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Electronic Structure of Vacancies in Transition Metals

By

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The electronic structure of vacancies in Fe, Ni, and Cu transition metals and in Al is calculated by linear augmented plane waves (LAPW) in muffin-tin Green function approach. The electronic structure of vacancies shows a strong hybridization with metallic d-states, and a considerable effect is observed on the s- and p-electrons in the density of states. The charge transfer differs from the similar case of the simple metals.

Die Elektronenstruktur von Leerstelle in den Übergangsmetallen Fe, Ni und Cu und in Al wird mit der LAPW-Methode in der Näherung der MT-Greenschen Funktionen berechnet. Die Elektronenstruktur der Leerstellen zeigt starke Hybridisierung mit den d-Zuständen der Metalle. Ein merklicher Effekt wird an s- und p-Elektronen in der DOS beobachtet. Der Ladungstransfer unterscheidet sich von dem in einfachen Metallen.

1. Introduction

As it is well known, vacancies play a significant role in mechanical properties of solids, especially in the defect stabilizing processes, and determine the plasticity and strength of materials. The electronic structure of vacancies must be calculated in order to determine the effects of vacancies on various physical properties. In our present paper the results of this calculation for vacancies in the metals Al, Cu, Ni, and Fe are shown.

The electronic structure of vacancies has been studied for a long time with methods based on the total calculation — from first principles and by quasi-empirical methods as well — of the electronic structure in a crystalline state with vacancies. In the jellium model [1 to 3], a vacancy is simulated as a "hole" in a positively charged environment, whereas the vacancy potential is assumed to be spherically symmetric and the crystal structure of the metal is ignored. The accuray of these calculations has been increased by the introduction of pseudopotential methods [3]. The electronic structure of a vacancy in Al matrix has been studied using a pseudopotential scheme [4, 5], in which the environment of the vacancy was simulated by a large super cell. The agreement of the calculated value (0.56 eV) and of the experimental one (0.66 eV) for the vacancy-formation energy is satisfactory [5].

The observation that the positron capture on vacancies increases the positron lifetime, has been studied using the APW calculation for Al, in which the vacancy environment was simulated by a supercell containing 27 atomic sites [6].

In transition metals the application of the above methods is rather difficult. The jellium model is unsuitable for electron states in transition metals which strongly differ from the free electron approximation. The major disadvantage of the supercell method is that it requires too much computer time and, in addition, the proper screening simulation of the defect interaction effects.

In the case of transition metals the simplest method would be the calculation by the Green function [7, 8], which can be used to find the self-consistent electronic density of states with the accurate treatment of the electronic structure of the host metal matrix. This was the method used for the calculations of Cu [9] and Al [10].

The ideal lattice Green function was calculated from self-consistent host band structures [9] (KKR Green-function method). Calculation were made in two ways: taking and not taking into account the perturbed potential of the Cu atoms closest to the vacancy. If taken into account, it has a great influence on the distribution of the electron density in the system. The perturbed potential of neighbouring atoms was also taken into account for the calculation of the electron density around the defect [10].

Thus, although the Green-function method has several obvious advantages, it is only one among several methods to calculate the electronic structure of vacancies in transition metals.

In our present paper the calculations on the electronic structure of vacancies in Al, Cu, Ni, and Fe, and their peculiarities are presented by the Green-function method. Contrary to [9], our approach is based on the LAPW method (linear augmented plane waves) for ideal crystals. Using a linear expansion of the radial solution for the Schrödinger equation in a MT sphere for the energy we achieved a high speed of numerical calculation without losing accuracy to a great extent.

2. Method of the Calculation

The ground-state properties are given, using the Green function of the system. The imaginary part of the Green function describes the density of states of quasi-particles and, if ignoring the attenuation, it gives directly the density of electron states.

The Green function of the crystal can be written as an expansion of the solution of the Schrödinger equation in a MT sphere $R_l^n(R; E) Y_L(r)$, where $L = (l, m)$ is the orbital quantum number, r the radius vector, E the energy, $Y_L(r)$, spherical harmonics with energy-dependent coefficients $G_{LL'}^{nn'}(E)$,

$$G(r + R^n, r' + R^{n'}, E) = -i\delta_{nn'}\varkappa \sum_L R_l^n(r_<, E) Y_L(r) H_l^n(r_>, E) Y_L(r')$$

$$+ \sum_{L, L'} R_l^n(r, E) Y_L(r) G_{LL'}^{nn'} R_{l'}^{n'}(r', E) Y_{L'}(r'), \tag{1}$$

where $r_< = \min(r, r')$, $r_> = \max(r, r')$, $L = (l, m)$ are the orbital quantum numbers, R and $R^{n'}$ are the atom positions, $\varkappa = \sqrt{E}$,

$$H_l^n(r, E) = R_l^n(r, E) + iN_l^n(r, E),$$

$$R_l^n(r, E)|_{r \to \infty} = j_1(r\varkappa) - i\varkappa t_l^n(E) h(r\varkappa),$$

$$H_l^n(r, E)|_{r \to \infty} = h_1(r\varkappa),$$

where the $G_{LL'}^{nn'}(E)$ are the energy-dependent coefficients of the Green function, $N_l^n(r; E)$ the nonregular solutions of the radial Schrödinger equation in the n-th MT sphere with centre R^n,

$$W[R_l^n(r, E), H_l^n(r, E)] = \frac{i}{r^2 \varkappa}. \tag{2}$$

With the help of the perturbed potential ΔV, the Green function of the system can be determined using the Dyson equation,

$$G = G^0 + G^0 \Delta V G, \tag{3}$$

where G and G^0 are the Green functions of the perturbed and unperturbed systems, respectively. With a single perturbed muffin-tin potential and taking into account only the s-, p-, and d-states, the Dyson equation (3) for the coefficient (1) takes the form of a scalar equation [8], as follows:

$$G_{LL}^{nn}(E) = G_{LL}^{0nn}(E) [1 - G_{LL}^{0nn}(E) \Delta t_l^n(E)]^{-1}, \tag{4}$$

where $\Delta t_l^n(E)$ is the deviation from the potential scattering matrix of the MT sphere. The density of states in the MT sphere of a vacancy Ω_v can be determined using the above calculated coefficients,

$$n(E) = \frac{-2}{\pi} \int_{V_{MT}} \text{Im } G(r, r, E) \, dr \tag{5}$$

and the electronic density can be calculated with the following formula:

$$n(r) = \frac{-2}{\pi} \int_{-\infty}^{E_F} \text{Im } G(r, r, E) \, dE. \tag{6}$$

The density functional theory can be applied for the calculation of the potential and the new electronic density produced by this potential. The self-consistent solution is obtained by a standard iteration technique. The exchange-correlation potential was treated by Vosko parameterization [11].

The electronic structure of the ideal crystal was calculated using a self-consistent LAPW method. The method is described in details elsewhere [12]. The imaginary part of the Green function can be obtained from the formula based on the expansion of the $R_l^n(r, E)$ with respect to energy [12].

The perturbed potential near a vacancy cannot be considered as small. Perturbations of the electron density and potential outside the MT sphere have to be taken into account. Best results were obtained using the condition of neutrality of the screened defect [10].

In our present calculations the perturbation of the electron density near to the defect is given by the following formula:

$$\Delta \varrho_{out}(r) = \frac{1}{r^2} (A + Br + Cr^2) \exp(-r/r_0), \tag{7}$$

where r_0 is the screening length of the electron gas for the area between spheres and the coefficients A, B, and C were selected from the following conditions:

A: continuity of $\varrho(r)$ on the boundary of the MT sphere;

B: continuity of the derivative $\varrho'(r)$ on the boundary of the MT sphere;

C: charge neutrality of the total system. The $\Delta\varrho_{out}(r)$ in [10] did not contain a term corresponding to the linear screening part, although the results of both approximations were almost the same — as will be shown later: the electron density increases in the centre of the MT sphere and the increase of the coefficients in the density of states are almost the same; and at the same time (7) corresponds to the known analytic result of the solution of the screening problem.

The value of r_0 has to be corresponded to some effective screening length. In a wide enough range of electron density, the characteristic value of r_0 for metals is about 0.65 at units [13]. In the case of a heterogeneous gas, an "average" value must be used in the calculations.

3. Results and Discussion

3.1 Aluminium

Conduction electrons in aluminium represent a practically homogeneous electron gas and can be described by the jellium model. In this case this calculation was the control of the validity of our present one. We have compared our results with the results of earlier investigations.

The density of states of electrons, taking and not taking into account the perturbation of the electron density around a vacancy, is shown for Al in Fig. 1. The calculated values of phase shfits, density of states at the Fermi level, partial charges, and residual resistances for all the metals considered are collected in Table 1. As has been expected, taking into account the perturbation around vacancies, we obtained a great charge transfer in the MT sphere of the vacancy, even greater than was estimated by other methods. The partial s- and p-charges have been doubled. The value of the electron density in the centre of the MT sphere has been increased from 4×10^{-3} to 19×10^{-3} at. units similarly as in earlier works:
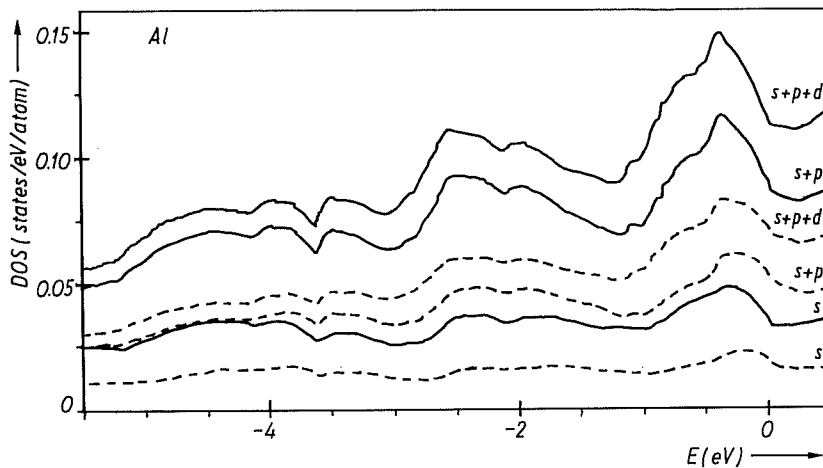

Fig. 1. Density of electronic states (DOS) around a vacancy in Al. Sets of perturbed (solid lines) and unperturbed (dashed lines) cases are given. The curves correspond to the s, s + p, and s + p + d density of states, from bottom to top, respectively (the energy zero fixed at E_F)

Table 1

Generalized phase shifts η_L (in rad), density of states at the Fermit level $n(E_F)$ (in electrons/atom), residual resistance ϱ/c (in $\mu\Omega$/cm/at%), partial charges $N_i(e)$, and the charge transfer into the Wigner-Seitz cell of the vacancy $\Delta Q(e)$ taking and not taking into account the perturbed potential near the vacancy. The results of [10] are also shown

parameter	Al		[10]
	without perturbation	with	
η_s	−1.15	−0.82	−0.83
η_p	−1.71	−0.52	−0.54
$n(E_F)$	0.98	1.57	
ϱ/c	0.92	0.50	0.52
N_s	0.12	0.26	
N_p	0.17	0.30	
N_d	0.07	0.11	
ΔQ	−1.15	−1.45	

22×10^{-3} at. units [10] and 25×10^{-3} at. units [6]. The phase shift of the potential of the vacancy and the residual resistance are very close to the values obtained in [10], but are lower than the experimentally observed ones (1.2 $\mu\Omega$/cm). We note that the peaks of the density of states have practically remained at the same place, no shift is observable.

Our results show that the given model exactly reproduces, for vacancies in Al matrix, the results of much more complicated and computer-time consuming calculations; while taking into account the perturbed potential near a defect, the distribution of the electron density is strongly influenced. We came to the conclusion that for all the peculiarities of the aluminium−vacancy system our model is effective, and shows the basic effects of the electron density.

3.2 Copper, nickel, and iron

The jellium model is totally inadequate for the calculation of the electronic structure of vacancies in transition metals because of the resonance d-states, which cannot be precisely described by the huge average of the jellium model. More satisfactory results can be achieved by our above-described muffin-tin Green-function (MTGF) method.

The results of the calculations of the density of electronic states for the metals Cu, Ni, and f.c.c.-Fe with vacancies, without and with taking into account the perturbation of the nearest neighbour atoms, are shown in Fig. 2 to 4. Fig. 2 shows also the density of electronic states for vacancies in Cu without taking into account the perturbation effect of (7). The calculation, as the figures show, results an increase of the partial coefficients and the shift of the characteristic features in the density of states to a lower energy level. This can be understood if we take into account the effect of perturbation, which leads to the potential dependence. In all the cases a strong hybridization of vacancy states at the d-states of metals was obtained, which is shown by the presence of three peaks in the density of states. The first (strongest one) has basically s-character. The calculated positions in energy are −4.15, −3.2, and −2.9 eV for Cu, Ni, and Fe, respectively. The generalized phase shifts
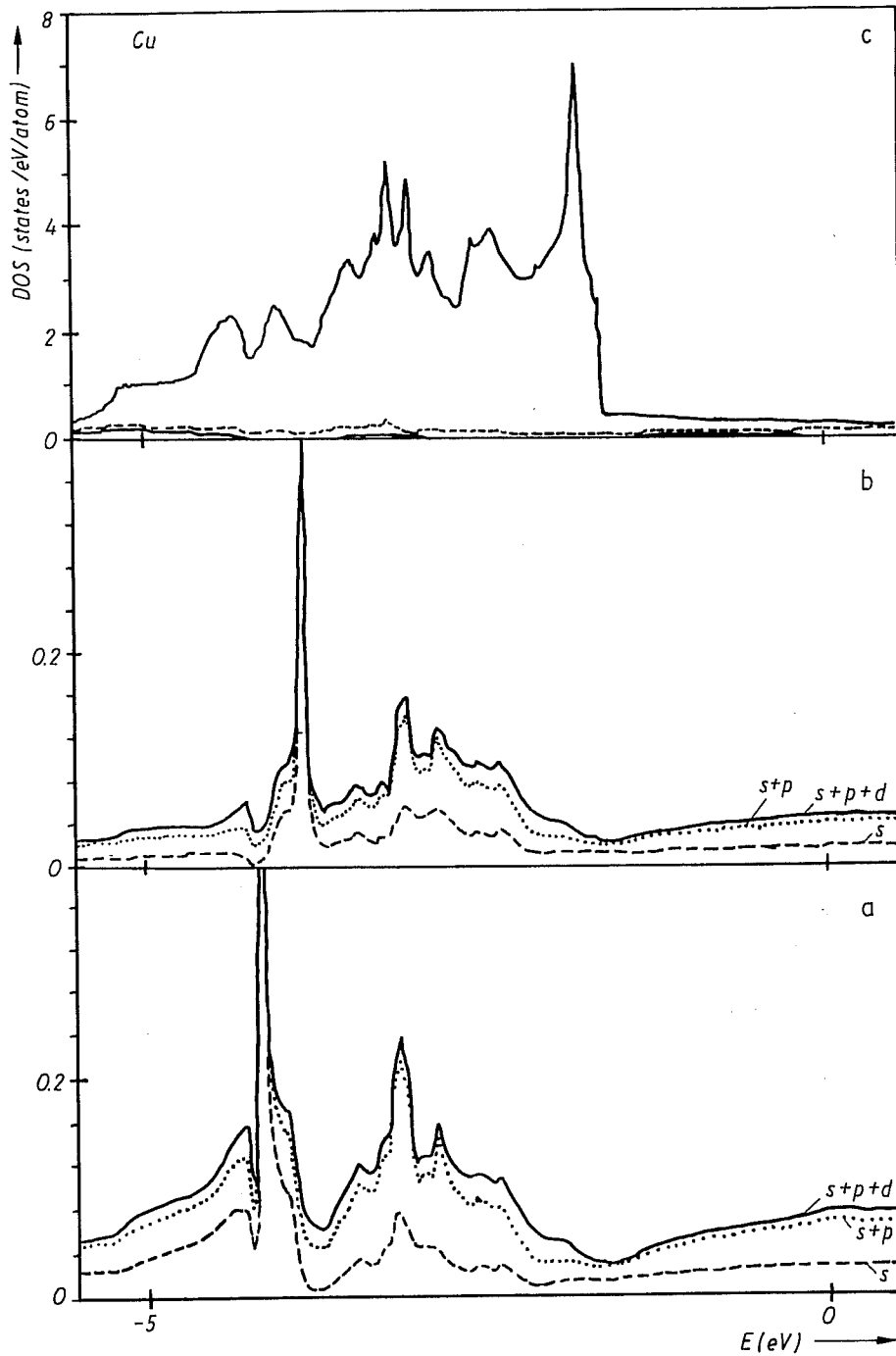
Fig. 2. DOS for vacancies in Cu a) with and b) without perturbations; c) DOS for Cu metal. The curves correspond to the partial DOS, from bottom to top, of s, s + p, and s + p + d states, respectively (energy zero fixed at E_F)
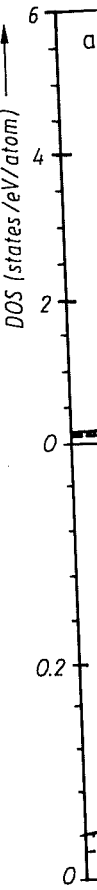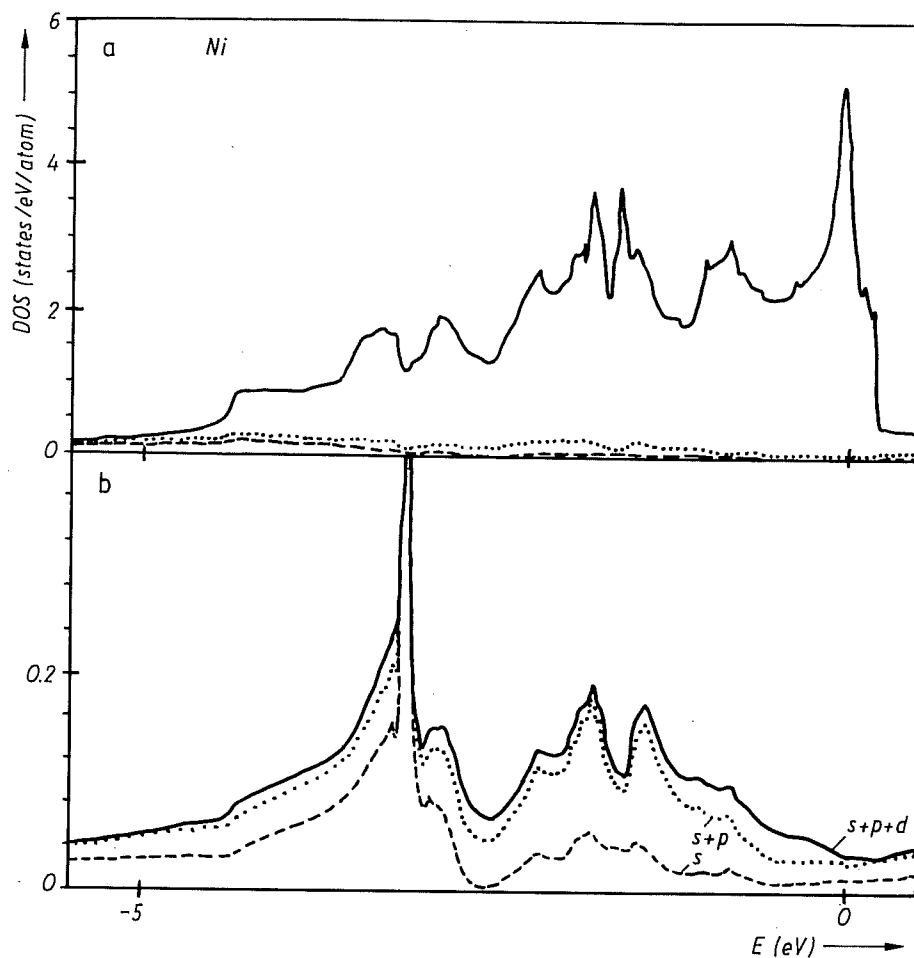
Fig. 3. DOS for a) vacancies in Ni with perturbations, b) Ni metal. The curves correspond to the partial DOS, from bottom to top, of s, s + p, and s + p + d states, respectively. (The zero energy is fixed at E_F)

for the potential of the MT sphere of vacancies, the density of states at the Fermi level, the partial charges of the Wigner-Seitz sphere, and parameters of the distribution of electronic density are shown in Table 2. The major effect for the density of states is caused by sp-states. The effect of s- and p-electrons, practically, are the same, while the effect of the d-electrons is slighter. The charge-transfer effect into the Wigner-Seitz cell has the value of about one electron. If the perturbation of atoms was taken into account in the first coordination sphere [9], the values of $\varrho(0)$ and $\varrho(R_s)$ are 5×10^{-3} at. and 17×10^{-3} at. units, respectively. For the density of electronic states the same peculiarities were determined (peaks appeared roughly with the same energies in relation to the Fermi level). Recently a semi-experimental calculation of the phase shifts for the potentials of vacancies in Cu was made by measuring the anisotropy of scattering effects, [14]. The s-phase and p-phase shifts are equal to 0.75 and 0.72 rad, respectively. Our results, as Table 2 shows, are lower. The reason for this discrepancy can be explained by the fact that the
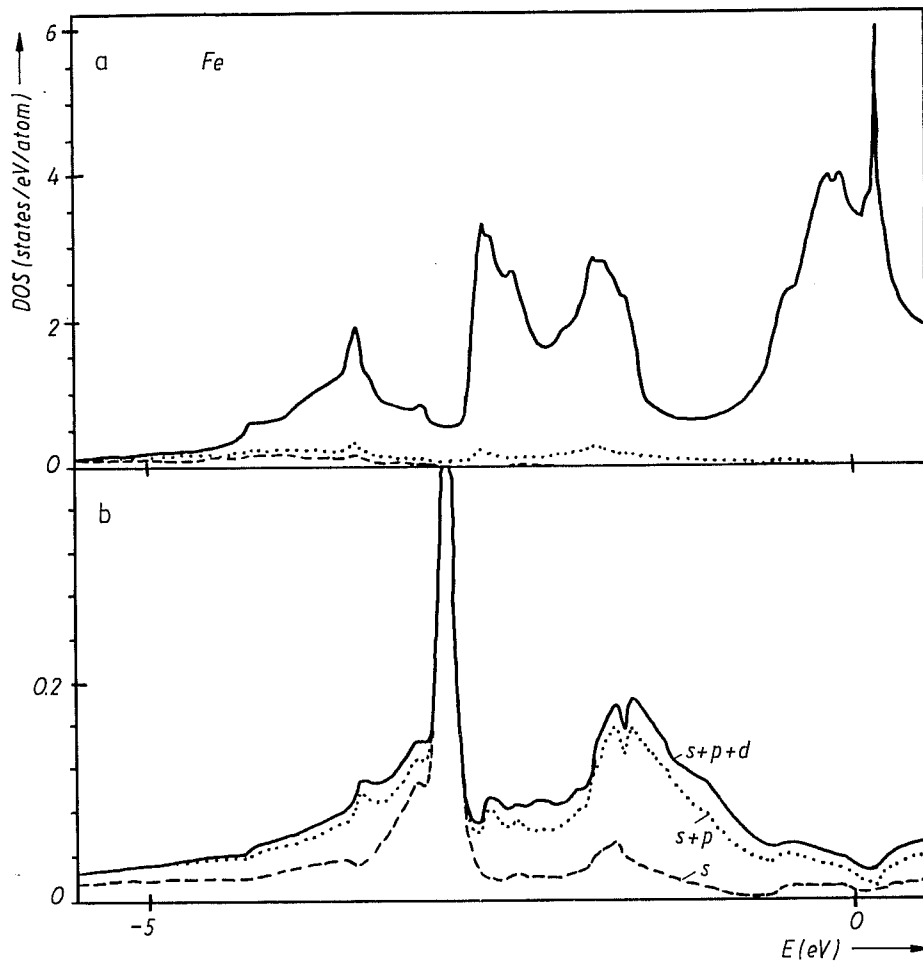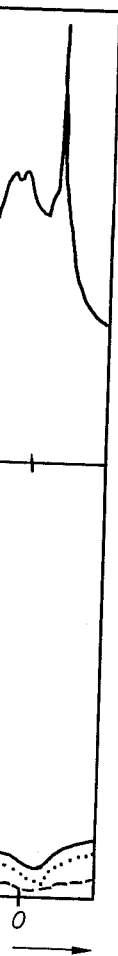
Fig. 4. DOS for a) Fe metal, b) vacancies in f.c.c.-Fe with perturbations. The curves correspond to the partial DOS, from bottom to top, of s, s + p, and s + p + d states, respectively (energy zero fixed at E_F)

determination of the phase shift of such a strong perturbation in the crystal will lose its clear "theoretical" sense. Phase shifts had been measured in experiments and must be compared to some average phase shifts for clusters of perturbed atoms.

4. Conclusion

In the frame of our present model, we got the result that the electronic structure of vacancies in transition metals has the following properties:

    a) strong hybridization of the vacancy states with the d-states of the metal is obtained;

    b) an s-peak appears in the density of states;

    c) great effect of the s- and p-electrons on the electron density is observed;

    d) the charge transfer in the Wigner-Seitz cell is about one electron and in general the effects of the perturbation in the first coordination sphere on the density of states cause characteristic effects.

Table 2

Generalized phase shifts η_L (in rad), density of states at the Fermi level $n(E_F)$, partial charges $N_i(e)$, the charge transfer into the Wigner-Seitz cell of the vacancy $\Delta Q(e)$, and the parameters of the distribution of the electron density: the density at the centre $\varrho(0)$ and on the boundaries $\varrho(R_s)$ of the MT sphere (10^{-3} at. units) for vacancies in Cu, Ni, and Fe

parameter	Cu	Ni	Fe
η_s	−0.37	−0.14	−0.12
η_p	−0.25	−0.08	−0.07
$n(E_F)$	1.05	0.48	0.44
N_s	0.29	0.31	0.23
N_p	0.25	0.27	0.22
N_d	0.07	0.09	0.07
sQ	−1.00	−1.12	0.77
$p(0)$	3.5	4.0	2.5
$p(R_s)$	16.5	19.9	13.2

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30*