Magnetic impurity states in simple metals: A study of the spin-polarization energy

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We report a systematic study of the spin-polarization energy of 3d impurities in monovalent simple-metal hosts, by means of self-consistent, local-spin-density-functional, impurity-in-jellium calculations, and propose a phenomenological model for the interpretation of our results. [S0163-1829(98)03424-9]

The spin-polarization energy of a magnetic system is defined as the difference between the total energy of the spin-polarized (ground) state and that of the hypothetical non-spin-polarized state of lowest energy of the system. This quantity plays a crucial role in the occurrence of magnetic energy anomalies in 3d systems,[1] and in the interaction of a magnetic impurity with another impurity or a vacancy.[2] Moreover, it determines the stability of the spin-polarized state. It is known, for instance, that lattice relaxation effects have a decisive influence on the magnetic moment of an iron impurity in aluminum, because of the relatively low spin-polarization energy: considering all the atoms at the ideal lattice positions, it is found that the impurity has a local magnetic moment of about 1.7μ_B, whereas, if structural distortion around Fe is taken into account, the ground state of the system turns out to be nonmagnetic.[3,4]

In this work we report a systematic study of the spin-polarization energy for 3d impurities in monovalent simple-metal hosts. We employ the jellium model, which enables us to describe reliably the magnetic properties of these systems gaining physical insight.[5] This model allows us to vary the host electron density $\bar{\rho}$ continuously from a critical value $\bar{\rho}_c$, beyond which the ground state of the system is nonmagnetic,[6,7] to 0, which corresponds to the case of a free impurity atom. A substitutional impurity in a jellium metal is described by creating a spherical hole with the volume of the host primitive unit cell in the jellium positive background, and inserting the nuclear charge of the impurity at the center of this vacancy. The electronic structure of the system is calculated self-consistently, within the framework of the density-functional theory, using a Green-function technique. Details about our method of calculation can be found elsewhere.[6] Here we restrict ourselves in noting that a range of perturbing impurity potential $S = 10$ a.u. and an angular momentum cutoff $\ell_{max} = 3$ are sufficient to obtain adequate convergence in the charge and magnetization densities $\rho(\mathbf{r})$ and $m(\mathbf{r})$, respectively, in all cases examined. For the exchange and correlation part $E_{xc}[\rho,m]$ of the total-energy functional $E[\rho,m]$, we employ the local-spin-density approximation (LSDA) with the parametrization of Vosko, Wilk, and Nusair.[8]

The calculation of the spin-polarization energy in a defect system, obtained by subtracting the total energy of the non-magnetic state from that of the magnetic state, is a delicate problem. Indeed, contrary to usual band-structure calculations of periodic systems, where charge neutrality is preserved by adjusting the Fermi energy E_F, in the case of dilute alloys E_F is fixed by the host. Charge perturbation is long ranged and, as a result, the total energy converges slowly as a function of the range of the perturbation considered in the calculation. This problem can be overcome by employing a generalized, grand-canonical energy functional, which is extremal for non-particle-conserving variations of the electron density.[9] An elegant and efficient alternative approach is the following. We consider the lowest-energy state of an impurity-in-jellium system constrained to have a given impurity magnetic moment M. This can be obtained by minimization of the generalized functional

$$E[\rho,m;M] = E[\rho,m] - H\left(\int_V d^3r \; m(\mathbf{r}) - M \right), \qquad (1)$$

where H is a Lagrangian multiplier having the dimensions of a magnetic field, and acts within the volume V of the crystal.[7] The lowest energy of the system, $E(M)$, is equal to the value of the functional (1) for the charge and magnetization densities, $\rho(\mathbf{r};M)$ and $m(\mathbf{r};M)$, respectively, which satisfy the appropriate Euler-Lagrange equations. Since at the energy minimum, $E[\rho,m;M]$ is stationary versus variations of ρ and m, we obtain, from Eq. (1),

$$\frac{dE(M)}{dM} = H. \qquad (2)$$

Thus the spin-polarization energy is given by

$$E_m = E(M_0) - E(0) = \int_0^{M_0} dM \; H, \qquad (3)$$

where M_0 is the ground-state magnetic moment in the absence of an external field. We can calculate $M = \int_V d^3r \; m(\mathbf{r})$ as a function of H, solving self-consistently the one-particle Euler-Lagrange equations deduced from minimization of the energy functional (1). The physical picture which underlies Eq. (3) is as follows. We apply an external magnetic field opposite to the direction of the impurity magnetic moment, and gradually increase its intensity until the moment vanishes. Equation (3) gives the work done by the external field during this process. This method is in principle exact. It focuses on the calculation of the magnetic energy itself, avoiding the computation of large total energies which involves the convergence problems mentioned above. However, the method has the disadvantage that, increasing the external field beyond a certain value, the mag-

netic moment abruptly changes direction instead of being further reduced, because in this way the system goes to a more stable configuration. Therefore, it is difficult to obtain configurations close to $M=0$ using conventional iteration schemes, and one should normally determine this part of the curve $H=H(M)$ by interpolation.

Another method, physically equivalent to the previous one but numerically nonproblematic, is based on the introduction of a coupling parameter λ, which switches on the spin-dependent part of the exchange-correlation energy.[1] Therefore one has to minimize the functional

$$E[\rho,m;\lambda]=E[\rho,m]+(\lambda-1)(E_{xc}[\rho,m]-E_{xc}[\rho,0]). \tag{4}$$

For $\lambda=0$ only the paramagnetic functional is included in the calculation, whereas $\lambda=1$ refers to the correct functional including the spin dependence. Substituting into Eq. (4) the charge and magnetization densities $\rho(\mathbf{r};\lambda)$ and $m(\mathbf{r};\lambda)$, respectively, which satisfy the appropriate Euler-Lagrange equations, we obtain the ground-state energy of the system $E(\lambda)$. The stationary property of the functional (4) versus variations of ρ and m, at the energy minimum, implies

$$\frac{dE(\lambda)}{d\lambda}=E_{xc}[\rho(\mathbf{r};\lambda),m(\mathbf{r};\lambda)]-E_{xc}[\rho(\mathbf{r};\lambda),0]. \tag{5}$$

By integrating over λ, we obtain the total-energy difference between the spin-polarized and non-spin-polarized states, i.e., the spin-polarization energy

$$E_m=\int_0^1 d\lambda\{E_{xc}[\rho(\mathbf{r};\lambda),m(\mathbf{r};\lambda)]-E_{xc}[\rho(\mathbf{r};\lambda),0]\}. \tag{6}$$

We applied both methods in some test cases, and the results were practically identical. Therefore we used the second one, which is computationally more efficient, to calculate the magnetic energy of all the $3d$ elements diluted in the monovalent simple metals: Rb ($\bar\rho=1.88\times10^{-3}a_B^{-3}$), K ($\bar\rho=2.37\times10^{-3}a_B^{-3}$), Na ($\bar\rho=4.39\times10^{-3}a_B^{-3}$), Li ($\bar\rho=7.57\times10^{-3}a_B^{-3}$), Ag ($\bar\rho=8.50\times10^{-3}a_B^{-3}$), and Cu ($\bar\rho=12.97\times10^{-3}a_B^{-3}$), as well as in two fictitious hosts with jellium densities: $\bar\rho=17.27\times10^{-3}a_B^{-3}$ and $\bar\rho=19.62\times10^{-3}a_B^{-3}$, where a_B is the Bohr radius. We also calculated the spin-polarization energy of the free impurity atoms, which corresponds to $\bar\rho=0$. Since the atomic states have a relatively short spatial extent, total-energy calculations are reliable, and can safely be used to evaluate the spin-polarization energy. In this respect, the LSDA ground state of the atom (magnetic configuration) and the LSDA atomic state of lowest energy, with equal occupancy of all the spin-up and the corresponding spin-down orbitals (nonmagnetic configuration), must be determined.

An alternative method to calculate the magnetic energy for free atoms is based on the concept of the transition state.[10,11] According to this, the energy needed to increase the number of electrons of a one-particle state, $|1\rangle$, from N_1 to N_1+n, by transferring n electrons from state $|2\rangle$, is given by
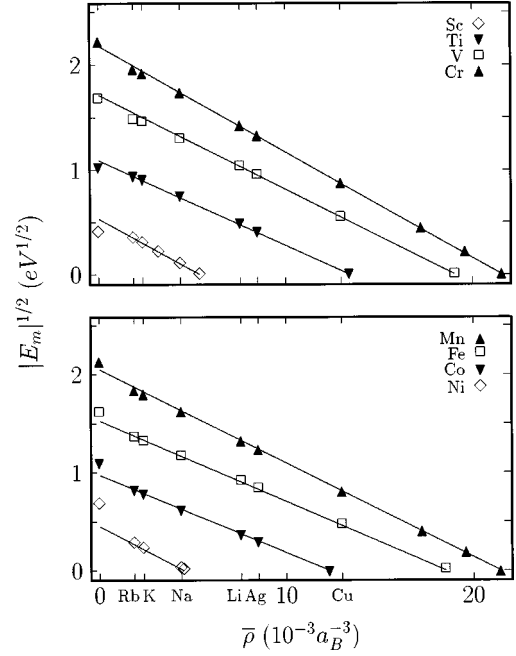

FIG. 1. Spin-polarization energy of the $3d$ substitutional impurities in monovalent simple metals vs the free-electron density of the host.

$$\Delta E=\int_{N_1}^{N_1+n} dn_1(\epsilon_1-\epsilon_2), \tag{7}$$

where ϵ_1 and ϵ_2 denote the energy eigenvalues of the corresponding one-particle states, as calculated for all the intermediate nonintegral occupancies. Suppose, for instance, that we want to find the spin-polarization energy of a Mn atom. In the ground-state configuration, according to Hund's rules, the $3d$ shell has five unpaired electrons in the spin-up state. The hypothetical nonmagnetic state of lowest energy turns out to have 2.5 electrons in the $3d$ shell with spin-up, and 2.5 electrons with spin-down. Starting from the nonmagnetic configuration, we gradually transfer 2.5 electrons from the $3d\downarrow$ to the $3d\uparrow$ state, determining at each intermediate configuration the energy eigenvalues $\epsilon_{3d\downarrow}$ and $\epsilon_{3d\uparrow}$ self-consistently. Then, using Eq. (7), we calculate a spin-polarization energy $E_m=-5.30$ eV. On the other hand, by directly subtracting the total energy of the nonmagnetic state from that of the magnetic state, we obtain $E_m=-5.26$ eV. The differences in the results obtained by the two methods are small, typically less than 1%. Therefore we have used the simpler, total-energy method.

Figure 1 shows our results for the spin-polarization energy of the $3d$ impurities as a function of the density $\bar\rho$ of the jellium host. It can be seen that the magnetic energy for each impurity varies quadratically with $\bar\rho$ within the whole range of metallic densities. It is also interesting to note that even the spin-polarization energy of a free impurity atom can in most cases be roughly estimated by extrapolation of the impurity-in-jellium results.

This systematic behavior can be understood as follows. We consider the lowest energy $E(M)$ of a given impurity in a jellium of density $\bar\rho$, constrained to have a magnetic moment M. The dependence of the magnetic moment on the

jellium density, in the immediate vicinity of the critical density $\bar{\rho}_c$, is most easily described by a Landau expansion of the energy in even powers of M with density-dependent coefficients.[12,7] Then

$$E(M) = E(0) + \alpha(\bar{\rho})M^2 + \beta(\bar{\rho})M^4 + \cdots . \qquad (8)$$

Both this phenomenological expansion of $E(M)$ and the LSDA calculations imply a mean-field theory. With truncation of the expansion (8) at fourth order, the minimum-energy condition for given $\bar{\rho}$ yields the ground-state impurity moment

$$M_0 = \left(-\frac{\alpha(\bar{\rho})}{2\beta(\bar{\rho})} \right)^{1/2} \quad \text{for} \quad \bar{\rho} < \bar{\rho}_c . \qquad (9)$$

Substituting Eq. (9) into Eq. (8), we find the magnetic energy

$$E_m = E(M_0) - E(0) = -\frac{\alpha^2(\bar{\rho})}{4\beta(\bar{\rho})} \quad \text{for} \quad \bar{\rho} < \bar{\rho}_c . \qquad (10)$$

The coefficient α is a measure of the curvature of $E(M)$ at $M = 0$. This must be negative for $\bar{\rho} < \bar{\rho}_c$ and positive for $\bar{\rho} > \bar{\rho}_c$, whereas $\beta(\bar{\rho})$ must be always positive, so that for $\bar{\rho} < \bar{\rho}_c$ the energy is minimized for a nonzero value of the magnetic moment M_0, and for $\bar{\rho} > \bar{\rho}_c$ there is no spontaneous magnetic moment. In the vicinity of $\bar{\rho}_c$, assuming that to leading order $\alpha(\bar{\rho}) = A(\bar{\rho} - \bar{\rho}_c)$ and $\beta(\bar{\rho}) = B$, where A and B are positive constants, from Eqs. (9) and (10) we obtain

$$M_0 = \left(\frac{A}{2B} \right)^{1/2} (\bar{\rho}_c - \bar{\rho})^{1/2} \quad \text{for} \quad \bar{\rho} < \bar{\rho}_c \qquad (11)$$

and

$$E_m = -\frac{A^2}{4B} (\bar{\rho}_c - \bar{\rho})^2 \quad \text{for} \quad \bar{\rho} < \bar{\rho}_c . \qquad (12)$$

Obviously, for $\bar{\rho} > \bar{\rho}_c$, $M_0 = 0$ and $E_m = 0$.

Our numerical results can be compared with those of the first-principles Korringa-Kohn-Rostoker (KKR) Green-function method in the case of an Ag host,[1] where KKR results are available. For Sc, Ti, V, Cr, Mn, Fe, Co, and Ni impurities, the jellium (KKR) results for the spin-polarization energy are, respectively, 0 (0), -0.1 (0), -0.9 (-0.6), -1.8 (-1.6), -1.6 (-1.9), -0.7 (-1.0), -0.1 (-0.3), and 0 (0), in eV. The agreement between jellium and KKR results is generally good. However, we can see that the jellium calculations systematically overestimate (underestimate) the tendency to spin polarization of the impurities of the beginning (end) of the $3d$ series. This is due to the hybridization between the low-lying $3d$ states of the silver host and the impurity $3d$ states, which is neglected in a jellium calculation.[6] Therefore we presume that the jellium results in the case of the alkali-metal hosts should be more reliable.

The systematic study of the spin-polarization energy reported in this work refers to substitutional impurities, without taking into account lattice-relaxation effects. However, especially in the heavy alkali metals, the large size differences between impurity and host atoms lead to unusually large lattice contractions around the impurity, which can be as large as 22% for the extreme case of Fe in Cs.[13] Lattice contraction leads to a stronger hybridization between the localized impurity d states and the host continuum states, thus reducing the tendency to magnetism. This effect of the local relaxation can be simulated in a first approximation by a homogeneous compression of the crystal, which is realized in our model by a different jellium density. In this way we find (see Fig. 1) that, for instance, a lattice contraction by 22% in the case of Fe in Cs ($\bar{\rho} = 1.44 \times 10^{-3} a_B^{-3}$) leads to a decrease of the magnitude of the spin-polarization energy by about 18%.

Recently, strong evidence has been reported that, in addition to substitutional positions, transition-metal impurities can also occupy interstitial sites in the heavy alkali metals.[14] Calculations for impurities at interstitial positions can be carried out rather easily by the jellium model.[5] In this case one has just to superimpose the nuclear charge of the impurity atom on the jellium background charge, instead of putting the impurity at the center of a spherical cavity in the positive background. As a result of the stronger impurity-host hybridization in the interstitial case, the impurity virtual bound state is broadened. On the other hand, there are more electrons around an impurity at an interstitial position because, then, the electrons have to screen, in addition to the impurity nuclear charge, the jellium positive background which is removed in the case of a substitutional impurity. This translates to a considerable charge transfer to the interstitial impurity, and the virtual bound state is shifted to lower energies in order to accommodate more electrons. For impurities with a more than half-filled resonant state, both effects discussed above tend to suppress magnetism in the interstitial case. Thus, for Mn in Rb, for instance, the spin-polarization energy changes from -3.4 eV (substitutional impurity) to -2.7 eV (interstitial impurity). In contrast to this, for the early $3d$ impurities the two effects act competitively, leading finally to a moderate enhancement of magnetism. For V in Rb, for instance, $E_m = -2.2$ (-2.3) eV in the substitutional (interstitial) case.

It should be pointed out that the LSDA, which is used in this work to describe effects of exchange and correlation, is known as a Stoner-type mean-field theory with exchange due to intra-atomic exchange interactions. Although the LSDA has been proven very successful for calculating ground-state properties of a wide range of materials, it tends to lose accuracy or break down in cases where local correlations are strong. Orbital polarization, for instance, which is normally connected with the ionic configurations occurring in free $3d$ atoms or even in the case of $3d$ impurities in heavy alkali metals,[15,16] cannot be obtained from our calculations. The electron-electron interaction (U) can also influence both the spin- and orbital-polarization energies.[16] However, we note that the values of the total energy obtained in the LSDA for isolated atoms do not differ drastically from those obtained in the Hartree-Fock approximation, despite the fact that the incomplete cancellation of self-interactions in the LSDA leads to a violation of Hund's rules for atoms. As the most striking example of this, we can cite that of the X_α approximation[17] where the parameter α was determined

from the equality between total energies in the X_α and the Hartree-Fock methods for free atoms. Therefore, one expects the LSDA also to yield reasonably accurate spin-polarization energies in the case of $3d$ impurities in heavy alkali metals or even in the case of isolated $3d$ atoms.

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