with bond angles roughly equal to 60°. The global energy minimum for a zigzag Ru chain is unstable relative to longitudinal-optical deformations with $q=0$. Besides the global energy minima, Au, Al, Rh, and Ru all exhibit one local zigzag minima, and Rh might have two. All these equilibria are stable relative to $q=0$ deformations and long-range longitudinal perturbations. Electronically, all the zigzag chains and linear chains are metallic, while dimerized chains are semiconducting.

In a real experimental situation, the chains are not infinite, and there may be finite temperature and bias voltage effects. To study the effects of finite temperatures, detailed molecular-dynamics calculations may yield useful information. An estimate of the influence of the bias voltage is difficult since we are assuming an infinitely periodic chain. Hopefully, future calculations of the finite chain, temperature, and voltage effects will be possible, but they are beyond the scope of the present calculation.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No.DMR-0087088, and by the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No.DE-AC03-76SF00098. Computational resources were provided by NCSA and by NERSC.

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