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Theoretical study of linear monoatomic nanowires, dimer and bulk of Cu, Ag, Au, Ni, Pd and Pt

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Abstract

The binding and electronic properties of monoatomic nanowires, dimers and bulk structures of Cu, Ag, Au and Ni, Pd, Pt have been studied by the projector augmented-wave method (PAW) within the density functional theory (DFT) using the local density approximation (LDA) as well as generalized gradient approximation (GGA) in both Perdew–Wang (PW91) and Perdew–Burke–Ernzerhof (PBE) parameterizations. Our results show that the formation of atomic chains is not equally plausible for all the studied elements. In agreement with experimental observations Pt and Au stand out as most likely elements to form monoatomic wires. Changes in the electronic structure and magnetic properties of metal chains at stretching are analyzed.

Keywords: Chain; Dimer; Bulk structures; Electronic and magnetic properties; DFT; Nanowires

1. Introduction

A proper understanding of the electronic properties of nanosized junctions is crucial for many domains of modern nanotechnology. Metal nanowires have recently attracted a great deal of attention due to their unusual properties and relative simplicity of fabrication. Most studied systems both experimentally [1-7] and theoretically [8-16] are free standing gold nanowires, which exhibit a quantized conductance at stretching and have peculiar structural properties. Unsupported and supported wires of Cu, Pd, Pt, Ag and Au have also been studied theoretically by means of *ab initio* and molecular dynamics methods [14], [17-22]. The influence of relativistic effects on the properties of Pd and Ag wires is analyzed in Ref. [23] and it is shown that fully relativistic and scalar relativistic calculations give very similar results. Comparison of binding energies per bond in bulk and chain structures of noble metals allowed Bahn *et al.*, to conclude that Au and Pt are more likely to form atomic chains than other noble metals [14].

Magnetic properties of metal chains have also attracted considerable attention [19], [23-32]. In particular, it has been suggested that a magnetic ordering in Pd chains determines the conduction properties of the system [26]. Studies have shown that Ag wires are non-magnetic at equilibrium bond length in contrast to Pd chains exhibiting the magnetic moment of $0.7 \mu\text{B}/\text{atom}$ at equilibrium interatomic separations [23]. The dependence of the magnetic moment on interatomic distance and wire structure has been studied in detail for Pd chains [24]. Short monoatomic Pd wires suspended between two Pd leads appear to have a moment of $0.3 \mu\text{B}$ whereas the coaxial nanowire is predicted to be non-magnetic [24]. Recently the density functional calculations employing the self-interaction corrected (SIC) LDA-functional have shown that the values of the magnetic moments for Pd wire are $0.45 \mu\text{B}$ and $0.69 \mu\text{B}$ at equilibrium and break separations, respectively [25]. It is interesting to compare these results with magnetic moment of the Pd dimer which from *ab initio* pseudopotential calculations was found to be $1 \mu\text{B}$ per Pd atom [28-30]. The same result was obtained using a semi-empirical tight-binding method and SIESTA code based on the linear combination of pseudoatomic orbitals [31]. At the same time, a tight-binding model within the Hartree–Fock approximation resulted in a non-magnetic solution for Pd dimer [32]. Fully relativistic *ab initio* calculations done for Pt wires indicate that magnetic moment for Pt monowire is about $0.6 \mu\text{B}$ at the equilibrium bond length of 2.48 \AA [20]. A review of electronic, magnetic, and structural properties of clusters including mono- and diatomic chains for metals in groups 10 and 11 is given in Refs. [30], [33-35].

Here, we present the results of a systematic *ab initio* study of the binding energies, equilibrium lattice parameters, break forces and magnetic properties of the linear infinite chains of Cu, Ag, and Au as well as Ni, Pd and Pt. We analyze the dependence of these properties on the degree of

wire stretching and compare them to those of dimer and bulk structures of corresponding materials.

2. Details of calculations

The calculations were performed by the projector augmented-wave (PAW) method [36] (as implemented in VASP [37] and [38]) based on the density functional theory (DFT) within the local density approximation (LDA) and generalized gradient approximation (GGA) using both Perdew–Wang (PW91) [39] and Perdew–Burke–Ernzerhof (PBE) [40] parameterizations. One-dimensional infinite wires were modeled by the three dimensional periodic tetragonal supercells with the wires aligned along the z-axis and separated in the x–y dimensions by 20 Å of vacuum. The unit cells consisted of one atom. Dimers were calculated using a large cell of 20 Å with the dimer aligned along the z-axis. The cutoff energies used in the calculations were 273 eV (Cu), 250 eV (Ag, Pd), 230 eV (Au, Pt), and 270 eV (Ni). The integration over the Brillouin zone was carried out using the special k-points method [41] with the k-meshes of $1 \times 1 \times 1$ (gamma point), $1 \times 1 \times 30$ and $10 \times 10 \times 10$ for dimers, chains and face-centered-cubic (fcc) bulk structures, respectively. Using these settings the total energies were converged within 1 meV/atom. All calculations allowed for spin-polarization.

The ground state properties (like equilibrium interatomic distances, binding energies, break distances and forces) can be estimated from the total energy calculations. In particular, forces needed to break bonds are defined as the maximum slope of the total energy *vs* bond length dependence. Though it is a crude estimate for the break force, especially in the case of bulk materials, it allows one to reveal trends for different structures.

3. Results and discussion

The binding energy curves for fcc bulk, linear chain and dimer structures calculated using LDA, GGA–PW91 and GGA–PBE are presented in Fig. 1. The obtained results on equilibrium lattice parameters, binding energies, break distances and forces are summarized in Table 1. It is worth noting that our calculated GGA bond length for the Pd dimer is in good agreement with the results of other DFT calculations [28-30] but somewhat lower than that from hybrid DFT calculations of Ref. [43] (2.53 Å for the triplet state). The bond length, 2.45 Å, obtained in the framework of the tight-binding method [31] is shorter than that from our GGA calculations, but it is larger than the calculated LDA bond length. The binding energy of the Pd dimers calculated within GGA perfectly matches the results of Refs. [28-30]: 0.611 eV [28], 0.63 eV [29], and 0.646 eV [30]. Both GGA–PW91 and GGA–PBE predict larger lattice parameters and break

forces but smaller binding energies compared to those obtained using LDA. The binding energies of bulk structures, if calculated per atom, are lower than those of linear chains (Fig. 1). However, if one recalculates these values per bond they turn out to be lower for chains than for bulk structures, in agreement with findings of Ref. [14]. The binding energies per atom calculated for dimers are higher than those of both chain and bulk structures. Having plotted properties for the considered elements (Fig. 2) we notice that binding energies, distances and forces follow similar trends within each group of elements. In particular, the middle elements, Ag and Pd, have the highest binding energies and lowest forces required to break their structures. Generally the larger the number of nearest neighbors is the larger the equilibrium interatomic separations are. This holds for all considered elements for Pd, for which the Pd–Pd distance in the dimer is slightly bigger than that in the Pd chain (Fig. 2). The break separation is generally larger for structures with higher atomic coordination, although, the dimers and chains of Pd and Pt show an exceptional behavior as the former are able to sustain larger distances than the latter (Fig. 2). We notice that this feature of the Pd and Pt structures is found in both spin-polarized and non-magnetic calculations. To compare binding properties of different structures we plot bulk/chain and chain/dimer energy and force ratios in Fig. 3. The smaller the bulk/chain binding energy ratio is the higher the relative stability of the chain structure with respect to the bulk is. Among the considered metals this ratio is lowest for Pt followed by Au that indicates an enhanced stability of linear Pt and Au structures compared to other metals. This is confirmed by the break force bulk/chain ratio showing the same trend. Although linear chains are not equilibrium structures for any metal, Pt and Au seem to be able to form atomic chains more readily than other studied elements that is in agreement with experimental observations and previous theoretical results [14]. The chain/dimer ratios behave more monotonically with some deviations seen for Pd structures.

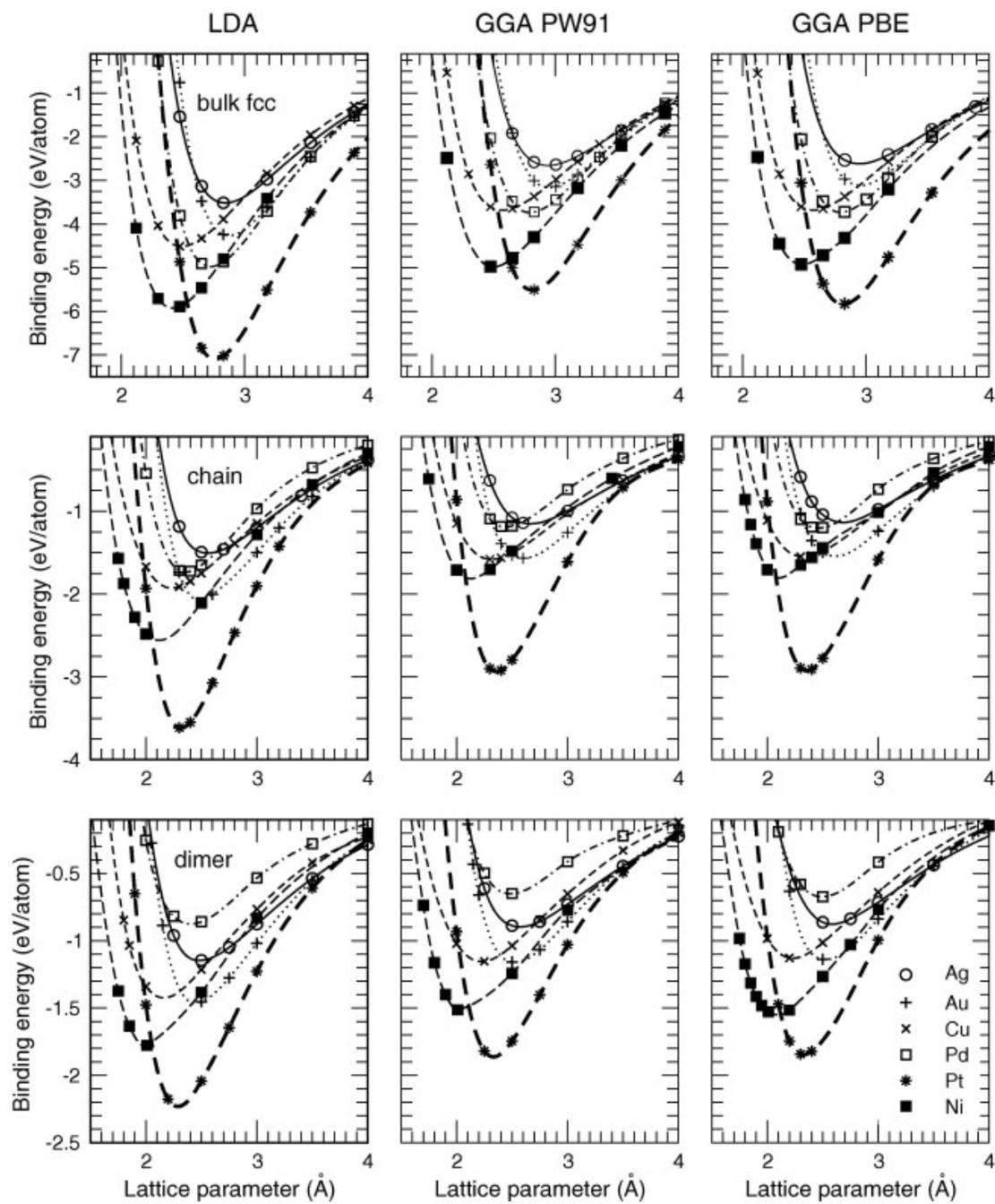


Fig. 1. Binding energy curves for fcc bulk, linear chain, and dimer structures of Cu, Ag, Au, Ni, Pd, Pt calculated within the LDA, GGA-PW91 and GGA-PBE approximations.

Table 1: Parameters calculated from the binding energy curves in Fig. 1. Equilibrium bonding length d_0 , binding energy E_0 per atom, break force F_0 , and interatomic distance d where the bond breaks.

Approximation	Element		Cu	Ag	Au	Ni	Pd	Pt
LDA	Bulk fcc	d_0 (Å)	2.49	2.84	2.87	2.42	2.72	2.76
		E_0 (eV)	-4.66	-3.59	-4.38	-5.53	-5.06	-7.04
		F_0 (eV/Å)	2.98	2.43	3.31	4.01	3.89	5.36
		d (Å)	3.0	3.25	3.30	2.91	3.14	3.17
	Chain	d_0 (Å)	2.23	2.56	2.48	2.12	2.35	2.31
		E_0 (eV)	-1.93	-1.51	-2.08	-2.56	-1.74	-3.62
		F_0 (eV/Å)	1.26	1.01	1.50	1.76	1.49	3.06
		d (Å)	2.76	2.99	3.07	2.49	2.82	2.71
	Dimer	d_0 (Å)	2.16	2.48	2.44	2.04	2.40	2.29
		E_0 (eV)	-1.42	-1.15	-1.46	-1.78	-0.88	-2.22
		F_0 (eV/Å)	1.86	1.46	2.11	2.50	1.53	3.42
		d (Å)	2.50	2.98	2.94	2.46	2.86	2.81
GGA PW91	Bulk fcc	d_0 (Å)	2.57	2.94	2.95	2.50	2.79	2.81
		E_0 (eV)	-3.69	-2.66	-3.17	-4.99	-3.74	-3.74
		F_0 (eV/Å)	2.35	1.74	2.45	3.24	2.90	4.30
		d (Å)	3.07	3.43	3.37	3.02	3.24	3.23
	Chain	d_0 (Å)	2.31	2.67	2.60	2.60	2.13	2.44
		E_0 (eV)	-1.58	-1.15	-1.57	-1.81	-1.19	-1.19
		F_0 (eV/Å)	1.04	0.75	1.16	1.58	1.06	2.61
		d (Å)	2.84	3.19	3.04	2.69	2.88	2.85
	Dimer	d_0 (Å)	2.23	2.57	2.52	2.08	2.48	2.33
		E_0 (eV)	-1.14	-0.93	-1.29	-1.54	-0.63	-1.85
		F_0 (eV/Å)	1.60	1.17	1.77	2.06	1.25	3.05
		d (Å)	2.70	3.11	2.97	2.43	2.87	2.81
GGA PBE	Bulk fcc	d_0 (Å)	2.57	2.95	2.96	2.48	2.79	2.81
		E_0 (eV)	-3.69	-2.67	-3.19	-4.93	-3.74	-5.53
		F_0 (eV/Å)	2.36	1.64	2.45	3.31	2.86	4.33
		d (Å)	3.08	3.18	3.17	3.07	3.23	3.21
	Chain	d_0 (Å)	2.33	2.68	2.61	2.11	2.46	2.35
		E_0 (eV)	-1.55	-1.14	-1.61	-1.93	-1.21	-2.93
		F_0 (eV/Å)	1.05	0.74	1.17	1.08	1.18	2.61
		d (Å)	2.87	3.0	2.99	2.26	2.87	2.84
	Dimer	d_0 (Å)	2.23	2.58	2.52	2.09	2.49	2.32
		E_0 (eV)	-1.14	-0.91	-1.22	-1.48	-0.65	-1.85
		F_0 (eV/Å)	1.54	1.14	1.81	1.93	1.38	3.30
		d (Å)	2.79	3.18	2.96	2.47	2.89	2.84
Experiment [42]	Bulk	d_0 (Å)	3.615	4.086	4.078	3.524	3.89	3.92

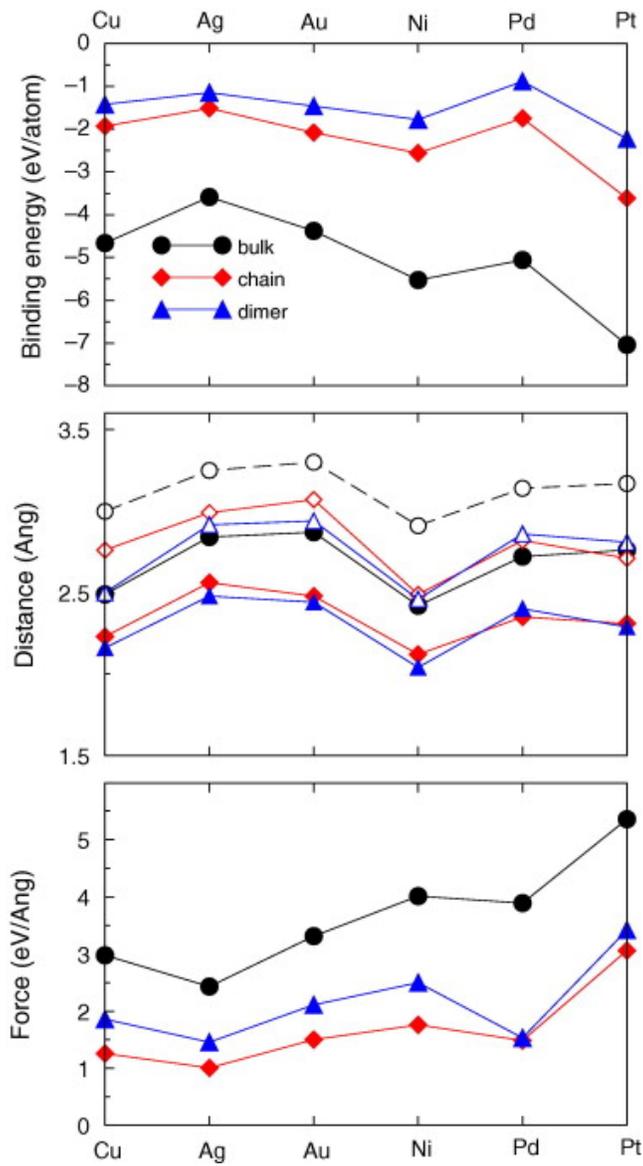


Fig. 2. Binding energies (a), equilibrium (solid symbols) and break (open symbols) distances (b) and break forces (c) calculated within LDA.

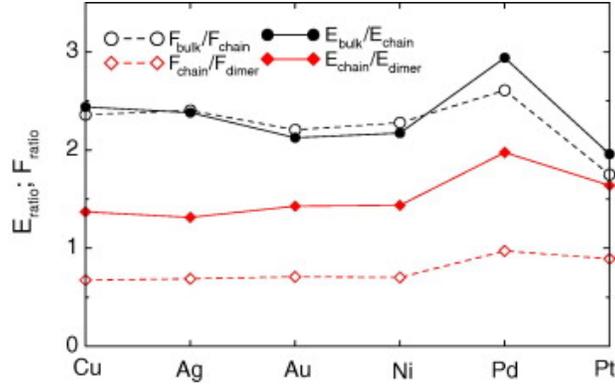


Fig. 3. Binding energy and break force ratios for bulk/chain and chain/dimer systems.

The LDA band structures and projected densities of states (PDOS) for the chains with the equilibrium interatomic separations are presented in Fig. 4. The band structures of the Cu and Au wires calculated for the corresponding equilibrium bond lengths resemble each other. Only one band, mostly consisted of d-states, is crossed by the Fermi energy (E_f) (Fig. 4a). In the case of the Ag chain the Fermi level also crosses just one band, but the band structure of this wire is appreciably different [44] and [45]. The band crossed by the Fermi level is mostly due to the s-states, while the d-states are filled and situated rather low in energy. Thus, the conductivity of the Ag chain is expected to be due to the s-states where as for the Au and Cu chains the d-states should also play an important role. Therefore, bonds keeping the Ag chain are in fact weaker than those in Cu and Au wires that is seen in their binding energies and break forces (Fig. 2 and Fig. 3). We note that in order to be able to describe the electronic transport through atomic chains one needs to apply more sophisticated approaches and consider more realistic structures [46]. Despite of a rather high PDOS at the Fermi energy for Cu and Au these wires do not become magnetic, but such a mounting of density at E_f indicates an unfavourableness of the linear structure for these wires [47] and [48].

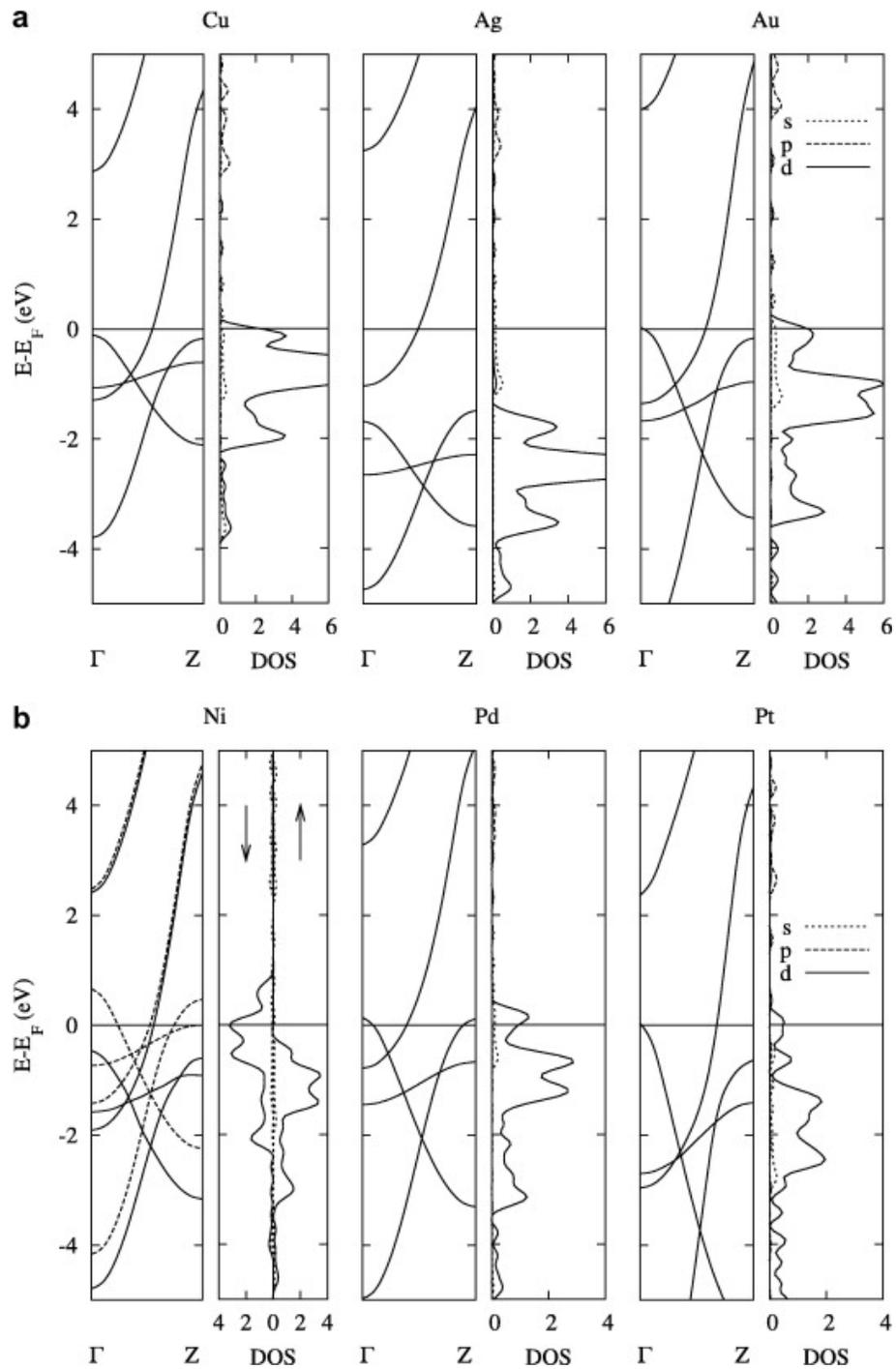


Fig. 4. LDA band structures and PDOS's for the linear Cu, Ag, Au (a) and Ni, Pd, Pt (b) chains with equilibrium interatomic distances. For band structure of Ni solid lines refer to spin - up electrons, and dotted lines stand for spin - down electrons. For DOS of Ni arrows up and down stand for spin-up, and spin-down states.

In the case of the Ni, Pd and Pt wires we find several bands, dominated by the d-states, being crossed by the Fermi level (Fig. 4b). The Ni chain of the equilibrium bond length is magnetic and the states at the Fermi energy mostly belong to one spin channel. PDOS of the Pd wire exhibits a broad peak at E_f due to d-bands. The equilibrium bond length for Pd chains as calculated in LDA is slightly shorter than the Pd–Pd separation for which magnetism appears in the Pd chains (2.5 Å). According to our GGA results, as well as previous GGA calculations [24], Pd chains with the equilibrium distances are magnetic. In this case, spin-polarization shifts some bands off E_f and, therefore, changes the number of conduction channels [24]. For the equilibrium Pt chains PDOS is mostly due to the d-states. However, the density of states at E_f is rather low compared to those for Ni and Pd wires.

In Fig. 5 the band structures and PDOS's for the wires just before breakage are shown. At stretching the electronic bands of the chains become flatter that leads to a narrowing of the valence band and its shift towards E_f . In the case of the Au wires stretching leads to the filling of the d-states. Consequently, the density of states at E_f becomes significantly lower. For Cu chains it is still dominated by the d-states in contrast to the Au chain whose DOS at E_f is mostly due to the Au s-states. No essential changes in the character of PDOS for the Ag chain is observed at stretching.

The electronic structure of stretched Ni, Pd and Pt wires is characterized by narrowing of the valence band and a larger split between up- and down-DOS's reflected in a growth of the magnetic moments for these chains. The density of states in the vicinity of E_f is still mostly due to the d-states, and E_f crosses high peaks in the DOS indicating an instability of these chains. This is easily understood if we recall that PDOS's shown in Fig. 5 belong to the wires stretched to the break point.

A decrease of coordination number and dimensionality can cause a dramatic change of the magnetic properties of a material. Similar to bulk Cu, Ag, Au the linear chains and dimers of these elements are non-magnetic at equilibrium and shorter separations (Fig. 6a). The magnetic moment of about 1 μ_B /atom appears in all the structures only at large expansion. The interatomic separations at which we observe the appearance of magnetic moment are smallest for Cu (4 Å) and largest for Au (5.5 Å) that is explained by the difference in the atomic radii of Cu and Au. Bulk Ni is magnetic whereas bulk Pd and Pt are not. The dimer structures of these elements are

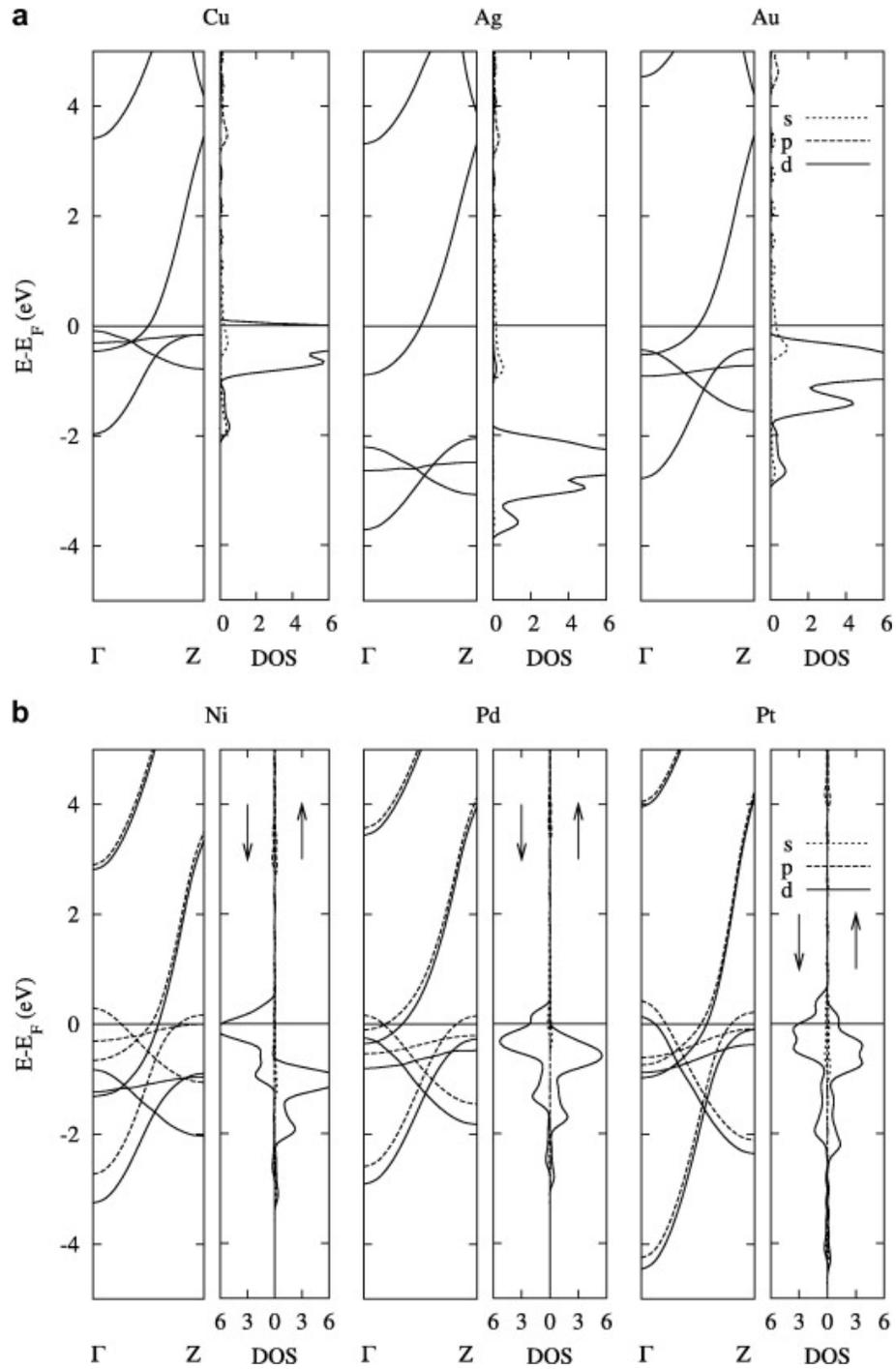


Fig. 5. LDA band structures and PDOS's for the linear Cu, Ag, Au (a) and Ni, Pd, Pt (b) chains stretched up to the break point. For band structure of Ni, Pd, and Pt solid lines refer to spin - up electrons, and dotted lines stand for spin - down electrons. For DOS of the metals arrows up and down stand for spin-up, and spin-down states.

found to be magnetic (Fig. 6b), although the dependence of the magnetic moment on the atomic separation is particular for each element. The Ni dimer has the moment 1 $\mu\text{B}/\text{atom}$ around equilibrium (1.98 \AA (LDA)), the moment starts to increase when the Ni–Ni separation increases above 3 \AA . The Pt dimer generally follows the same pattern, although the moment changes from 1 to 2 $\mu\text{B}/\text{atom}$ in an abrupt manner when the Pt–Pt distance exceeds 4 \AA . The Pd dimer shows a different trend as its magnetic moment rapidly decreases from 1 $\mu\text{B}/\text{atom}$ down to almost zero when the Pd–Pd separations are above 3 \AA . This behavior is in sharp contrast with the properties of atomic and bulk Pd, which are known to be non-magnetic. The magnetism of Pd dimers has also been obtained in earlier calculations [28-30], [43] and [48]. The hybridization of atomic s and d states leading to appearance of an open-shell-like behavior is responsible for the magnetism of Pd dimers. Other clusters of Pd have also been shown to be magnetic, with magnetic moment reaching its maximum for Pd dimer and steadily decreasing as the number of atoms in the cluster becomes larger [49].

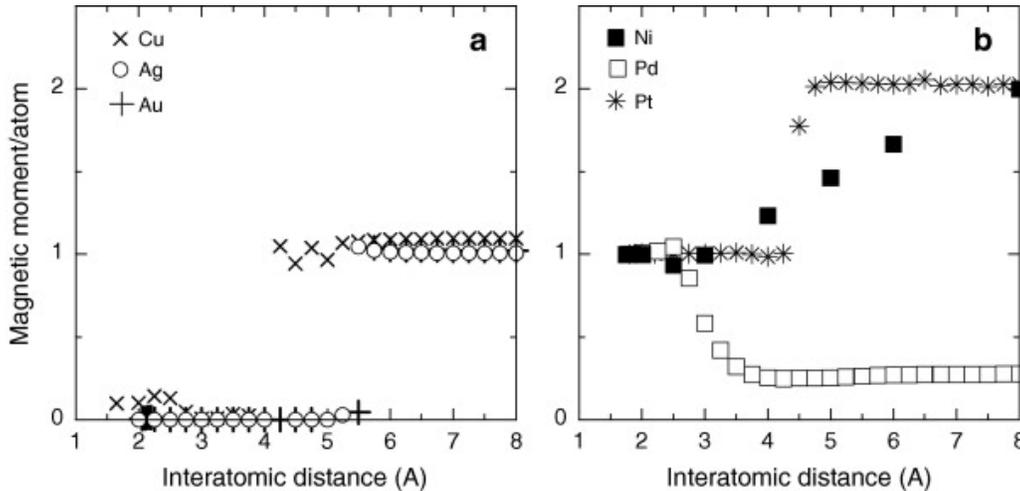
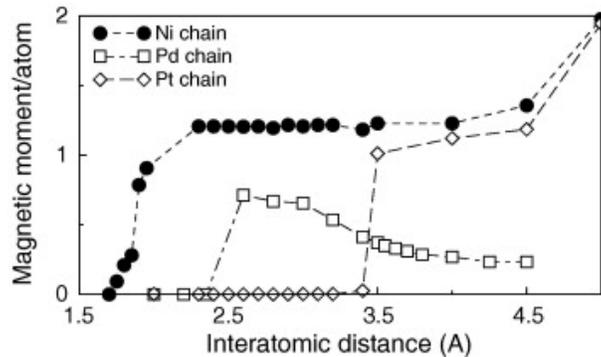


Fig. 6. Dependence of magnetic moment on interatomic separation for Cu, Ag and Au (a) and Ni, Pd and Pt (b) dimers calculated using the LDA approximation.

The Pd chain, where each atom has two neighbors, is magnetic as well, although magnetic moment never reaches 1 $\mu\text{B}/\text{atom}$ and it strongly depends on the Pd–Pd distance (Fig. 7). Depending on the used exchange-correlation potential we find slightly different Pd–Pd distances for which Pd chains become magnetic. This conclusion is in agreement with the results of recent ab initio calculations using different methods, including hybrid functionals [43] with gaussian orbitals giving the triplet state for the Pd dimer, and GGA functionals [28-30]. In the case of the LDA approximation magnetic moment appears at larger Pd–Pd separations (2.5 \AA) than the equilibrium distance 2.35 \AA but in the GGA approximations magnetic moment exists already at the equilibrium bonding length 2.46 \AA (GGA–PBE). The magnetic moment of the Pd chains

quickly decreases at both stretching and compression. The maximal value of the magnetic moment is about $0.76 \mu\text{B}/\text{atom}$ (LDA), or $0.85 \mu\text{B}/\text{atom}$ (GGA–PBE). Ni chains are found to be magnetic around equilibrium with the moment $1.2 \mu\text{B}/\text{atom}$, which quickly decreases down to zero at compressions corresponding to Ni–Ni separation below 2 \AA (Fig. 7). At stretching above 4.5 \AA the moment becomes $2 \mu\text{B}/\text{atom}$ that is similar to the behavior observed for Ni dimers. The Pt chain starts being magnetic only for the distances larger than 3.5 \AA when the moment jumps from zero to 1, and further to $2 \mu\text{B}/\text{atom}$ when the Pt–Pt distance becomes larger than 4.5 \AA . One should notice, however, that the Pt wire breaks at the Pt–Pt separations of 2.7 \AA (LDA) or 2.84 \AA (GGA–PW91; GGA–PBE), thus these magnetic transitions are highly hypothetical as they take place beyond the interval of the wire stability. We notice that spin-orbit interaction may affect magnetism of heavier elements like Au and Pt, although its overall contribution is generally expected to be small. But Au is found to be non-magnetic. Au is found to be non-magnetic even in the calculations including SO interaction. The magnetic moment for Pt chains with SO turns out to be negligible at equilibrium (2.31 \AA (LDA)) and it reaches $0.76 \mu\text{B}/\text{atom}$ before wire breakage (2.71 \AA (LDA)).



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