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Electronic Structure of Transition Metal Surfaces: Ni(001)*

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〈Abstract〉

Using the recursion method, the densities of states at (001) surfaces of Ni are calculated. Including the effect of charge transfer and asymmetry for the surface atoms, the surface density of states at Ni (001) is smaller root mean square widths than the bulk. The need to include second neighbours and the relative unimportance of third neighbours can be seen more clearly.

The narrowing relative to the bulk is greatest for the surface yz/zx density of states. Our results are compared with angular resolved photoemission theory and experiment.

전이금속 표면의 전자구조 ; Ni(001)

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〈요 약〉

Recursion 방법으로, Ni(001)표면의 상태밀도를 계산한다. 표면의 전자구조를 계산할 때 고려되어야 할 두개의 중요한 효과, 비대칭성과 전하의 전이를 포텐셜에 고려하면, Ni(001)면의 상태밀도가 고체내부보다 폭이 줄어듦을 본다. 가장 가까운 원자와 다음 가까운 원자의 영향이 지배적이며 그 다음 가까운 원자의 영향은 무시할 수 있다.

내부 DOS에 비해서 yz/zx 궤도의 d전자가 가장 현저히 줄어든다. 우리의 계산결과를 광전자 사출효과의 실험과 비교한다.

I. Introduction

Up to now, most calculations of the electronic structure of metal surfaces have been based on an LCAO approach[1~5]. The resulting tight-binding Hamiltonian may either be solved by moment methods[1,2], or in the case of layer calculations by straightforward matrix diagonalization[3~5]. Other calculations have been carried out using pseudopotentials, and the Schrödinger equation is then solved by considering a periodic arrangement of layers to restore translational symmetry[6]. None of these methods is ideal for finding the electronic structure of a transition metal surface in which we wish to include both the sp- and the d-electrons and their hybridization, in an accurate way. In this paper we shall use the recursion method[7].

In the independent electron theory, the eigenstates of a system are given by the solutions of the Schrödinger equation

$$(-\nabla^2+V(\boldsymbol{r}))\Psi(\boldsymbol{r})=E_n\Psi_n(\boldsymbol{r}) \qquad (1)$$

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where $V(r)$ is the one-electron potential and is independent of the other electron states in the system.

Eq. (1) has a solution provided the matrix $(EI-H)$ can be inverted. Given the matrix elements of Hamiltonian H, we may define the resolvent matrix by

$$G=[EI-H+i\delta]^{-1} \tag{2}$$

It is a standard result that the local densities of states are related to the Green function matrix elements:

$$N_i=\frac{1}{\pi}\mathrm{Im}G_{ii} \tag{3}$$

The total DOS (density of States) of the system is

$$N(E)=\sum_i N_i(E)=-\frac{1}{\pi}\sum \mathrm{Im}G_{ii} \tag{4}$$

$$=-\frac{1}{\pi}\mathrm{Im}\ \mathrm{Tr}(G) \tag{5}$$

or

$$N(E)=\sum_i\sum_n \delta(E-E_n)|\langle\phi_i|\Psi_n\rangle|^2 \tag{6}$$

$$=\sum_n \delta(E-E_n) \tag{7}$$

That these two expressions are equivalent can be seen by writing $\mathrm{Tr}(G)$ in the representation where the basis vectors are eigenvectors of the System.

The evaluation of the quantities $G_{i\alpha}$ is a problem of inverting a large sparce matrix, H. It has been demonstrated that the most efficient way to achieve this is the recursion method of Haydock et al[7,8]. We define a change of basis from the localised orbitals $\phi_{i\alpha}(\equiv\phi_\alpha(\gamma-\gamma_i))$ to a new basis Ψ_n via the recursion algorithm

$$b_{n+1}\Psi_{n+1}=(H-a_n)\Psi_n-b_n\Psi_{n-1} \tag{8}$$

If we require $G_{i\alpha}$, we start the algorithm with $\Psi_0=\phi_{i\alpha}$ and $b_0=1$, $a_0=0$, and determine the successive $\{a_n, b_n\}$ by demanding that the functions Ψ_n are orthogonal.

It is important to get a clear understanding of the clean surface and the factors which enter a clean surface calculation. Compared to the monatomic bulk material there are two new factors which must be considered in a surface calculation. First is the effect of charge transfer. Due to the changed environment the local density of states at the surface is different to that in the bulk. A simple calculation will therefore usually lead to a different number of electrons being associated with the surface atoms compared to the bulk atoms. If the effect of this charge on the energy levels of the surface atoms is not included in the calculation in some self-consistent manner highly unphysical surface charges are obtained and the shape of the local density of states may also be altered significantly[9,10]. This point has been understood for some time and calulations now usually allow it somehow. The second new factor in a surface calculation has, until very recently, not generally been considered for the transition metal surfaces. The bulk of a cubic material is a highly symmetric situation but at the surface this symmetry is broken by the presence of the vacuum, leading to an asymmetric or 'aspherical' enviroment for the surface atoms. Not surprisingly, the shape of the potential in the region of the surface and its asymmetry play an important part in determining the surface electronic structure and need to be fully included in a surface calculation.

The potential for the calculation was obtained according to the Mattheiss prescription[11] using the atomic configuration $(3d^9\ 4s^1)$ for the Ni atoms. The program was easily adapted to give the muffin-tin potential for the surface atoms and this was found to be indistinguishable from the bulk except towards the muffin-tin edge where the surface potential was a bit higher, due to the decreased number of neighbours. Towards the centre of the potential the effect of neighbours is negligible compared to the strength of potential of the atom itself. The effects are sufficiently small for the spherical approximation still to be good within the muffin-tin.

Charge transfer was included in the potential by allowing the input charge configuration for

the surface atoms in the potential calculation to vary in the same way as the surface charge distribution obtained from the local density of states calculation varied relative to the bulk Ni distribution.

In the present calculation this aspherical potential can be included at two stages. Firstly it could be included in the one site potential V_I for calculating the surface optimum local orbital-giving a local orbital which would no longer be a pure spherical harmonic. Secondly it could enter in V_{rest} for the surface atom the difference between the true potential and the one site potential V_I. Either way the effect of this aspherical potential is included in defining the hopping parameters for the surface atoms as well as their self-energies.

In Ⅱ we describe charge transfer on the surfaces, and in Ⅲ we calculate the DOS of bulk nickel and find the Fermi energy. In Ⅳ we calculate surface density of states at Ni (001) and in Ⅴ we compare this calculation with photoemission spectroscopy. Our conclusion are presented in Ⅵ.

Ⅱ. Charge Transfer

The approach to charge transfer (or perhaps charge redistribution is a better expression) outlined above and discussed in more detail below, is a simple one. It considers $d \leftrightarrow sp$ transfer but ignores redistribution of charge within the d-levels when calculating the potential and, in common with all d-band only calculations, it is making implicit assumptions about the behaviour of the sp-band without actually calculating it. However this behaviour is as far as possible built into the calculation of the potential for the new charge distribution (even though approximate) the approach is a significant improvement of previous calculations.

Their usual approach has been to include a single parametric shift of the energy level of the surface atom in order to satisfy the Friedel sum rule[9] or to give surface charge neutrality[4] with no direct reference to the potential. Inglesfield[12] improved on this in principle by bodily shifting the potential of the surface atoms in a matching Green's functions calculation, but did not consider charge redistribution changing the shape of the potential.

Previous d-band only calculations[2] used the criterion that the d-band alone showed overall charge neutrality (thus assuming the same for the sp-band alone). In the present calculation this unphysical assumption is not made, though the behaviour of the sp-band is still being assumed complementary to the behaviour of the d-band so that between them overall charge neutrality is preserved. For a starting potential from the Mattheiss program corresponding to the atomic configuration on all atoms a surface d-band density of states is calculated and filled to the bulk Fermi level. The filling of the Ni d-level input for the surface atom in the Mattheiss program is then altered by the amount this surface band filling differs from the bulk band filling. Since the overall input configuration for the potential calculation must remain neutral the difference is taken up by also changing the number of 4s electrons input for the surface atoms. It is by this process that the required complementary behaviour of the sp-band is being to some extent built into the potential. Self-consistency is reached when for example the potential derived with a configuration $3d^{9-x}4s^{1+x}$ yields a surface d-band containing $9.4-x$ electrons. (The potential being calculated using atomic (9 : 1) configuration, not bulk (9.4 : 0.6) but the important point being that the charge transfers are the same in both cases.) As stated above, it was found that to avoid unreasonable charging of the subsurface atoms the self-consistency procedure had to be applied to them also (concurrently with the

surface layer as the two are not independent). This is another point which has previously been neglected parameters usually being shifted for the surface atoms only and often the charging of the subsurface atoms not even being considered.

The decrease in the number of neighbours at the surface and their replacement by a more repulsive potential causes an increase in the energy of the *d* electrons. Charge thus flows from the *d*-band into the conduction band retaining effective charge neutrality throughout (since charge neutrality is always maintained in metallic systems). This charge transfer makes the surface potential more attractive to the *d* electrons thus lowering their energy giving a stable self-consistent system. The calculated orbital resonance energy, E_r, is thus lowered relative to that for no $d \leftrightarrow s$ charge transfer, though in the present calculation it remains above the bulk value. (The band self-energies, E_n, are further raised by the inclsion of the non-muffin-tin potential).

Why should the *sp*-band be prepared to accept more charge, whereas the *d*-band loses charge? The reason is that the *sp* electrons in the bulk are highly pressurised by overlap repulsion[14] which raises their self-energy. At the surface where there are no neighbours the overlap repulsion is greatly decreased and the *sp* electrons spill out towards the vacum-lowering their energy because of lack of overlap repulsion and thus accomodating more charge. The effect of the less attractive potential towards the vacuum is relatively unimportant. For the *d* electrons which are far more localised the decrease in overlap repulsion is less significant-indeed the interaction of the *d* electrons with neighbouring atoms must be an attractive interaction or under the repulsive force of the *sp* electrons the material would fly apart[14]. The energy of the surface *d* electrons is therefore raised because of neighbours, and the relatively high potential, more than it is lowered by the decreased overlap repulsion. The picture described in the paragraph above is hence a consistent one.

Ⅲ. DOS of bulk Nickel

The Ni bulk density of states thus calculated is shown in Fig. 1. We obain the Fermi energy, $E_F = 0.64$Ryd. (Fig. 2.) using Zornberg's parameter (Table 4).

For detailed calculations such as are being undertaken here it is often necessary to include second neighbour interactions. The reason for this can be seen for the present case by comparing the band density of states calculated using only first neighbour interactions (Fig. 3) with that including second neighbours(Fig. 4).

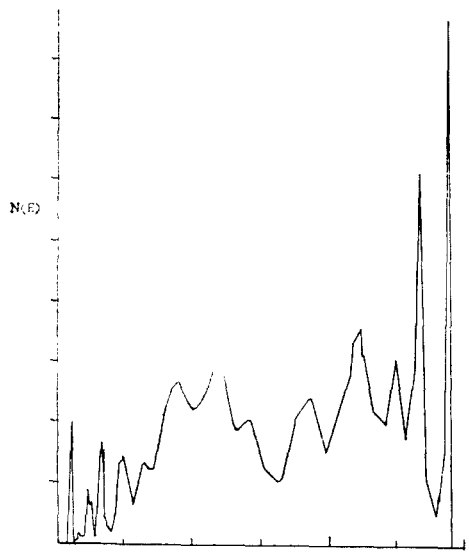

Fig. 1. D. O. S. as a function of energy C. F. S. 40 position NiBDOS 870 atoms cluster.

Table 1. Parameters for the Ni calculations. (Units: Rydbergs)

ddσ	−0.0167	−0.038	−0.038
ddπ	0.0076	0.0173	0.0173
ddδ	−0.0008	−0.0017	−0.0017

1) From Mattheiss[15] on first column
2) From Zornberg.[16] Crystal field terms adveraged. on 2nd and 3rd column

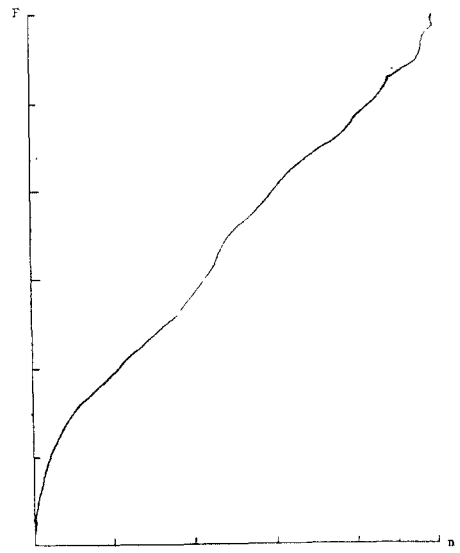

Fig. 2. **Fermi energy as a function of filling of the band NiBDOS position 870 atoms cluster.**

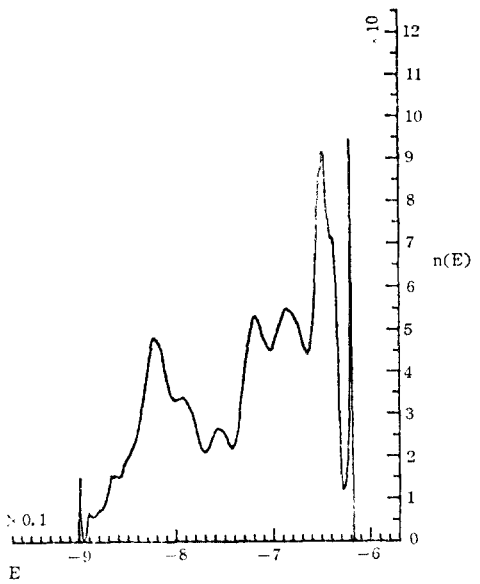

Fig. 3. *d*-band density of states for bulk Ni, calculated using; first ueighbours only.

Evidently the effect of second neighbours is significant. What then of third neighbours since it is usual for fcc to stop at first neighbours or include both second and third[13]. Fig. 5. shows the density of states calculated including third neighbours and although there is

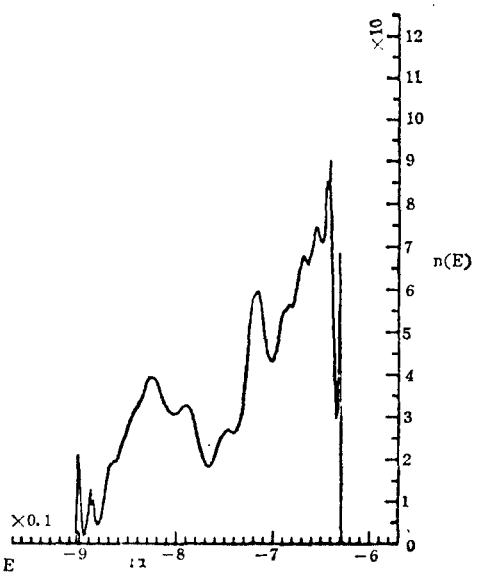

Fig. 4. *d*-band density of states for bulk Ni, Calculated using first and second neighbours.

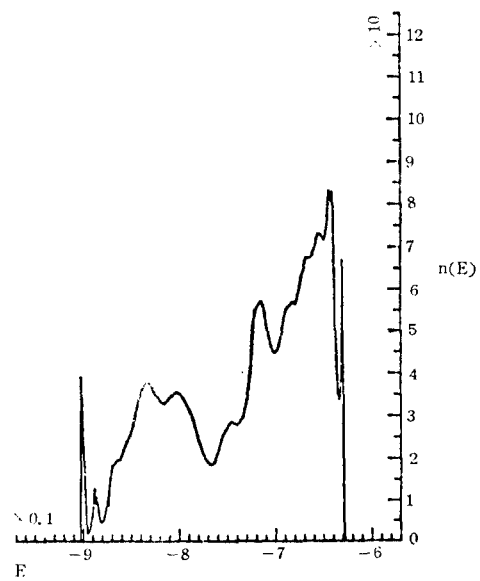

Fig. 5. *d*-band DOS for bulk Ni Calculated using first, second, third neighbours.

still some change it is no where near so great as on inclusion of second neighbours.

Energy, E, in Ryd., density of density of states, $n(E)$, in states per atom per Ryd., These and all subsequent densities of states are normalised to 10 d electron states per atom. The spikey structure at the band edges which appears here and in some other figures is due to individual eigenvalues of the cluster being resolved by the recursion method: these have negligible weight and will not be mentioned further. Cluster size 1098 atoms, 25 levels of the continued fraction.

The need to include second neighbours and the relative unimportance of third neighbours can be seen even more clearly in the filling of the separate symmetry bands.

Table 2. gives the final band self-energies E_n.[17] Those for the surface and subsurface layers each contain a constant (i.e. symmetry independent) shift due to charge self-consistency. To show only the effects of the altered shape of the potential at the surface compared to the bulk potential, column 3 gives, for the surface atoms, the change in self-energy relative to the bulk having removed this shift. For the subsurface atoms the potential is screened sufficiently quickly and the basis orbitals are sufficiently localised that the crystal field corrections for the subsurface layer have been taken the same as for the bulk.

Table 2.

Nickel surface and bulk band self-energies E_n(Ryd.)

	Bulk	Surface	Subsurface
xy	−0.7326	−0.7168	−0.7340
yz	−0.7326	−0.6969	−0.7340
zx	−0.7326	−0.6969	−0.7340
x^2-y^2	−0.7298	−0.7068	−0.7312
$3z^2-r^2$	−0.7298	−0.6976	−0.7312

It can be seen that the effects of the aspherical potential are even marked in the surface self-energies than in the interaction parmeters. By symmetry only the yz/zx orbitals remain degenerate at an (001) surface of an fcc crystal.

Two other attempts have been made to include corrections to the bulk self-energies at the surface. For Ni(001) Dempsey and Kleinman[5,18] in a tight-binding calculation estimated the relative shifts for the different d orbitals according to how much their lobes would be affected by the vacum potential, and used the criterion of charge neutrality for the surface layer to determine the overall shift. Their results are very like those obtained above, especially considering the relative shifts were only estimated on symmetry grounds and their whole calculation was ferromagnetic and included the sp-bands. The shifts they obtained were all positive, were of similar order of magnitude to those in table 2 and, most significantly had the same order according to size i.e.

$$yz/zx > 3z^2-r^2 > x^2-y^2 > xy$$

Although not given in detail it would appear their resoning was probably similar to that used above in discussing the calculated results. It is curious thought they do not appear to have considered any similar effects for the sp-band which was in their calculation, and they still obtain a d-band filling at the surface which is greater than in the bulk.

Table 3 gives the orbital-orbital interaction matrices which go to make up the secular matrix for certain pairs of atoms. The matrices are the result for an orbital on atom i of acting the hamiltonian on an orbital on atom j. They are calculated from Slater and Koster's interaction matrix[19]. for a given starting atom j. But the bulk parameters for bulk and surface self-energies for surface are used. First and second neighbour Ni interactions are included.

Table 3.

Nickel surface and bulk interaction matrices(Ryd.)

$R_i - R_j = (1/2,\ 0,\ -1/2)$

Acting on a surface atom j, result on a bulk atom i.

	xy	yz	zx	x^2-y^2	$3z^2-r^2$
xy	0.0110	−0.0175	0.0	0.0	0.0
yz	−0.0162	0.0120	0.0	0.0	0.0
zx	0.0	0.0	−0.0220	0.0098	0.0054
x^2-y^2	0.0	0.0	0.0092	−0.0008	−0.0156
$3z^2-r^2$	0.0	0.0	0.0045	−0.0174	0.0189

Bulk atoms.

	xy	yz	zx	x^2-y^2	$3z-r$
xy	0.0111	−0.0154	0.0	0.0	0.0
yz	−0.0154	0.0111	0.0	0.0	0.0
zx	0.0	0.0	−0.0220	0.0090	0.0052
x^2-y^2	0.0	0.0	0.0090	−0.0009	−0.0149
$3z^2-r^2$	0.0	0.0	0.0052	−0.0149	0.0162

$R_i - R_j = (1,\ 0,\ 0)$ (Second neighbour)

Surface atoms. (acting on j, result on i)

	xy	yz	zx	x^2-y^2	$3z^2-r^2$
xy	0.0021	0.0004	0.0	0.0	0.0
yz	−0.0002	0.0007	0.0	0.0	0.0
zx	0.0	0.0	−0.0018	−0.0042	0.0025
x^2-y^2	0.0	0.0	0.0039	−0.0024	0.0026
$3z^2-r^2$	0.0	0.0	−0.0029	0.0024	0.0021

(1, 0, 0) (Second neighbour) continued

Bulk atoms.

	xy	yz	zx	x^2-y^2	$3z^2-r^2$
xy	0.0038	0.0	0.0	0.0	0.0
yz	0.0	−0.0011	0.0	0.0	0.0
zx	0.0	0.0	0.00038	0.0	0.0
x^2-y^2	0.0	0.0	0.0	−0.0053	0.0051
$3z^2-r^2$	0.0	0.0	0.0	0.0051	0.0006

$R_i - R_j = (0,\ 0,\ -1)$ (Second neighbour)

Acting on surface atom j, result on bulk atom i.

	xy	yz	zx	x^2-y^2	$3z^2-r^2$
xy	−0.0013	0.0	0.0	0.0	0.0
yz	0.0	0.0044	0.0	0.0	0.0
zx	0.0	0.0	0.0044	0.0	0.0
$x-y$	0.0	0.0	0.0	0.0040	0.0
$3z^2-r^2$	0.0	0.0	0.0	0.0	−0.0088

Nickel surface and bulk interaction matrices (Ryd.)

Bulk atoms.

	xy	yz	zx	x^2-y^2	$3z^2-r^2$
xy	−0.0011	0.0	0.0	0.0	0.0
yz	0.0	0.0038	0.0	0.0	0.0
zx	0.0	0.0	0.0038	0.0	0.0
x^2-y^2	0.0	0.0	0.0	0.0036	0.0
$3z^2-r^2$	0.0	0.0	0.0	0.0	−0.0082

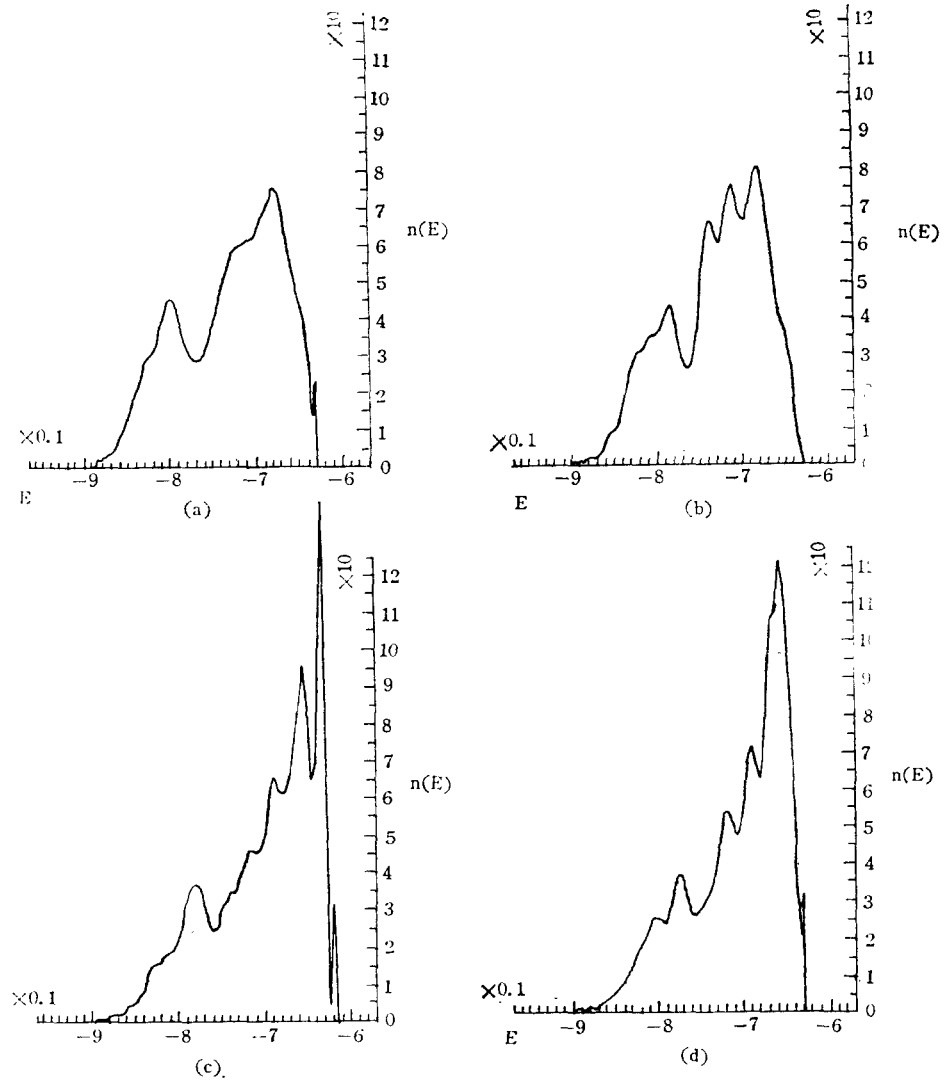

Fig. 6. Local densities of states for the Ni(001) surface, calculated using a) bulk parameters: b) aspherical potential corrections at the surface in the inter-atom interaction matrices only; c) as b) but corrections in the self-energies only; d) all aspherical potential corrections in the surface parameters. Energy, E, in Ryd., density of states, $n(E)$, in states per atom per Ryd. normalised to 10 electron states. Cluster size 591 atoms, 25 levels of the continued fraction.

Ⅳ. Surface density of States at Ni(001)

The surface density of states shows directly the effects of the surface on the electronic structure, and is important experimentally for understanding surface effects in photoemission[20], as well as being relevant to surface energies[21] and chemisorption theory[22]. In this section we shall calculate Ni(001) surface using the recursion method. We can obtain the full surface density of states $N(E)$ (4) from summing over the Ni(E).

Fig. 6. gives the band local densities of states for an atom in the (001) surface plane of Ni calculated using bulk parameters(fig. 6. a) including the effect of the aspherical potential in the interaction matrices and self-energies separately (fig. 6b, c), including all aspherical potential corrections in the surface parameters (fig. 6. d).

Plots of the symmetry resolved local densities of states for the bulk, surface and subsurface layers are shown in fig. 7, and their properties are discussed below.

The surface densities of states have smaller root mean square widths than the bulk densities of states whereas the subsurface densities of states have roughly the same root mean square widths as the bulk. Moreover the narrowing relative to the bulk is greatest for the surface yz/zx density of states. This is in agreement with the result that second moment of the density of states equals the sum of the squares of the hopping parameters to nearest neighbour orbitals[23,24]. As noted by Davenport et al[9] the yz symmetry orbitals have lost the greatest proportion of important nearest neighbours and thus their local density of states shows most narrowing. Conversely the subsurface atoms have a full complement of first nearest neighbours and thus have about the same square width to their local densities as found in the bulk. Comparison with previous

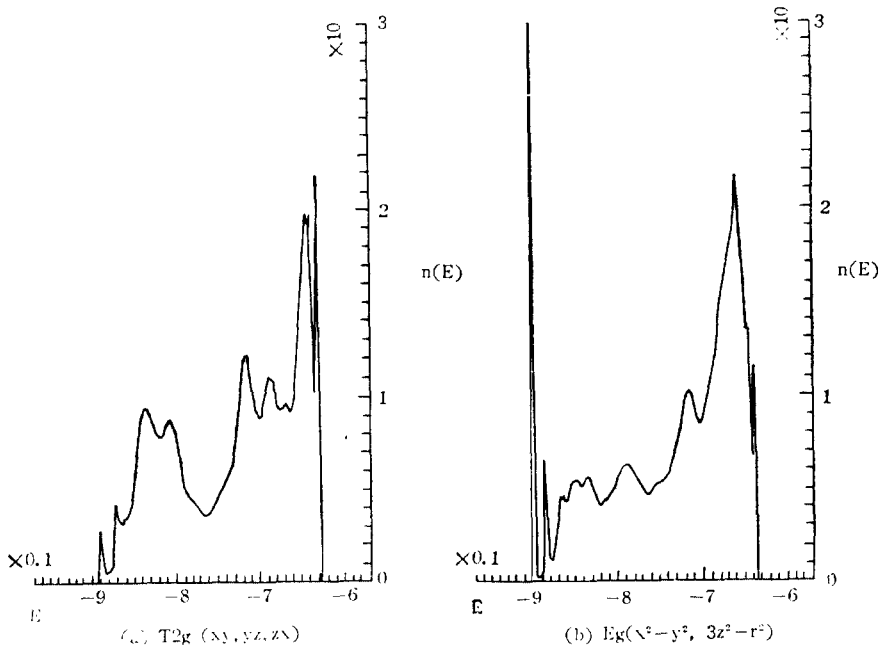

Fig. 7. Symmetry resolved local densities of states for Ni. 7(a, b) bulk $xy/yz/zx$, $x^2-y^2/3z^2-r^2$ respectively.

surface calculations (e.g. those cited above) and of fig. 6a with fig. 6d shows that the narrowing appears to be greater than that obtained using ordinary bulk parameters at the surface.

Energy. E. in Ryd., density of states, $n(E)$, in states per atom per Ryd., normalised to 10 d electron states per atom. Cluster size 591 atoms, 25 levels of the continued fraction.

V. Photoemission and the surface density of states

The process of photoemission, in which a photon excites an electron out of a solid, can be dominated by either bulk or surface effects, depending largely on the mean free part of the excited electron inside the solid[30]. When the mean free path is long it is believed that bulk processes dominate, in which the electrons undergo K-conserving transitions, and it is well known that this explains as a function of energy and angle in angular resolved photoemission experiments on Cu(001)[25]. On the other hand when the mean free path is shortened by many electron effects so that the wavevector perpendicular to the surface need not be conserved, the emitted electrons can reflect the surface density of states. Features in photoemission spectra which are in sensitive to photon energy are usually due to the surface electronic structure rather than K-conserving bulk transitions. On the Ni (001) surfaces Pendry has calculated the photocurrent over a wide range of emission angles and obtained good agreement with photoemission experiments[27]. And Woodruff et al[26] have demonstrated the feasibility of K-resolved inverse photoemission spectroscopy (KRIPES) on Cu (001) and Ni (001)[26]. The normal-incidence KRIPES data for Ni(001) are shown in Fig. 8, and they have shown that the observed energy dispersion and relative peak intensities can be understood in terms of a rather simple model based on bulk band structure.

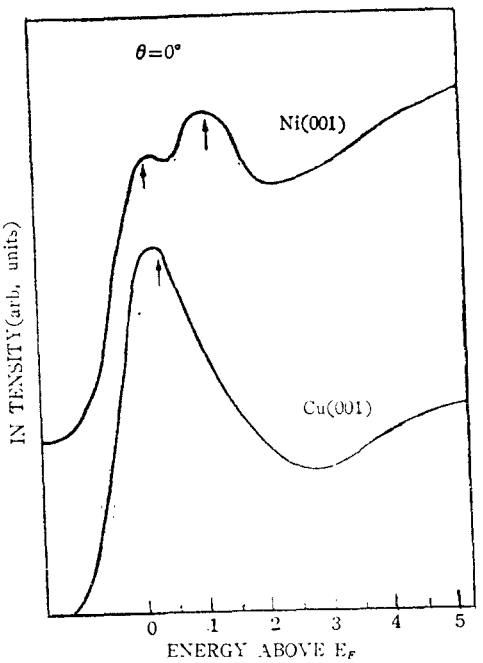

Fig. 8. Comparison of the normal incidence isochromat spectra for Ni(001) and Cu (001). The arrows indicate the final energies for possible direct transitions.

VI. Conclusion

Our calculations have clearly demonstrated the recursion method to describe surface states of transition metals based upon a LCAO. The parameters for the calculation are obtained including two important factors, the effect of charge transfer and aspherical environment for the surface atoms. The Ni bulk density of states and Fermi energy are obtained and d-band DOS also obtained. LDOS for an atom in the (001) surface plane of Ni are calculated for the bulk, surface and subsurface layers. The surface densities of states have smaller root mean square widths than the bulk densities of states. We obtain good agreement with photoemission experiments.

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