First-principles study of electronic properties of interfacial atoms in metal–metal contact electrification*

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The mechanism of contact electrification between metals was studied using the first-principles method, taking the Ag–Fe contact as an example. Charge population, charge density difference, the orbitals and densities of states (DOS) were calculated to study the electronic properties of the contacting interfacial atoms. Based on the calculation, the amount of contact charge was obtained. The investigation revealed that the electrons near Fermi levels with higher energies transfer between the outermost orbitals (s orbitals for Ag and d orbitals for Fe). Meanwhile, polarized covalent bonds form between the d electrons in the deep energy states. These two effects together lead to an increase of charge magnitude at the interface. Also, the electrons responsible for electrification can be determined by their energies and orbitals.

Keywords: contact electrification, first-principles calculations, charge transfer, metal–metal contact

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1. Introduction

Contact electrification is a familiar phenomenon in nature, and has been studied for quite a long time.[1–3] Various experiments have been performed to study the mechanism of electrification and the effects of different experimental factors.[4–7] It is believed that the charge transfer between dissimilar metals is due to the difference of their Fermi levels.[1,2,7] However, the transfer detail of the electrons, such as the energy variation of the interfacial atoms, electron redistribution at the interface, and the energies and oribitals of the transferred electrons, have not been specified. Moreover, although the polarities of the transferred charge could be determined by simply comparing the Fermi levels of the two metals, the value of the transferred charge cannot be measured during contact using existing methods. The experimental methods can only be used to measure the charge remaining on the surface after the separation of the contacting metals, while part of the charge might flow back.[8–10] What happened to the contacting atoms during contact? What are the electronic properties of the interfacial atoms, and what is the amount of the electrification charge during contact? Answering these questions is valuable to further reveal the mechanism of contact electrification and to explain the change that occurs in the material surface during contact. Thus, a method capable of exploring the electronic properties of the interfacial atoms during contact is required.[11,12]

The first-principles method is an effective way to study the electronic properties of the interface, providing the information of electrons' distribution, charge population, electron states, and electron orbitals. It has been widely applied in studying the transportation properties of the electronic devices. Band structure, electrostatic potential, conductance, and the I–V characteristics of the interface have been hot topics of research.[13–17] Even so, the intrinsic charge transfer between the materials at the interface was not studied in detail. Even if the charge transfer was considered, it was investigated as a tool to demonstrate or explain the variation of electronic properties, such as the work function, dipole formation,[18,19] and chemical bonding.[20,21] However, the amount and the origin of transferred charge have not been studied with this method.

In this paper, the first-principles method is used to study the electrification of a metal–metal contact, and an Ag–Fe contact was taken as an example due to the good lattice match between Ag and Fe. It has been reported that the structural and magnetic properties of Fe–Ag monatomic multilayer have been studied using the first-principles method,[22,23] while the electron transfer at the interface has not been investigated. Electronic characteristics of the contacting atoms are described and magnitude of electrification charge during contact is calculated. According to these results, the electrons responsible for electrification are determined, and the mechanism of contact electrification is discussed.

2. Computational methods

According to a previous work,[24] electron transfer occurs only at the outermost atomic layers of metal surfaces. The interior atoms in the bulk materials were found not to be involved in the contact electrification process. Therefore, for studying contact electrification, first-principles calculations of electronic properties of the contact interface are valid for both bulk materials and thin solid films.

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First-principles calculations were performed with the spin-polarized density functional theory (DFT), using the CASTEP program,[25] which is based on the plane-wave ultrasoft pseudopotential method.[26] The generalized gradient approximation (GGA) as parameterized by Perdew–Burke–Ernzerhof was employed for the exchange–correlation energy.[20,27–29] This was because, compared to the local density approximation (LDA), GGA better characterizes the electronic properties of the transition metals, and is more accurate in calculating the band gaps. Calculations of the parameter tests, such as the $\boldsymbol{k}$-point density, the cutoff energy, and the number of surface layers, were performed and the optimized computational parameters were obtained. Based on the calculation results, the primitive unit cells of fcc Ag and bcc Fe were first built, respectively. The atomic positions and the lattice parameters were relaxed, with a cutoff energy of 380 eV and the Monkhorst–Pack $\boldsymbol{k}$-point meshes of 6×6×6. The convergence threshold of energy change between optimization cycles was 2×10^{-6} eV per atom. The computational results of lattice constants for Ag and Fe were 4.17 Å and 2.76 Å, which were in good agreement with the experimental results from the references (4.09 Å for Ag, and 2.89 Å for Fe).[30]

The unit cell after optimization was sliced into 7 layers of atoms by the low-index surface. Surface slabs of Ag (111) and Fe (100) were built to simulate the surface layers of the bulk materials, where material deformation under the contact load was not considered in this paper. As the lattice parameters of the surface slabs were different, the Ag (111) 1×1 cell, Fe (100) 1×2 cell, and 20-Å vacuum layer were constructed, and they were combined together. The lattice parameters of the combined slab were averaged in 5.31 Å×2.85 Å×48.7 Å with the maximum lattice mismatch of 6.7%. Based on this combined contact model, different geometries with the Fe interfacial atom located at hollow, bridge, and atop sites of the interfacial Ag layer were calculated. According to the relaxation results, the hollow geometry has the minimum systematic energy, so it is taken to be the optimal geometry. Ag–Fe distances ranging from 2 Å to 4 Å were also calculated. The optimal Ag–Fe interfacial spacing was 2.31 Å, and the Ag–Fe distance was 2.77 Å. The relaxation of these contact models was performed under the cutoff energy of 300 eV, the convergence energy change of 1×10^{-5} eV per atom and the Monkhorst–Pack $\boldsymbol{k}$-point meshes of 7×4×1. After relaxation, the interfacial rumpling effect was observed, the atoms in the interface and subsurface layers were relaxed due to the interaction of the interfacial atoms.

The optimized Ag–Fe contact model was shown in Fig. 1. Using this model, the electronic properties were calculated under the same computational parameters as in the relaxation calculation.

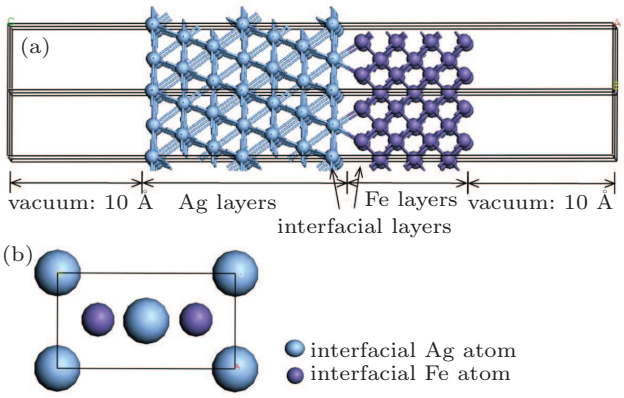


Fig. 1. Optimized Ag (111) 1×1–Fe (100) 1×2 contact model. (a) The side view of the contact model. (b) Cross-section of the contact interface.

3. Results and discussion

Charge populations of the atoms in the Ag (111)–Fe (100) contact model were calculated by Hirshfeld population analysis. The results are shown in Fig. 2.

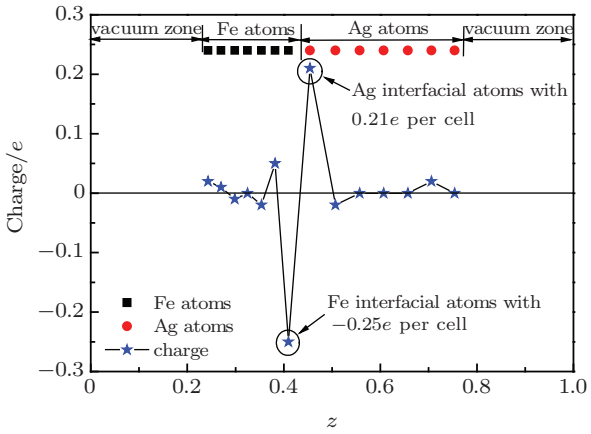


Fig. 2. (color online) Charge population of atoms in the Ag (111)–Fe (100) contact model with the z coordinate along the height of the crystal cell.

The transferred charge was localized at the interfacial layers. The interfacial Ag atoms carry $0.21e$ per cell, and the interfacial Fe atoms carry $-0.25e$ per cell, e is the electron charge. The nonconservation of the calculated charge in the contact model is because of the inaccurate determination of the atomic space in the Hirshfeld method,[31] due to the possible overlap between two contacting atoms. According to this charge population, the transferred charge density on the Ag–Fe contact interface during contact could be calculated by

$$\rho = \frac{eq}{S}. \tag{1}$$

Here, ρ is the transferred charge density, q is the number of electrons at the interface of the contact model, and S is the surface area, which was calculated by the lattice constants of 5.31 Å and 2.85 Å. According to the results from Fig. 2, the charge magnitudes on the Ag and Fe interfaces are different, so the transferred charge density was separately calculated

according to the results of the charge population calculation for Ag and Fe, respectively. The values from 0.22 C/m^2 to 0.26 C/m^2 were derived. It is suggested that the transferred charge density is between these two values.

Electronic characteristics were analyzed according to the computational results of density of states (DOS). In order to find out the change of the electrons' dissipation and their energy states during contact electrification, the DOS results of the surface slab and the contact model were compared and shown in Fig. 3. The dashed line at 0 eV in the figure represents the Fermi level.

Figure 3(a) represents the DOS for s, p, and d electrons of Ag atoms, respectively. The p electrons of the interfacial Ag atoms and the surface Ag atoms are of similar distribution, and there is no significant difference, while the distribution of the s and d electrons change greatly after contact. For s electrons, the DOS magnitude in the surface slab near Fermi level is larger than that in the contact model, which means that the number of the nearly-free s electrons decreases after contact for Ag interfacial atoms. The d electrons in the surface states of the Ag surface slab have relatively high energy, when Ag comes into contact with Fe, the DOS peak shifts toward the low energy direction, and the d-DOS peaks redistribute. The surface states disappear, and new DOS peaks appear at around −5.1 eV and −4.3 eV.

Figure 3(b) represents the DOS for s, p, and d electrons of Fe atoms. The DOS magnitude for s and p electrons of the Fe atoms are small and the difference between the surface atoms and interfacial atoms can be neglected. While for the d electrons, the DOS magnitude near the Fermi level in the surface slab is significantly smaller than that of the contact model, which means that the number of nearly-free electrons increases after contact. The DOS peaks below Fermi level also redistribute due to the interaction with the Ag interfacial atoms.

The total DOS results are shown in Fig. 3(c). After contact, the DOS magnitude near Fermi level decreases for Ag atoms and increases for Fe atoms, implying the charge transfer from Ag to Fe atoms. Specifically, the s electrons of Ag interfacial atoms transfer to the d orbitals of Fe interfacial atoms, resulting in the charge transfer of contact electrification. The transferred electrons near the Fermi level are the outermost electrons of the elements, which have the highest energy states. Another consequence of the contact is the presence of common DOS peaks generated for both Ag and Fe interfacial atoms at around −5.1 eV and −4.3 eV in the contact model, implying the formation of a Ag–Fe covalent bond between the interfacial atoms, and the bonding electrons are mainly d electrons.

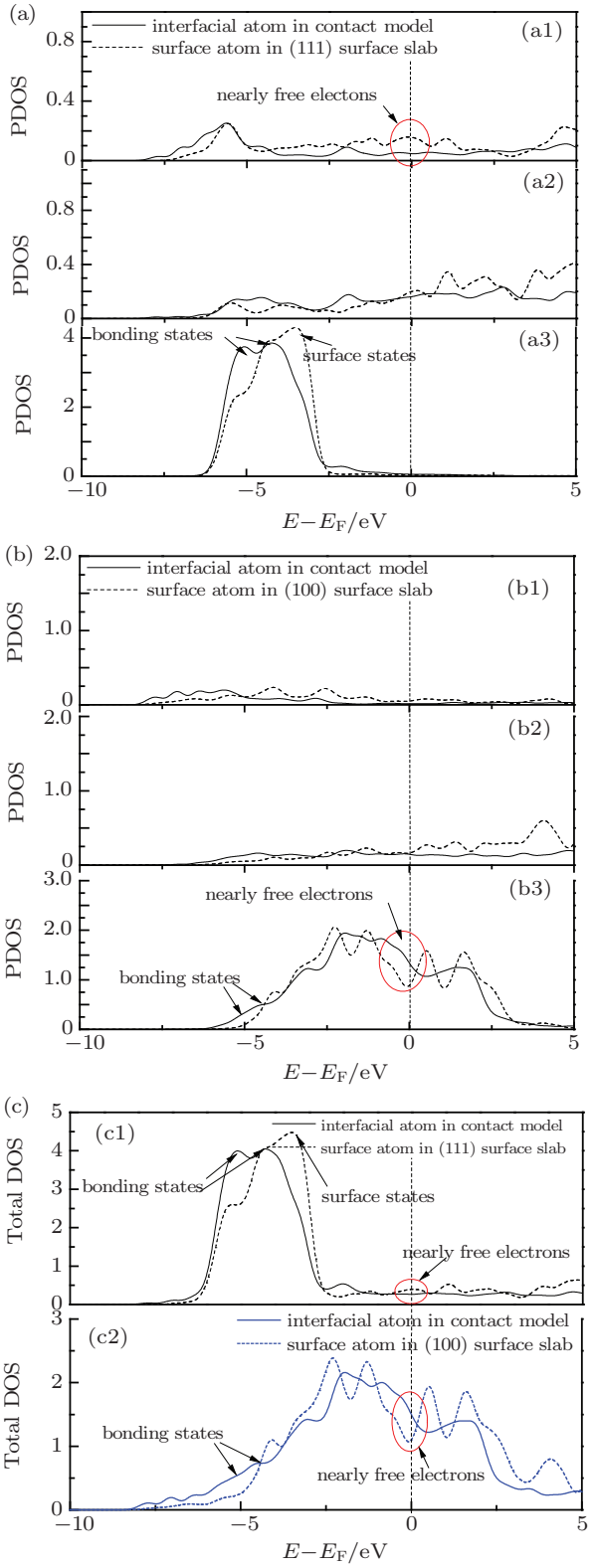


Fig. 3. (color online) Comparison of the DOS for interfacial Ag and Fe atoms in the contact model (solid line) and for the atoms in surface slab (dotted line). PDOS of (a1) 5s, (a2) 5p, and (a3) 4d electrons of Ag atoms. PDOS of (b1) 4s, (b2) 4p, and (b3) 3d electrons of Fe atoms. The total DOS results for (c1) Ag atoms and (c2) Fe atoms.

To further understand the electron dissipation, the charge density difference of the contact model was calculated and the result is shown in Fig. 4. It can be seen that the electron density decreases in the region around the Ag atoms and increases

in the region around the Fe atoms, which means that the Fe atoms carry a negative charge and Ag atoms carry a positive charge, as in the results of the charge population calculation. An evident increase of the electron density is clearly seen at the interfacial region between the Ag and the Fe atoms, indicating the electron accumulation and the formation of Ag–Fe covalent bonds. The bond is polarized and the electrons incline toward the Fe atoms. From the shape of the charge density difference of Ag interfacial atoms, which is not a circle as it is both for the s orbitals that lose their free electrons and for the typical d orbitals that share the bonding electrons, it could be suggested that the charge transfer during contact is attributed to the synergistic effect of the free electron transfer and formation of polarized covalent bonds.

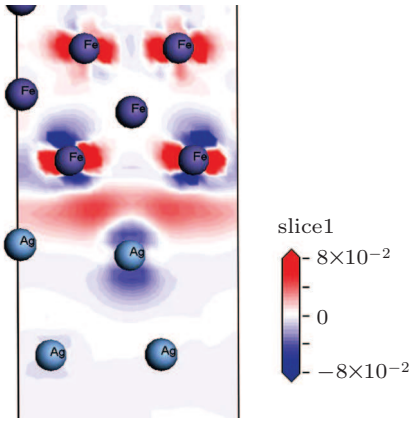


Fig. 4. Charge density difference of the Ag–Fe contact model.

The dissipation of electrons could also be determined by the orbitals' shape as shown in Fig. 5. Figure 5(a) shows the electrons at the DOS peak from −5.22 eV to −4.91 eV in Fig. 3(c) (pointed out by arrows). The electron orbitals of the nearest-neighboring interfacial atoms are overlapped, and their directions are different from the usual orientation (perpendicular to the surface plane), which illustrates the formation of polarized covalent bonds during contact. The Ag electrons are in the d_z^2 orbitals, and the Fe electrons are in the d_{yz} orbitals. At the energy range from −4.64 eV to −4.18 eV, Ag electrons participate in the covalent bond through d_{yz} orbitals, and Fe electrons through the $d_{x^2-y^2}$ orbitals, as shown in Fig. 5(b). Electrons in the energy range from −0.54 eV to 0.08 eV are the nearly-free electrons across the Fermi level, these electrons are concentrated at the interfacial region around Fe atoms, and they are in the mixture of the d orbitals.

Based on the above analysis, the mechanism of the contact electrification between Ag and Fe could be described as follows: when Fe and Ag are brought into contact, the electrons near the Fermi level with the highest energy transfer between the outermost orbitals (s orbitals for Ag and d orbitals for Fe). At the same time, polarized covalent bonds also form between the d electrons in the deep energy states.

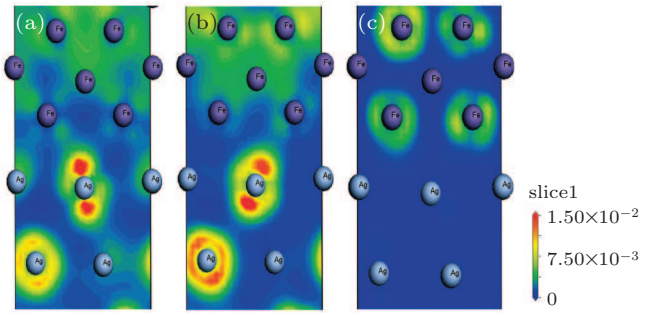


Fig. 5. Projection of electron orbitals in the xz plane in different energy ranges: (a) from −5.22 eV to −4.91 eV, (b) from −4.64 eV to −4.18 eV, and (c) from −0.54 eV to 0.08 eV.

4. Conclusion

In conclusion, the contact electrification between Ag and Fe was investigated using the first-principles method. Calculation of charge population shows that electrons transfer from Ag to Fe interfacial atoms. The transferred charge density ranging from 0.22 C/m^2 to 0.26 C/m^2 for the Ag–Fe contact was theoretically derived. According to the DOS and orbital analysis, the transferred electrons could be specified from their energies and orbitals. The mechanism of contact electrification was revealed to be a synergistic effect of nearly-free electrons transferring at Fermi levels and the formation of polarized covalent bonds between the interfacial atoms.

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