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LETTER TO THE EDITOR

Self-diffusion of adatoms on Ni(100) surfacesC M Chang¹, C M Wei² and J Hafner³¹ National Centre for High-Performance Computing, Hsinchu, Taiwan 30077, Republic of China² Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan 11529, Republic of China³ Institut für Materialphysik, Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria

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Abstract

Using *ab initio* calculations, we find that the calculated energy barrier for exchange diffusion of Ni adatoms on Ni(100) surfaces shows a surprisingly large dependence on the size of the surface unit cell. It decreases from 1.39 to 0.78 eV when the cell size changes from (2×2) to (6×6) . This is due to the long-ranged strain field created by the transition state for atomic exchange, which needs a larger cell to relax. The hopping diffusion energy, on the other hand, shows only a very small size effect and remains approximately constant at 0.82–0.86 eV, independently of the cell size. Our results indicate that Ni diffusion on Ni(100) occurs by the exchange mechanism and this is consistent with recent experiments. Previous results obtained using (3×3) or (4×4) unit cells did not converge sufficiently well to yield correct conclusions.

Diffusion of adatoms on metal surfaces is important for understanding many surface phenomena such as thin-film and crystal growth, heterogeneous catalysis, phase transitions, segregation, and sintering [1]. Surface diffusion on fcc (100) surfaces may take place either by a hopping mechanism (an adatom hopping between minima on the potential energy surface; see figures 1(a) and 1(b)), or by an atomic exchange mechanism [2] where an adatom replaces a nearby surface atom which is pushed out of its equilibrium position and then moves up to an adsorption site; see figure 1(c). Although the atomic exchange mechanism was first found by Bassett and Webber [3] on fcc (110) surfaces, it attracted great interest only after a similar atomic exchange mechanism was found experimentally to occur on the highly symmetric and fairly smooth (100) surfaces of fcc Pt [4] and Ir [5], and predicted theoretically for the Al(100) surface [6]. In recent years, considerable progress has been achieved in the investigation of surface diffusion and related phenomena, owing to significant improvement in experimental techniques [7]. Although a considerable amount of experimental information is now available for single-atom diffusion [2], experimental data for self-diffusion on fcc (100) surfaces are still quite scarce. On the Rh(100) surface, the self-diffusion mode of adatoms was found by field-ion microscopy (FIM) experiments to be the hopping mechanism [8]. However, for Ir(100) and Pt(100) surfaces, FIM experiments demonstrated that the self-diffusion of adatoms proceeds by the atomic exchange mechanism.

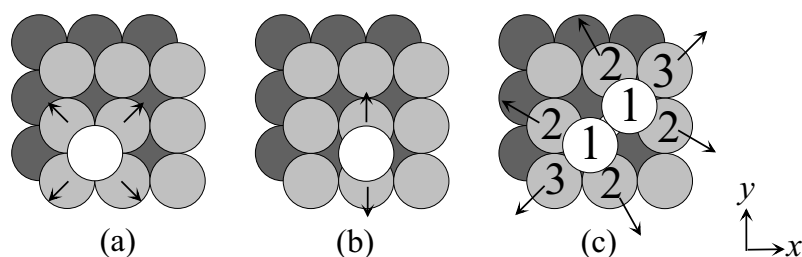


Figure 1. The top view of an adatom at (a) the fourfold hollow site, (b) the transition state (bridge site) for hopping diffusion, and (c) the transition state (with a dimer on top of a surface vacancy) for exchange diffusion. Arrows in (a), (b), and (c) indicate the directions of lateral relaxations of surface atoms surrounding the adsorbed atom, and the atoms at the hopping and exchange transition states, respectively. The numbers in (c) are labels used to identify atoms whose the bond distances and lateral relaxations are listed in table 2—see later.

Why is the hopping mechanism favoured on Rh(100) surfaces but the exchange mechanism favoured on Ir(100) and Pt(100) surfaces? This is still an open question that physicists have been attempting to answer for a long time. The first theoretical prediction of exchange diffusion on fcc (100) surfaces was made for self-diffusion of Al/Al(100) [6]. Feibelman concluded that the exchange mechanism is favoured for Al/Al(100) because strong covalent bonds are formed at the transition state of exchange diffusion. However, Yu and Scheffler [9] argued that covalent bonding might not explain the low exchange diffusion barrier on the (100) surfaces of the 5d transition metals Ir and Pt. From density-functional calculations on Ag(100) and Au(100) surfaces, they concluded that the tensile surface stress plays a crucial role for the exchange diffusion and explains why the exchange process is favourable for the late 5d, but not for 3d and 4d fcc (100) metal surfaces. Recently, using *ab initio* calculations, Feibelman and Stumpf [10] showed that the tensile surface stress itself does not appear to be useful for achieving an understanding of the diffusion mechanism on transition metal (100) surfaces. They showed that exchange diffusion is favoured when the adsorption-induced lateral relaxation (see figure 1(a)) is large, as had been proposed by Kellogg *et al* [11]. Feibelman and Stumpf found that hopping diffusion occurs on the (100) surfaces of the 4d metals Rh(100) and Pd(100), whereas the exchange mechanism is favoured for the same surfaces of the 5d metals Ir and Pt. However, a very recent FIM experiment by Fu and Tsong [12] showed that on the (100) surface of the late 3d transition metal Ni, self-diffusion of an adatom is accomplished by the exchange mechanism with an energy barrier of 0.59 eV. This surprising result revealed that exchange diffusion not only exists on the (100) surfaces of late 5d metals, but also on the late 3d metal Ni, in apparent contradiction to all theoretical expectations.

In the present work, we use *ab initio* density-functional theory (DFT) [13] to study the self-diffusion behaviour of Ni adatoms on a Ni(100) surface. We find that atomic exchange is the favoured diffusion mode for Ni/Ni(100). We also find that the calculated exchange diffusion energy shows a surprisingly large dependence on the size of the surface unit cell used in the calculations. The exchange diffusion is energetically unfavourable when using (4×4) or smaller surface unit cells and becomes favoured for (5×5) or larger cells. The DFT calculations reported here were performed by using the Vienna *Ab initio* Simulation Package (VASP) [14], using a plane-wave basis and ultrasoft pseudopotentials [15] for describing the electron-ion interaction. The exchange-correlation functional is treated in the local density approximation (LDA) [16] using the functional based on the quantum Monte Carlo simulations of Ceperley and Alder, as parametrized by Perdew and Zunger [17]. The influence of the choice of the exchange-correlation functional was checked by using the generalized gradient

approximation (GGA) proposed by Perdew *et al* [18], and also using the spin-polarized LDA (LSDA). The wave functions are expanded in a plane-wave basis set with a kinetic energy cut-off of 17.8 Ryd for all calculations. The calculated equilibrium lattice constants are $a = 3.43 \text{ \AA}$, 3.43 \AA , and 3.52 \AA for the LDA, LSDA, and GGA, respectively. The bulk modulus is $B = 1.72 \text{ Mbar}$, 1.69 Mbar , and 1.95 Mbar for the LDA, LSDA, and GGA, respectively. These bulk properties agree well with the experimental values of $a = 3.52 \text{ \AA}$ and $B = 1.86 \text{ Mbar}$. We note in particular the tendency of the GGA to correct the overbinding present in the LDA. The supercell geometry used to study the self-diffusion on the Ni(100) surface consists of periodically repeated slabs of five atomic layers of Ni, separated by a vacuum region with a width of at least 10 \AA . The adatom is adsorbed only on one side of the slab. In all the calculations, the adatom and the top three atomic layers are fully relaxed. All the other atoms are kept at bulk positions. The relaxations are performed using the exact forces on the atoms derived from the Hellmann–Feynman theorem. The geometry is optimized until the total energy is converged to 10^{-5} eV . The convergence with respect to the thickness of the slab is checked by performing calculations with six atomic layers. The diffusion energy difference is less than 0.03 eV between five and six atomic layers (see cases 5 and 7 in table 1). In the lateral directions we increase the periodicity from (2×2) , (3×3) , (4×4) , (5×5) to (6×6) surface unit cells. For k -point summations in the surface Brillouin zone we use different sets of Monkhorst–Pack k -point meshes [19] based on the size of surface unit cell (see table 1) chosen such as to keep the same density of grid points in k -space for all cells. The convergence of the sampling density was also checked (for example, see cases 1 and 2 in table 1), and the results are found to be well converged.

Table 1. The calculated lateral relaxation (ΔS) around an adatom, adsorption height (Z_{ads}) of the adatom, height of the adatom at the transition state for hopping (Z_{hop}) and exchange (Z_{exc}) diffusion, bond length of the dimer at the exchange transition state (D_{exc}), and diffusion energy of the hopping (E_{hop}) and exchange (E_{exc}) mechanisms calculated using surface unit cells of different sizes. The last column gives the experimentally determined diffusion energy for Ni/Ni(100), and the diffusion proceeds by the exchange mechanism. The lateral relaxation is given as a percentage of the nearest-neighbour spacing of the bulk crystal; the height of the adsorbed atom and of the atoms in transition states is given as a percentage of the bulk layer spacing. N_l is the number of atomic layers used in the supercell. EC stands for the exchange–correlation functional treated in the LDA, GGA, or LSDA.

Case	Cell size	k -point mesh	N_l	EC energy	ΔS (%)	Z_{ads} (%)	Z_{hop} (%)	Z_{exc} (%)	D_{exc} (\AA)	E_{hop} (eV)	E_{exc} (eV)	E_{exp}^a (eV)
1	2×2	5×5	5	LDA	1.59	84.30	96.99	64.30	2.17	0.86	1.39	0.59
2	2×2	6×6	5	LDA	1.57	84.30	96.81	63.97	2.17	0.85	1.39	Exchange
3	3×3	4×4	5	LDA	1.99	84.43	94.70	48.03	2.13	0.84	1.07	
4	4×4	3×3	5	LDA	2.25	83.95	93.84	39.38	2.10	0.82	0.87	
5	5×5	2×2	5	LDA	2.11	84.80	94.26	36.79	2.11	0.83	0.80	
6	6×6	2×2	5	LDA	2.36	84.55	94.19	35.51	2.11	0.82	0.78	
7	5×5	2×2	6	LDA	2.16	84.65	94.75	38.01	2.12	0.84	0.77	
8	4×4	3×3	5	GGA	1.89	85.29	95.24	43.72	2.19	0.73	0.82	
9	5×5	2×2	5	GGA	1.84	85.38	95.83	42.20	2.20	0.72	0.77	
10	2×2	5×5	5	LSDA	1.40	84.79	97.24	64.68	2.19	0.84	1.37	

^a Reference [5].

We first calculate the total energy for the adatom at the fourfold hollow site. For hopping diffusion, we calculate the diffusion barrier from the total energy when the adatom is in the transition state, i.e., at the twofold-coordinated bridge site (figure 1(b)). For the exchange process, the diffusion barrier is given by the total energy of the transition state in which a

dimer is placed diagonally above a surface vacancy (see figure 1(c)). The diffusion energies for the hopping (E_{hop}) and exchange (E_{exc}) mechanisms are both obtained by subtracting the total energy of the adsorption state from that of the transition state. Feibelman and Stumpf [10] have demonstrated that an asymmetric transition state might have a higher barrier than that for the symmetric transition state, which is only a local minimum. However, this is not the case for Ni/Ni(100). When we displace the dimer a little bit from the symmetric transition state, it becomes very unstable and one of the dimer atoms moves all the way back to the fourfold hollow site, while the other atom moves down to the lattice site. This indicates that for Ni/Ni(100), the symmetric transition state is a local maximum (saddle point) for the exchange diffusion. The diffusion energies calculated for various surface unit cells are summarized in table 1. We can see from this table that for the LDA results with the (2×2) , (3×3) , and (4×4) surface unit cells, the hopping diffusion has lower barriers than the exchange diffusion. However, when the surface unit cell is expanded to (5×5) and (6×6) , the exchange diffusion is favoured over hopping diffusion. We plot these LDA results in figure 2. We see clearly that the exchange diffusion energy decreases as the size of the surface unit cell increases. This means that the calculated exchange diffusion energy has a strong dependence on the size of the surface unit cell used in the calculations. In contrast, the hopping diffusion energy has a very small size effect and remains almost constant. By analysing the local geometry of the adsorption and transition states for hopping and exchange diffusions, we find that the adatom in the fourfold hollow site has almost the same height, independently of the size of the surface unit cell. The same holds for the height of the adatom at the twofold bridge site. Hence the geometries of the equilibrium adsorption site and of the transition state for hopping diffusion are insensitive to the size of the surface unit cell. For the transition state for exchange diffusion, the height of the dimer above the surface decreases as the surface unit cell increases (see table 1 and figure 3). We have analysed the interatomic distances and the relaxation of atoms surrounding

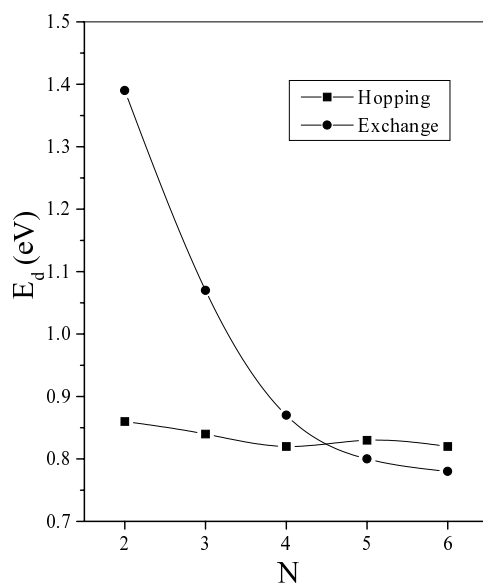


Figure 2. A plot of diffusion energy versus size of surface unit cell ($N \times N$). The hopping diffusion energy remains almost constant (between 0.82 and 0.86 eV) when the surface unit cell increases from (2×2) to (6×6) . The exchange diffusion energy has a big size effect; the energy decreases from 1.39 to 0.78 eV when the surface unit cell increases from (2×2) to (6×6) .

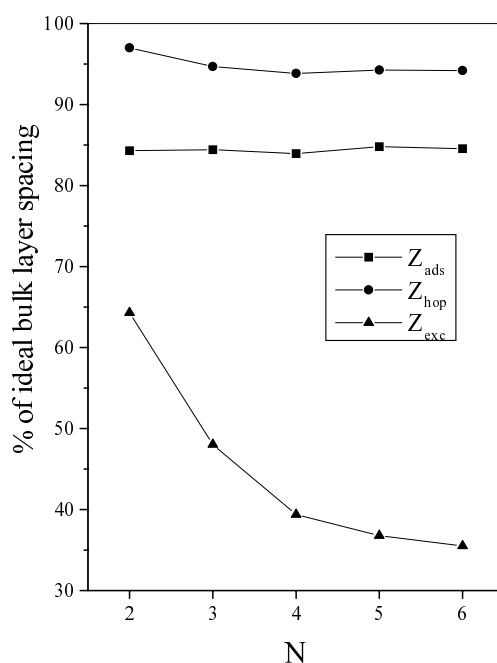


Figure 3. A plot of the heights of adatoms in the fourfold hollow site (Z_{ads}), of adatoms in the transition state for hopping diffusion (Z_{hop}), and the height of the dimer at the transition state for exchange diffusion (Z_{exc}) versus the size of the surface unit cell ($N \times N$).

the exchange dimer (see table 2) and found that the surrounding atoms will relax further away from the dimer atoms as the surface unit cell is increased (figure 4). This shows that the exchange transition state creates a long-ranged strain field, which will be released only by a long-range relaxation of the atoms in the vicinity of the exchange dimer. The lateral relaxation of surface atoms adjacent to the adsorbed hollow site (ΔS) and to the bridge site (the hopping transition state— ΔB) are also shown in figure 4. Both ΔS and ΔB change little and are converged within about 2.2% and 5.2% of the nearest-neighbour spacing, respectively, as the surface unit cell increases from (3×3) to (6×6) . In order to verify the role of the long-ranged lateral relaxations in the exchange diffusion more clearly, we use the (5×5) surface unit cell and then allow only the atoms within the (2×2) , (3×3) , and (4×4) cells, centred at adatoms or exchange dimers, to undergo lateral relaxations (relaxations in the perpendicular direction are allowed for all atoms). We find that the total energy for the fourfold hollow adsorption state is almost unchanged (within 0.03 eV of each other) as we allow more atoms to relax in lateral directions. However, the total energy for the exchange transition state decreases very quickly, and therefore the exchange diffusion barrier decreases from 1.36, 0.87, to 0.86 eV as we allow the atoms within (2×2) , (3×3) , or (4×4) cells to relax, and finally decreases to 0.80 eV for the fully relaxed (5×5) cell. The energy barriers of 0.87 and 0.86 eV for lateral relaxation allowed within (3×3) and (4×4) cells are so close because in the surface layer only the same atoms are allowed to relax. From these results we can see that in the transition state for exchange diffusion there are long-ranged strain fields which can be released only by long-range relaxations. A large lateral relaxation of the atoms surrounding the exchange dimer creates more space around the surface vacancy and permits the dimer to sink deeper into the substrate, and this makes the exchange diffusion more favourable.

Table 2. Bond distances (in Å) and lateral relaxation of the atoms in the surface layer (as percentages of the nearest-neighbour distance in the bulk) surrounding the exchange dimer for various surface unit cells calculated using the LDA. The labels (1, 2, and 3) correspond to the nomenclature used in figure 1(c).

	R_{12} (Å)	R_{13} (Å)	ΔE_{2x} (%)	ΔE_{2y} (%)	ΔE_2 (%)	ΔE_3 (%)
3×3	2.15	2.45	4.4	4.7	6.4	-2.0
4×4	2.15	2.44	3.8	7.7	8.6	-1.0
5×5	2.17	2.44	3.2	9.3	9.8	-0.4
6×6	2.18	2.44	2.8	10.8	11.2	-0.1

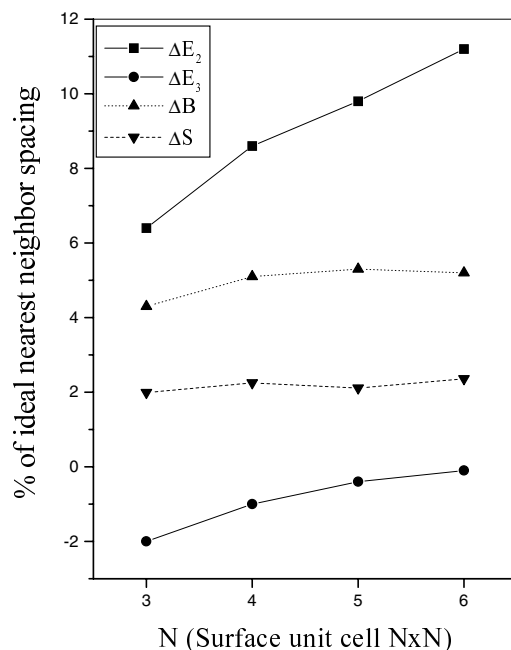


Figure 4. A plot of the lateral relaxation of surface atoms surrounding the adsorption atom ΔS , the bridge site (transition state for hopping diffusion) ΔB , and the dimer of the exchange transition state (ΔE_2 and ΔE_3) as indicated in figure 1 versus the size of the surface unit cell (N).

We checked the results for a (2×2) surface unit cell by using spin-polarized calculations, and find that the results are hardly affected by spin polarization (see cases 1 and 10 in table 1). We also performed GGA calculations with (4×4) and (5×5) surface unit cells. From the GGA results (cases 8 and 9 in table 1), we can see that although the exchange diffusion energy decreases from 0.82 to 0.77 eV, it is still larger than the hopping diffusion energy of 0.72 eV. Hence the GGA results favour hopping diffusion, in contradiction to the LDA results and experiment. This is a bit surprising. Since the GGA lattice constant (3.52 Å) is larger than the LDA value (3.43 Å), this contradicts Yu and Scheffler's conclusion [9] that exchange diffusion becomes favoured if the lattice is expanded. The reason might be that the increase in the dimer bond length for the exchange transition state is 5.2%, whereas the lattice constant increases by only 2.6% on going from the LDA to the GGA. This could lead to strain fields that are even more long ranged in the GGA than in the LDA. For a (5×5) cell, the exchange diffusion energy decreases by 0.05 eV compared to that for a (4×4) cell. A further decrease by about

the same amount would bring the GGA results into agreement with the LDA calculations and with experiment. However, this would make it necessary to expand the surface cell to a (7×7) geometry, exceeding our present computer resources.

In summary, we have studied the self-diffusion behaviour of Ni/Ni(100) by means of DFT calculations. The LDA results show that the diffusion of Ni on Ni(100) occurs through the atomic exchange mechanism, which is consistent with FIM experiments [12]. The exchange diffusion energy has a large size effect and changes from 1.39 to 0.78 eV when the size of the surface unit cell increases from (2×2) to (6×6) . In contrast, the hopping diffusion energy has very weak size dependence and changes only from 0.86 to 0.82 eV. The large size effect of the exchange diffusion is due to the long-ranged strain field created at the exchange transition state, and thus a large surface unit cell is needed to allow long-ranged relaxations to release the strain. Our results indicate that previous calculations using (3×3) or (4×4) surface unit cells are not sufficiently well converged to yield correct conclusions about the self-diffusion mode on fcc (100) surfaces. We also find that GGA results for diffusion of Ni on Ni(100) obtained for (4×4) and (5×5) unit cells lead to a slightly lower barrier for the hopping mechanism, which is the wrong diffusion mode according to experimental findings. This suggests that due to the weaker bonding in the GGA, the relaxation around the transition state will be even more long ranged than in the LDA and that even larger cells will have to be used to recover the LDA result and to establish agreement with experiment.

Preliminary results for a number of 3d, 4d and 5d transition and noble metals and for Al suggest that the size effect discussed here is a very general result. For the 5d metals and for Al exchange, diffusion is favoured already on the basis of calculations for rather small cells, but the barrier height for exchange diffusion continues to decrease as the cell is expanded. Hence, so far, the results reported in the literature are confirmed. For the 3d and 4d metals the situation is more complex, but at least for Rh(100), hopping diffusion remains favoured even for the largest cells studied so far. Further extended calculations will be needed to decide whether the size effect is strong enough on other surfaces besides Ni(100) to affect the prediction of the surface diffusion mechanism.

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References

- [1] Zangwill A 1988 *Physics at Surfaces* (Cambridge: Cambridge University Press)
- [2] For a collection of works on diffusion on metal surfaces, see, for example, Kellogg G L 1994 *Surf. Sci. Rep.* **21** 1
- [3] Bassett D W and Webber P R 1978 *Surf. Sci.* **70** 520
- [4] Kellogg G L and Feibelman P J 1990 *Phys. Rev. Lett.* **64** 3143
- [5] Chen C L and Tsong T T 1990 *Phys. Rev. Lett.* **64** 3147
- [6] Feibelman P J 1990 *Phys. Rev. Lett.* **65** 729
- [7] See, e.g., the collection of articles published in Tringides M C (ed) 1997 *Surface Diffusion: Atomistic and Collective Processes* (New York: Plenum)
- [8] Ayrault G and Ehrlich G 1974 *J. Chem. Phys.* **60** 281
- [9] Yu B D and Scheffler M 1997 *Phys. Rev. B* **56** R15 569
- [10] Feibelman P J and Stumpf R 1999 *Phys. Rev. B* **59** 5892
- [11] Kellogg G L, Wright A F and Daw M S 1991 *J. Vac. Sci. Technol. A* **9** 1757
- [12] Fu T Y and Tsong T T 2000 *Surf. Sci.* **454–456** 571
- [13] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [14] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558

- Kresse G and Hafner J 1994 *Phys. Rev. B* **49** 14 251
Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11 169
- [15] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
- [16] See, for example,
Lundqvist S and March N H (ed) 1983 *The Theory of the Inhomogeneous Electron Gas* (New York: Plenum)
Pickett W E 1989 *Comput. Phys. Rep.* **9** 115
- [17] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
as parametrized by
Perdew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [18] Perdew J P 1991 *Electronic Structure of Solids '91* ed P Ziesche and H Eschrig (Berlin: Akademie)
Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pedersen M R, Singh D J and Fiolhais C 1992 *Phys. Rev. B* **46** 6671
- [19] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188