Magnetic behavior of transition-metal impurities in alkali-earth metals

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We present density-functional calculations within the local-density approximation for all transition-metal impurities in the divalent hosts Ca, Sr, and Ba. Our results predict sizable moments, even for impurities of the 4*d* and 5*d* series, being only slightly smaller than the moments obtained in the corresponding alkali metals.

I. INTRODUCTION

Considerable progress has been achieved during the last decade in the study of the local magnetism of dilute nonalloying systems, both from the experimental[1–10] and from the theoretical[8–17] point of view.

On the experimental side, the time-differential perturbed γ-ray angular distribution technique has been extensively used to probe the local magnetic properties of impurities implanted by recoil into the host crystal, following heavy-ion reactions. This method allows microscopic studies of the local magnetism of extremely dilute impurities in hosts where alloying by more conventional methods is very difficult or not possible at all.[1–10]

Investigation of the magnetic behavior of 3*d* and 4*d* impurities in alkali metals attracted considerable interest. Due to the extremely large atomic volume and, consequently, the very dilute free-electron gas of a heavy alkali metal, the impurities exhibit the phenomena of ionic ground states in *LS* coupling, large orbital contributions,[2–6] mixed valence,[5] and crystal field smaller than the *LS* coupling[2–6] in these exotic systems. Therefore, one faces the challenging question, how the localized configuration of the free atom matches continuously its itinerant behavior in a solid-state environment. Alkali metals constitute ideal model hosts to study this problem, since their atomic volumes cover a wide range of values. Moreover, their energy bands are very much free-electron-like, so that simple model calculations, allowing physical insight, are applicable.[11] It is, however, worth to notice that the important size differences between the impurity and the large atomic volume of the late alkali-metal host might lead to unusually large lattice relaxation of the neighboring atoms, as discussed by Gross, Riegel, and Zeller.[8] There is also strong experimental evidence that, in addition to substitutional configurations, transition-metal impurities can occupy interstitial positions.[7]

The formation of a local impurity moment results from the competition between intra-atomic exchange interaction and interatomic electron motion. It has been shown that, if the host metal is likened to a jellium, the local impurity moment starts to develop at a critical host free-electron density, following a square-root behavior as the host density decreases.[11,12,15,16] The electronic structure and the magnetic properties of impurities in alkali metals were systematically investigated by first-principles local-spin-density-functional calculations.[8–16] These calculations give results for the local-spin moments in good general agreement with the available experimental data. Moreover, they predict the existence of magnetic 5*d* and *sp* impurities with well developed spin moments in the heavy alkali metals, both on substitutional and interstitial configurations.[16] These theoretical studies cannot, however, account for the observed ionic ground-state configurations, since orbital degeneracy is inherent in the traditional local-spin-density approximation used in these works. First-principles calculations employing improved density functionals, including intra-atomic correlations between the localized orbitals, have been also reported for the 4*d* impurities in Rb.[17] The results obtained clearly show the existence of ionic ground-state configurations for the localized impurity states, in agreement with the experimental findings.

By comparing with the experiments, one should bear in mind that the theoretical calculations provide a static picture for the ground-state magnetic properties of the system, in the framework of a one-electron theory. While, the local susceptibility data are analyzed in the context of the theory of spin fluctuations[2–10] using a Kondo temperature, below which the magnetic moment is rapidly fluctuating. However, when experiments show no sign of magnetism it is not clear if the impurity moment is very rapidly fluctuating or if it actually does not exist.

Impurities in alkali-earth metals also attracted experimental[1,4] and theoretical[14] interest which arise from the fact that the alkali-earth metals represent the link between the alkali metals and the transition metals and that the impurities show a very different behavior in these two systems. Recently, Guenzburger and Ellis[14] calculated the electronic structure and the magnetic properties of an Fe impurity in alkali-earth hosts using the discrete-variational embedded-cluster method in the framework of the local-spin-density-functional theory. The divalent alkali earths are also typical examples of *sp* band metals

which, however, exhibit noticeable deviations from a free-electron description, resulting in a deep minimum close to the Fermi level.[18] The big atomic volumes available allow one to expect that transition-metal impurities in the late alkali-earth metals also exhibit a pronounced magnetic behavior.

In this work we carry out a systematic study of the electronic structure and the magnetic properties of all the transition-metal impurities in Ca, Sr, and Ba, by means of first-principles, local-spin-density-functional Green's-function calculations.

II. CALCULATIONAL METHOD

Systematic calculations of the electronic structure and the magnetic properties of all the $3d$, $4d$, and $5d$ substitutional impurities in the late alkali-earth metals: Ca, Sr, and Ba are carried out self-consistently, within the framework of density-functional theory.[19] Exchange and correlation effects are included through the local-spin-density approximation, with the parametrization of Vosko, Wilk, and Nusair.[20] For the heavy $4d$ and $5d$ impurities relativistic effects were taken into account in the scalar-relativistic approximation,[21] thus neglecting spin-orbit interaction.

We employ the Korringa-Kohn-Rostoker (KKR) Green's-function method to describe the electronic structure of a single substitutional impurity atom surrounded by an infinite lattice of host atoms, neglecting lattice relaxations around the impurity atom. The details of the method have been reported elsewhere.[22] Here, we restrict ourselves to note that potential perturbations on the impurity atom and its first 12 neighbors in the case of the fcc hosts Ca and Sr or its 14 first and second neighbors in the case of bcc Ba host, are determined self-consistently, including angular momenta up to $l_{\max}=3$. The correct embedding of the perturbed cluster is given by the Green's function of the host crystal.

In addition to the KKR calculations, we have also calculated self-consistently the electronic structure of the impurities using the impurity-in-jellium approach, which has been described in detail in previous work.[11] Within this scheme, the alkali-earth metal is considered as a jellium. A substitutional impurity is described by removing the positive background within the Wigner-Seitz sphere and inserting the nuclear charge of the impurity in the center of the resulting "vacancy." The electronic structure of the system is determined self-consistently using a Green's-function approach. An angular momentum cutoff $l_{\max}=3$ and a range of perturbing potential $S=10$ a.u. are sufficient to obtain good convergence in all the cases examined.

III. RESULTS AND DISCUSSION

A. Magnetic moments

With two electrons per primitive cell, calcium, strontium, and barium are typical examples of metals with *nearly*-free-electron bands, where the effective lattice potential induces important deviations from the free-electron band structure in the vicinity and above the Fermi energy. In Fig. 1 we have plotted the local densities of states for Ba host, the deviations from the free-electron behavior are manifested by the presence of a sharp minimum at the Fermi level, which separates two high peaks in the density of states, features which are also common in Ca and Sr hosts.[18]

The importance of the band-structure effects of the alkali-earth hosts on the formation of a spin moment in the vicinity of an impurity can be estimated if we compare the results obtained with the realistic KKR Green's-function method, with the impurity-in-jellium calculations where a free-electron band structure is explicitly assumed. The overall agreement between KKR and jellium results is satisfactory, with the jellium moments being in general about 10% higher than the KKR ones. This can be explained as follows: As mentioned above, due to the presence of the high peaks, the host density of states is on the average larger in the vicinity of the Fermi energy, as compared with the corresponding free-electron density. This means that in the jellium approach, the host-impurity hybridization is underestimated, thus leading to an overestimation of the impurity magnetic moment. In the following the discussion will be restricted to the more realistic KKR results.

In Fig. 2 we show the local spin-moments of all $3d$, $4d$, and $5d$ impurities in Ca, Sr, and Ba. In each host, the magnetic moment shows a parabolic behavior as we move across a given transition series of impurities, with the strongest spin polarization occurring for the elements with a half-filled d shell. Moreover as we change the host in the sequence Ca, Sr, Ba the impurities exhibit somewhat higher magnetic moments, because the hybridization between the impurity d states and the host states becomes weaker with increasing host atomic volume. These changes are, however, not large, since the calculated spin-moments of the impurities are already nearly saturated, especially the moments of the $3d$ impurities. This suggests the occurrence of almost atomic

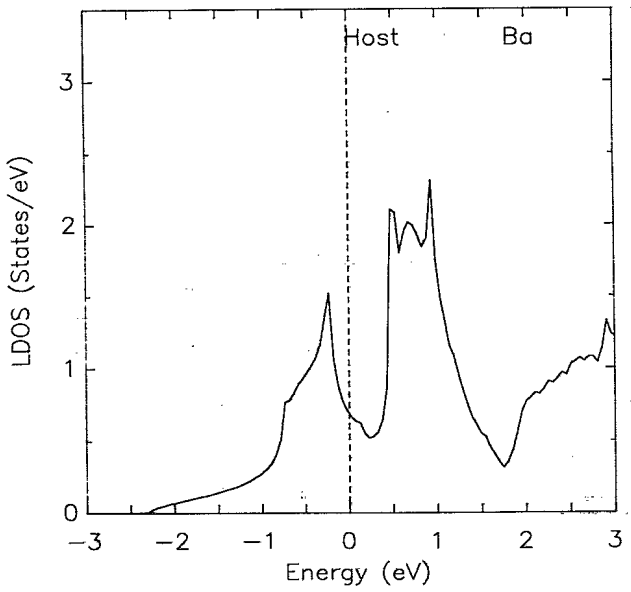

FIG. 1. Densities of states of pure Ba (bcc). The energies are counted relatively to E_F.

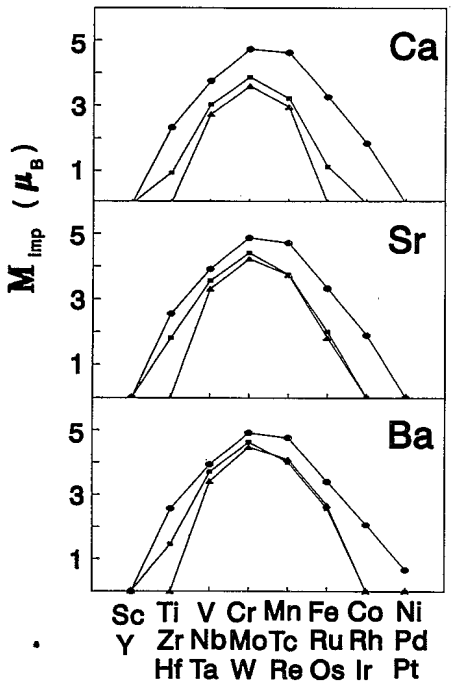

FIG. 2. Calculated magnetic moments for the 3*d* impurities (Sc, Ti, V, Cr, Mn, Fe, Co, Ni) [circles], 4*d* impurities (Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd) [squares], and 5*d* impurities (Hf, Ta, W, Re, Os, Ir, Pt) [triangles] in Ca, Sr, and Ba hosts.

configurations, with spin and orbital moments nearly as large as required by Hund's first and second rules for the free atoms. This can also be seen in Fig. 3 where we have plotted the spin-polarized densities of states for 3*d* impurities in the Ba host. The dilute environment in the Ba host allows for the very strong localization of the impurity virtual bound state. Band-structure effects however play an important role in the case of V impurity since they considerably broaden the occupied majority state. Additionally we observe a crystal-field splitting between V $d-e_g$ and $d-t_{2g}$ states. The systematic behavior of the magnetic moment confirms the usual observation that the 3*d* impurities have a stronger tendency for magnetism, as compared with their 4*d* and 5*d* counterparts. This is due to the weaker hybridization of the 3*d* impurity states with the host *sp* states and can be seen better if we compare the widths of the virtual bound state in the case of 3*d* impurities (Fig. 3), with the widths of the 4*d* and 5*d* impurities shown in Fig. 4 where we have plotted the spin-polarized densities of states for the middle elements of the 4*d* and 5*d* series. Comparing isoelectronic impurities, i.e., Mo and W with Cr, we can see that the 4*d* and 5*d* majority virtual bound states are somewhat more broadened compared with the 3*d* one. This is due to the fact that the 4*d* and 5*d* wave functions are spatially more extended than the corresponding nodeless 3*d* wave functions. The largest difference is, however, found in

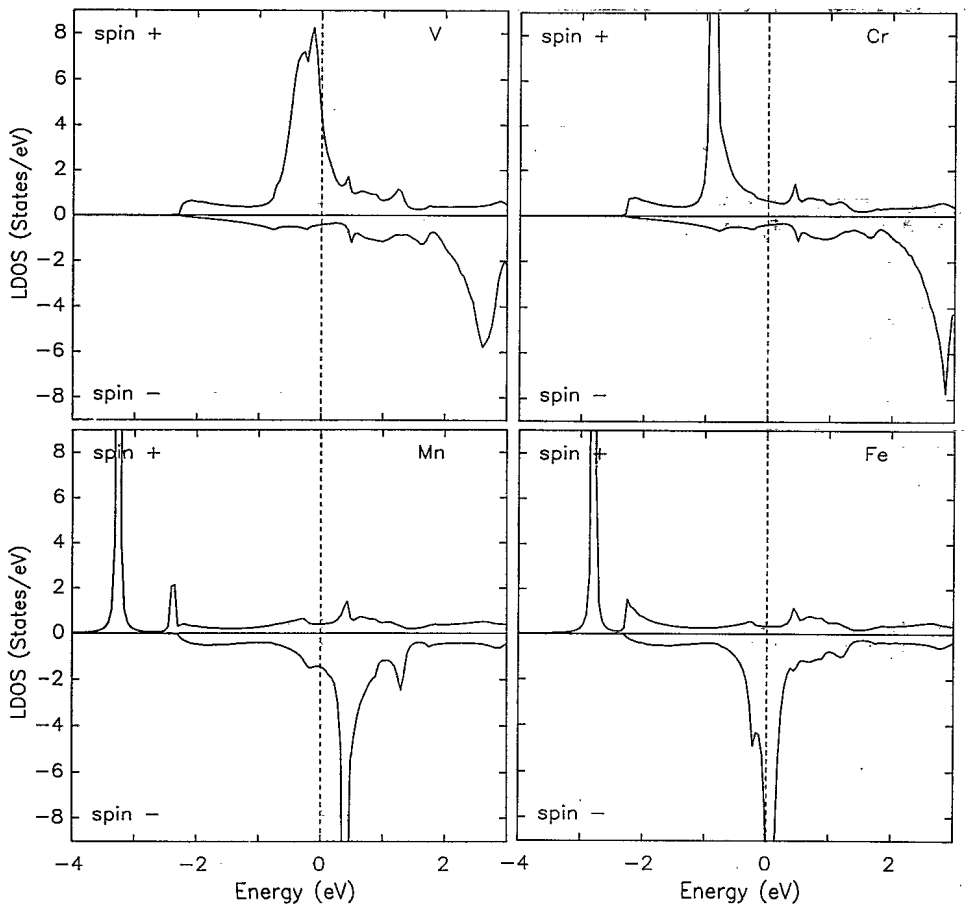

FIG. 3. Local densities of states for majority (+) and minority (−) spin directions of 3*d* impurities V, Cr, Mn, and Fe in Ba host.

the minority band. For instance, for Cr a strong minority peak shows up at about 3 eV, whereas for the isoelectronic impurities Mo and W we observe two peaks at about 1 and 2 eV. Thus in the 4*d* and 5*d* series the exchange splitting is considerably lower, being partly a result of the smaller moments and partly due to the reduced exchange integrals.

The small peaks seen in Figs. 3 and 4 at the band minimum arise from the localized or nearly localized valence *s* states. The spin splitting of these states indicates that the impurities also have a small *s* moment, being of the order of $0.1\mu_B$ and relevant for the hyperfine fields of these impurities (see below).

A close look at Figs. 3 and 4 reveals subtle changes in the positions of the majority *d* and *s* peaks for the different series. If we again concentrate ourselves on the isoelectronic impurities Cr, Mo, and W, we see that the *d* peak of Mo is lower than the *d* peak of W and even lower than the Cr peak, despite the fact that the Cr moment and the relevant exchange splitting is larger. On the other hand the *s*-peak of Mo is higher than the one of W. This is basically an atomic effect. As compared to the 3*d* elements, in the 4*d* series the *d* levels are moved to lower energies, whereas the valence *s* levels are moved up. In contrast to this, in the 5*d* series relativistic effects move the *d* levels again up to higher energies and the *s* levels down. These trends can be clearly seen by comparing the majority local density of states of Cr, Mo, and W in Figs. 3 and 4. As a result, we obtain in the 4*d* series somewhat larger *d* counts resulting in a slight shift of the corresponding local moment curve to smaller valences (see Fig. 2), an effect which has also been found for the 4*d* and the 5*d* impurities in the alkali metals.[16]

The host band structure causes the strong hybridization that we see in the unoccupied high-energy states of Mo and W, while for Tc and Re impurities we have a sharp virtual bound state in the energy region of the minimum of the host density of states close to the Fermi energy. However the position and half-width of the impurity states for the 3*d* impurities in Ba, with the exception of V, are very close to the ones previously obtained in the more dilute K host.[15]

The differences between the local moments in the various alkali-earth metals are relatively small, despite the fact that the impurity-host hybridization decreases with increasing host volume. Therefore in general the moments in Sr are somewhat larger than the moments in Ca, but smaller than the ones in Ba. An exception in the Zr impurity, having a larger moment in Sr than in Ba. This is due to the strong structure of the host density of states of Ba around E_F indicating a stronger deviation from the free-electron behavior than Sr and Ca.

It is interesting to compare the moment formation in the alkali-earth metals with the situation in the alkali metals. This is most simply done in the jellium model, where the average electron density is the most important

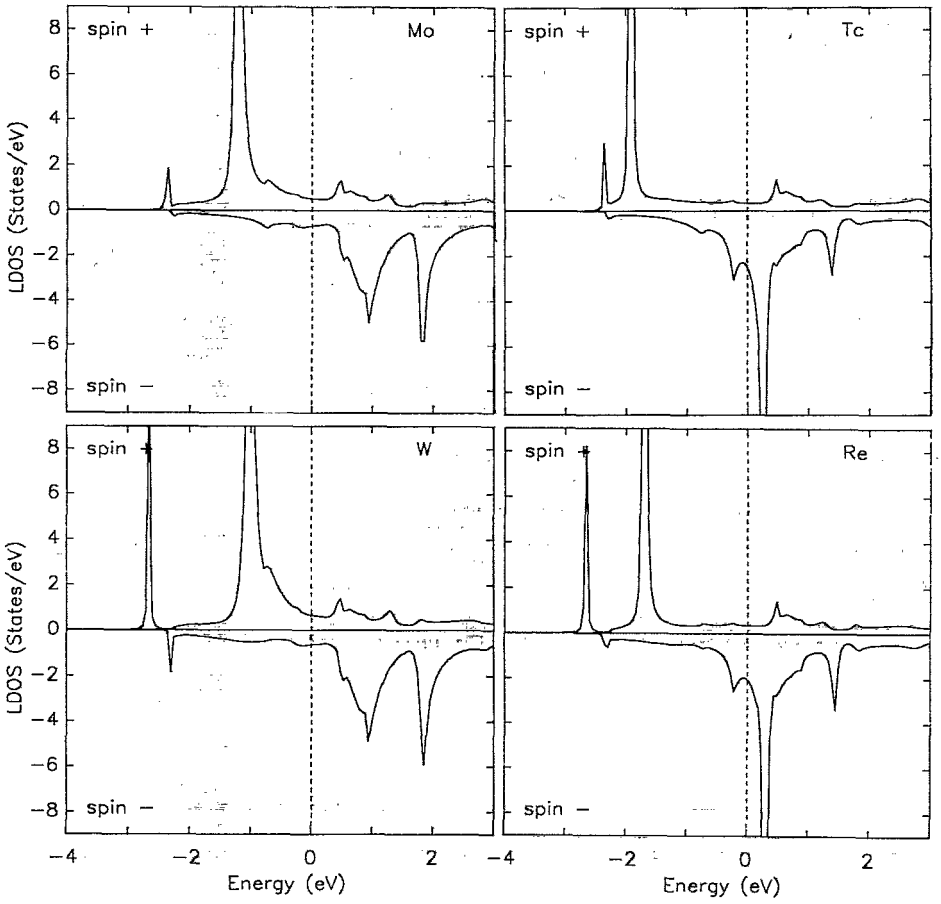

FIG. 4. Local densities of states for majority (+) and minority (−) spin directions of Mo, Tc, W, and Re impurities in Ba host.

parameter. It is therefore reasonable to compare two hosts with similar electron densities, e.g., Na with Ba the electron density of which is only 6% larger than the one of Na. However for the substitutional impurity calculation the jellium density is not the only relevant parameter, since by creating the defect one has to remove the background charge in one elementary volume. For the divalent Ba this volume is about twice as large as the one of Na, thus reducing the hybridization of the impurity with the jellium. Nevertheless the calculated moments of the 3*d*, 4*d*, and 5*d* impurities in Ba are very similar to the ones obtained in Na,[15,16] so that the reduction of the hybridization is not very important. Larger differences are only observed at the beginning and end of the series. For instance, the Ni impurity is nonmagnetic in Na, whereas the present calculations give a moment of $0.67\mu_B$ in Ba. Thus for Ni, with relatively localized *d* orbitals, the reduction of the hybridization due to the larger "vacancy" volume becomes important. The opposite effect is, however, observed at the beginning of the series. For instance, Zr has a moment of 2.18 μ_B in Na (Ref. 15) but a smaller moment of $1.47\mu_B$ in Ba. Similarly the 5*d* impurity Hf has a moment of $1.69\mu_B$ in Na,[16] whereas no moment is obtained in Ba.

Guenzburger and Ellis[14] also calculated the local magnetic properties of an Fe impurity in Be, Mg, Ca, and Sr, using an embedded-cluster approach. For Fe in Ca, they obtain an impurity moment which grows from $2.78\mu_B$ (19-atom cluster) to $2.93\mu_B$ (43-atom cluster), whereas our calculation yields $3.28\mu_B$. Moreover, for Fe in Sr, a 19-atom cluster calculation gives an Fe moment of $3.01\mu_B$ somewhat smaller than our result ($3.33\mu_B$). These discrepancies between the calculations are presumably due to the uncertainties introduced by the finite size of the clusters considered.

B. Hyperfine fields

The strong localization of the impurity *d* states, when dissolved in the late alkali-earth metals, suggests the occurrence of atomiclike configurations with unquenched orbital moments. As a result, one expects strong positive orbital contributions to the hyperfine field of the impurity, which is in line with the available experimental results.[1] Unfortunately, orbital degeneracy is inherent in the local-spin-density-functional theory employed in this work and, consequently, we cannot calculate orbital contributions to the hyperfine field. Therefore, we restrict ourselves to study the variation of the hyperfine field on a Mo impurity dissolved in Ca, Sr, and Ba. Molybdenum is an element with a half-filled *d* shell and clearly has a vanishing orbital moment. The calculated hyperfine fields are listed in Table I, separately for the core and the valence contributions, together with the local magnetic moments per symmetry. The core polarization which arises from the intra-atomic *s-d* exchange is expected to vary linearly, but oppositely in sign, with the local *d* moment. This is indeed confirmed by our calculations (see Table I). On the other hand, the positive valence hyperfine field increases rapidly with the increasing spin polarization, as we proceed in the sequence Ca, Sr, Ba, and dominates over the negative core contribution. However, the local-density approximation does not allow an accurate calculation of the hyperfine field, e.g., in the case of Fe the core contribution seems to be underestimated by about 30%.[23] Nevertheless our calculations indicate that due to the increasing *s* polarization in the heavier hosts the hyperfine fields of Mo tends to become positive.

TABLE I. Angular momentum decomposition of the local moments of a Mo impurity in Ca, Sr, and Ba hosts (units: μ_B) and hyperfine field (core and valence contributions) on the impurity (units: kG).

Host	Ca	Sr	Ba
M_s	0.10	0.13	0.15
M_p	0.11	0.13	0.11
M_d	3.67	4.15	4.38
M_{tot}	3.88	4.41	4.64
H_{core}	−599	−673	−711
H_{val}	730	895	978
H_{tot}	131	222	266

IV. CONCLUSION

We have presented local-density-functional calculations for the magnetic properties of all transition-metal impurities in Ca, Sr, and Ba, by applying the KKR Green's function method. In total we find a very strong tendency for magnetism, being only slightly reduced compared to the behavior found in the alkali metals. Even impurities from the middle of the 4*d* and 5*d* series have large moments in all three hosts, with the moments of Mo and W being close to $5\mu_B$ in Sr and Ba.

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