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Electronic Structure of Impurities in Cu, Calculated Self-Consistently by Korringa-Kohn-Rostoker Green's-Function Method

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We report calculations of the electronic structure impurities in Cu by appying the Korringa-Kohn-Rostoker Green's-function method. We use a self-consistent host band structure for the calculation of the Green's function. The additional effort for calculating the impurity problem self-consistently is considerably smaller than for calculating the host band structure. As examples, the local densities of states for Ni, Zn, Ga, and Ge impurities in Cu are presented.

Because of the technological importance of point defects in metals, there is a great need for a proper theoretical understanding of their electronic properties. Previous theoretical work has been mainly limited to simple metals to which pseudopotential theory of jellium models[1] can be applied. Exceptions are cluster calculations, which are restricted to a small number of atoms, or supercell models exhibiting a periodic arrangement of defects. For instance, such a model has been used recently by Gupta and Siegel[2] for vacancies in Al. Both methods have serious disadvantages: In cluster calculations the embedding in the ideal lattice is neglected whereas supercell calculations necessarily include interaction effects between the periodically arranged defects. A Green's-function method is more appropriate to treat the defect problem, since it takes full advantage of the periodicity of the host lattice and the short range of the impurity potential.

For metals a Green's-function method based on the Korringa-Kohn-Rostoker (KKR) band-structure formalism has been proposed by Dupree,[3] Beeby,[4] and others.[5] The host lattice is represented by a periodic array of muffin-tin potentials and the impurity is described by a single perturbed potential. Calculations based on this method have been performed by Harris,[6] Lasseter and Soven,[7] Terakura,[8] and Coleridge, Holzwarth, and Lee.[9] Similar calculations based on a pseudo Green's-function approach have been performed by Smith.[10] One unsolved problem in these calculations is the choice of the potentials. Normally the potentials are constructed with the Mattheiss prescription from atomic charge densities. They depend on the chosen atomic configuration which, however, may be changed considerably in a solid.

In this Letter we report calculations based on the KKR Green's-function method for Ni, Zn, Ga, and Ge impurities in Cu for which we have determined the potentials self-consistently. We have employed the Hohenberg-Kohn-Sham formalism in the local-density approximation with the exchange-correlation potential of Hedin and Lundqvist.[11] Our method can be applied to both transition and simple metals and represents in a sense an analog to the recently developed Green's-function method for semiconductors.[12]

The electronic charge density, which is needed for a self-consistent determination of the potential, is related to the one-electron Green's function of the perturbed crystal

$$\rho(\vec{r}) = -(2/\pi)\int_{-\infty}^{E_F} dE\, \operatorname{Im} G(\vec{r},\vec{r},E). \tag{1}$$

Similarly the local density of states in a volume V is obtained as

$$n_V(E) = -(2/\pi)\int_V d^3r\, \operatorname{Im} G(\vec{r},\vec{r},E). \tag{2}$$

We will briefly outline the basic equations for the KKR Green's function.[13] In each unit cell m,n the Green's function G is expanded into eigensolutions of the local muffin-tin potential:

$$\begin{aligned} G(\vec{r}+\vec{R}^m,\vec{r}\,'+\vec{R}^n) = {} & (E)^{1/2}\delta_{mn}\sum_L Y_L(\vec{r})Y_L(\vec{r}\,')R_l^m(r_<,E)H_l^m(r_>,E) \\ & + \sum_{LL'} Y_L(\vec{r})R_l^m(r_1E)G_{LL'}{}^{mn}(E)R_{l'}{}^n(r',E)Y_{L'}(\vec{r}\,'). \end{aligned} \tag{3}$$

Here $\vec{r}$ and $\vec{r}\,'$ are restricted to the Wigner-Seitz cell, and $r_<$ or $r_>$ are the smaller or larger of $|\vec{r}|$ and $|\vec{r}\,'|$. Y_L are real spherical harmonics. The radial eigenfunctions $R_l^m(r,E)$ are regular at the origin and are given outside the muffin-tin radius R_{mt} by a combination of spherical Bessel and Neumann functions: $\cos\delta_e{}^m j_l((E)^{1/2}r) - \sin\delta_l{}^m n_l((E)^{1/2}r)$.

$H_l{}^m = N_l{}^m - iR_l{}^m$ is the analog to the spherical Hankel function and also contains a nonregular solution $N_l{}^m$ which is given asymptotically by $\sin\delta_l{}^m j_l((E)^{1/2}r) + \cos\delta_l{}^m n_l((E)^{1/2}r)$. Here $\delta_l{}^m(E)$ are the phase shifts for the muffin-tin potential in cell m. The only unknowns in Eq. (3), the Green's-function matrix elements $G_{LL'}{}^{mn}(E)$, can be obtained by a Dyson equation from the matrix elements $G_{LL'}{}^{0\,mn}(E)$ of the Green's function G^0 for the ideal crystal

$$\tilde{G}_{LL'}{}^{mn}(E) = \tilde{G}_{LL'}{}^{0\,mn}(E) + \textstyle\sum_{L''} \tilde{G}_{LL'}{}^{0\,m0}(E)\,\Delta t_{l''}(E)\,\tilde{G}_{L''L'}{}^{0n}(E), \tag{4}$$

where $\tilde{G}_{LL'}{}^{mn}(E) = G_{LL'}{}^{mn}(E)\exp(-i\delta_l{}^m - i\delta_l{}^n)$. $\Delta t_l = t_l - t_l{}^0$ is the difference between the on-shell t matrices of the impurity, which is assumed to be at the origin, and the host atoms and can be expressed by the phase shifts ($t_l = -E^{-1/2}\sin\delta_l \exp i\delta_l$). Equation (4) is relatively simple to solve, once the ideal Green's function is known, since the perturbation is localized at the impurity cell only. For most applications one only needs the impurity Green's function $\tilde{G}_{LL'}{}^{00}$ which for cubic symmetry is diagonal in angular momentum, if $l, l' \leq 2$. The Dyson equation then decomposes into four scalar equations for s, p, d-T_{2g} and d-E_g scattering.

The major problem is the determination of the ideal Green's-function elements $G_{LL'}{}^{0\,mn}(E)$. By inserting the KKR *Ansatz* for the wave function

$$\psi_{\vec{k}\nu}(\vec{r} + \vec{R}^m) = \exp(i\vec{k}\cdot\vec{R}^m)\textstyle\sum_L i^l \varphi_L(\vec{k}\nu) Y_L(\vec{r}) R_l(r, E)$$

in the spectral representation for the Green's function

$$G^0(\vec{r}, \vec{r}', E) = \sum_\nu \int_{\mathrm{BZ}} d^3k\, \frac{\psi_{\vec{k}\nu}(\vec{r})\,\psi_{\vec{k}\nu}{}^*(\vec{r}')}{E + i0^+ - E_{\vec{k}\nu}}, \tag{5}$$

one immediately obtains for the imaginary part

$$\mathrm{Im}\,G_{LL'}{}^{0\,mn}(E) = (E)^{1/2}\theta(E)\delta_{mn}\delta_{LL'} - \pi \textstyle\sum_\nu \int_{\mathrm{BZ}} d^3k\, \delta(E - E_{\vec{k}\nu})\,\varphi_L(\vec{k}\nu)\,\varphi_{L'}(\vec{k}\nu)\, i^{l-l'} \exp[i\vec{k}\cdot(\vec{R}^m - \vec{R}^n)]. \tag{6}$$

The real part can be obtained by a Kramers-Kronig integration:

$$\alpha_{ll'}(E)\,\mathrm{Re}\,G_{LL'}{}^{0\,mn}(E) = \pi^{-1}\textstyle\int_{-\infty}^{\infty} dE'\,P(E' - E)^{-1}\alpha_{ll'}(E')\,\mathrm{Im}\,G_{LL'}{}^{0\,mn}(E'), \tag{7}$$

with

$$\alpha_{ll'}(E) = \textstyle\int_0^{R\mathrm{mt}} dr\, r^2 R_l(r, E) R_{l'}(r, E).$$

In actual calculations the integration in (7) cannot be done up to infinite energies and one has to choose a cutoff energy E_c. For $m = n$ this means that above E_c one replaces the Green's function by that for free electrons. Alternatively one can evaluate the Green's-function elements by a Brillouin-zone (BZ) integration over the reciprocal KKR matrix

$$\begin{aligned} G_{LL'}{}^{0\,mn}(E) = {} & -\delta_{LL'}[t_l{}^0(E)]^{-1} \\ & -[t_l{}^0(E)\,t_{l'}{}^0(E)]^{-1} V_{\mathrm{BZ}}{}^{-1} \textstyle\int_{\mathrm{BZ}} d^3k [(E)^{1/2}\cot\delta_l{}^0\delta_{LL'} + A_{LL'}(\vec{k}, E)]^{-1} \exp[i\vec{k}\cdot(\vec{R}^m - \vec{R}^n)]. \end{aligned} \tag{8}$$

Contrary to (7), the integrand is only needed in the desired energy range. However, an additional difficulty arises due to the strong E and $\vec{k}$ depencence of the KKR structure constants.

We have calculated the imaginary part of the Green's function according to Eq. (6) and the real part by both methods. The BZ integrations were performed with the tetrahedron method[14] with 6144 tetrahedrons in the irreducible part of the Brillouin zone. For this the KKR matrix in Eq. (8) was expanded into eigenvectors.[7] Figure 1 shows that both methods agree very well, so that the much faster Kramers-Kronig integration with a cutoff at about 1 Ry can be used.

By applying this method to impurities in Cu, we have used the density-functional formalism with the local exchange-correlation approximation of Hedin and Lundqvist.[11] For this choice of the exchange-correlation potential, the self-consistent host potential of Cu has been calculated by Moruzzi, Janak, and Williams[15] and is used to generate the Cu band structure and the ideal Green's functions. The impurity potential is then calculated self-consistently from the charge density. For this a density change only in the impurity muffin-tin cell is assumed. The core states of the impurity are frozen and taken

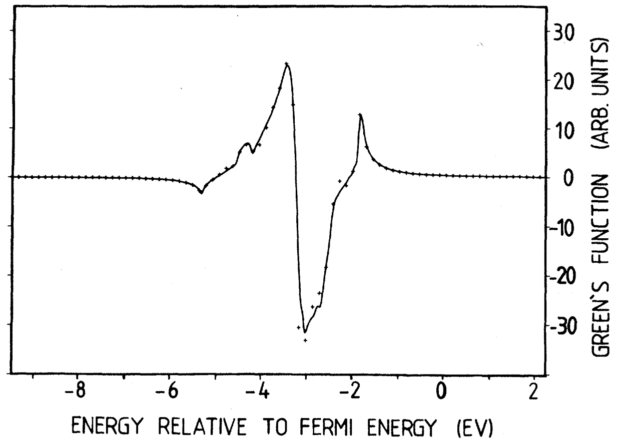

FIG. 1. Real part of the Green's function for d-E_g symmetry and $m=n$ (i.e., $\alpha_{22}\mathrm{Re}G_{E_g}^{mm}$) as function of the energy relative to the Fermi energy. The self-consistent potential of Moruzzi, Janak, and Williams (Ref. 15) was used. Solid line, Kramers-Kronig integration: pluses, direct integration of Eq. (8).

from an atomic calculation. As usual self-consistency is achieved by iteration, i.e., solving Eq. (4), calculating a new impurity potential, etc. Obviously the Green's-function method is of considerable advantage for this self-consistency procedure: For each iteration only the relatively simple one-center problem for the impurity has to be recalculated, whereas the Green's functions for Cu have only to be determined once.

As a result of our calculations, Fig. 2 shows the local densities of states within the muffin-tin sphere for Ni, Zn, Ga, and Ge impurities in Cu. For comparison the density of states for pure Cu is also given.

For Ni, our calculations give a virtual bound state centered at 1.10 eV below the Fermi energy with a half width of $\Delta = \frac{1}{2} \times 0.35$ eV. Experimental values for the peak position are 1.0 eV (soft-x-ray scattering measurements of Durham *et al.*[16]) and 0.8 eV (x-ray photoelectron spectroscopy measurements of Hüfner, Wertheim, and Wernick[17]).

For Zn the virtual bound state appears at 8.2 eV. This is about 1.5 eV higher than the recent experimental value of Norris and Williams.[18] This error, which is even more pronounced for Ga and Ge, seems to be a general shortcoming of the local-density approximation. Similar effects occur in band-structure calculations.[19] Within the energy range of the Cu d band the s and p densities of states are strongly structured. This effect, already discussed by Terakura,[8] is due to the hybridization of the impurity s and p electrons with the d electrons of the host Cu atoms. It is more pronounced for Ga and Ge.

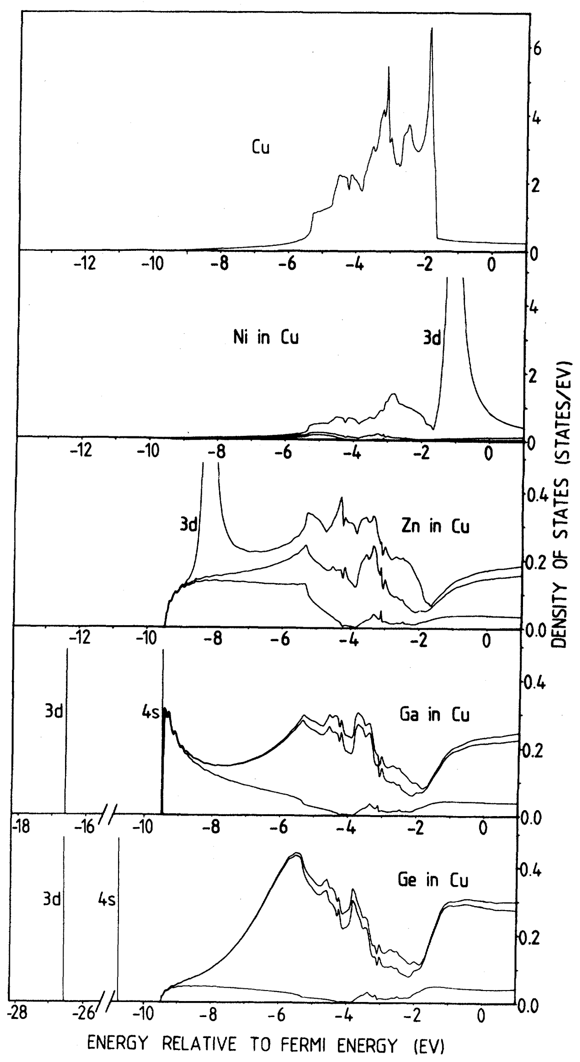

FIG. 2. Local densities of states for Ni, Zn, Ga, and Ge impurities in Cu. The lowest curve gives the s contribution, the second one the sum of the s and p contributions, and the highest one of the total local density of states as the sum of the s, p, and d contribution. The density of states for pure Cu is given at the top.

For Ga the s density is shifted to lower energies and a localized 4s state appears just below the bottom of the Cu valence band. The energy of the localized 3d state, 16.6 eV, is about 2.0 eV higher than the experimental value.[18]

For Ge the energies of the localized states are further decreased ($E_{4s}=10.7$ eV, $E_{3d}=26.6$ eV; the experimental value is $E_{3d}=29.2$ eV[19]). The position of the p density of states remains practically unchanged from Zn to Ge. Its visible increase is expected from the atomic configurations.

Our calculations indicate that the assumption that only the impurity potential is perturbed, is not of major importance, since the impurity is to a large extent screened in its own muffin-tin sphere. E.g., for Ni the impurity Wigner-Seitz cell contains 10.03 electrons (instead of 10), and even for the tetravalent Ge only 0.22 electrons are missing in the impurity cell.

In conclusion, we have shown that self-consistent *ab initio* calculations of the electronic structure of impurities in transition metals are possible. The calculations can be extended to cases where the potentials at neighboring atoms are also disturbed. The effort of such a calculation would be comparable to a cluster calculation with the same number of atoms. Contrary to the cluster method, however, the Green's-function method described the embedding of the perturbed cluster in the infinite ideal crystal exactly.

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