Coordination Dependence of Hyperfine Fields of 5sp Impurities on Ni Surfaces

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We present first-principles calculations of the magnetic hyperfine fields \( H_{hf} \) of 5sp impurities on the (001), (111), and (110) surfaces of Ni. We examine the dependence of \( H_{hf} \) on the coordination number by placing the impurity in the surfaces, on top of them at the adatom positions, and in the bulk. We find a strong coordination dependence of \( H_{hf} \), different and characteristic for each impurity. The behavior is explained in terms of the on-site \( s\)-\( p \) hybridization as the symmetry is reduced at the surface. Our results are in agreement with recent experimental findings.

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The understanding of the magnetic properties of solids on the atomic level is a challenge for experiment and theory. The magnetic hyperfine interaction of the electronic magnetization with the nuclear magnetic moment of an atom is such a property, and it is known to depend in turn on the properties of the atom as well as on the neighboring atomic environment. In particular, for impurities in the bulk of the ferromagnetic materials Fe, Co, Ni, the trends of magnetic hyperfine field \( H_{hf} \) have been well understood and the experimental and theoretical results extend practically over the whole periodic table. The relation of \( H_{hf} \) to the local magnetic moment and to the atomic environment is not trivial. Therefore, for the interpretation of the trends, first-principles, all-electron methods have been extremely useful, since they can describe the charge density and magnetization near the atomic nucleus self-consistently. \( H_{hf} \) measurements for probe atoms at interfaces or surfaces can also provide unique information on the local structure, especially in combination with relevant calculations.

One of the modern powerful experimental techniques allowing the study of the hyperfine interaction of impurities at surfaces or interfaces is the perturbed angular correlation spectroscopy. It has a high enough sensitivity that allows accurate measurements from highly diluted probe atoms (\( 10^{-4} \) – \( 10^{-5} \) of a monolayer), so that these form practically isolated impurities. In a recent experimental publication, the coordination number dependence of \( H_{hf} \) of Cd impurities in Ni host was studied, by comparing data from Cd positioned on several Ni surfaces. The conclusion was that the \( H_{hf} \) of Cd strongly depends on the coordination number. Although this might be expected, since the magnetic moment of the Cd impurity is not intrinsic but rather induced by the environment, the data show neither a linear dependence nor an increase with the number \( N \) of Ni neighbors. On the contrary, \( H_{hf} \) is measured to be strongest for \( N = 3 \), while as \( N \) is progressively increased \( H_{hf} \) seems to change sign and has a parabolic behavior.

In order to interpret this puzzling behavior, we have performed first-principles calculations for all 5sp and the early 6s impurities (Ag to Ba) on various Ni surfaces and in bulk Ni in a substitutional position. The impurity positions studied are given in Table I together with the coordination numbers. In this way we aim to understand the trends of \( H_{hf} \) not only on the coordination number, but also on the impurity atomic number as has been done in the past in the bulk and on (001) surfaces. In all cases the impurities were assumed to be on the ideal lattice positions with the experimental fcc Ni lattice constant; relaxations were not accounted for.

The calculations are based on the local spin density approximation of density-functional theory. The full-potential Korringa-Kohn-Rostoker Green function method for defects in bulk or at surfaces is employed, with an exact description of the atomic cells. In short, after calculating the electronic structure of the host medium (bulk or surface) self-consistently, we use the Green function of this reference system to calculate the electronic structure of the distorted system containing the impurity via an algebraic Dyson equation. The power of the method lies in that it works in real space with the boundary condition of the infinite host included, rather than in \( k \)-space with a supercell construction. The Green function \( G_{lm,nm'}^{nn'}(E) \) is described in cell-centered coordinates around cells \( n \) and \( n' \) and expanded in cell-centered solutions of the Schrödinger equation with angular momenta \( (l, m) \) and \( (l', m') \). The impurity and a cluster containing the 12 first neighbors is perturbed in our calculations; this is enough because the fcc crystal structure is close packed. Increasing the cluster to contain the second neighbors in a test case brought insignificant changes to our results. A truncation of the angular mo-

| Surf | (111) | (001) | (110) | (110) | (001) | (111) | (110) |
|------|-------|-------|-------|-------|-------|-------|-------|
| Pos  | S+1   | S+1   | S+1   | Kink  | S     | S     | S+1   |
| \( N \) | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 11    | 12    |
mentum to $l_{\text{max}} = 3$ was taken. In a final step, the trace of the Green function is used to obtain the $(l, m)$ decomposed charge density and magnetic moment. We use the scalar relativistic approximation, which takes into account the relativistic effects other than the spin-orbit interaction and retains spin as a good quantum number.

In the case of spin magnetism, the dominant contribution to $H_{\text{hf}}$ is the Fermi contact interaction relating it directly to the spin density at the nucleus, $m(r = 0)$. In a non-relativistic treatment this has the simple form

$$H_{\text{hf}} = \frac{8\pi}{3} m(r = 0).$$

In a scalar relativistic treatment, as in the present paper, Breit’s formula has to be used instead to average $m(r)$ over the Thomson radius of the nucleus. In any case the magnetization at or near the nuclear position is important, and determined by the $s$ wavefunctions alone, since the states of higher $l$ vanish at $r = 0$.

In $sp$ impurities, which possess no intrinsic magnetic moment, the magnetization is transferred by the neighboring magnetic atoms. This has almost no effect on the contribution to $H_{\text{hf}}$ from $s$ bound states of the ionic core, but affects the contribution from the valence states strongly. This is found in our calculations, in agreement to previous results; in fact, the valence contribution to $H_{\text{hf}}$ is proportional to the local $s$ moment. Thus we focus on the behavior of the valence $s$ states.

Our starting point is the interpretation of the trends of $H_{\text{hf}}$ as a function of the impurity atomic number $Z$, as it has been understood generally for defects in the bulk of ferromagnetic hosts in the past. Relevant results are shown in Fig. (bottom-right) together with experimental data taken from Ref. The central issue is the so-called $s$-$d$ hybridization of the impurity $s$ orbitals with the $d$ states of the magnetic host, forming bonding (lower in energy) and antibonding (higher) hybrid states. In this way the $s$ local density of states (LDOS) of the impurity is affected, differently for every spin due to the exchange splitting of the host $d$ band. We denote the host majority spin as spin-up and the minority as spin-down. In the beginning of the series (Ag) the bonding hybrids for both spins are occupied while the antibonding ones unoccupied. Because the host spin-down $d$ band is higher in energy than the spin-up, the spin-down bonding hybrids are more $s$-like than the spin-up ones. Then the impurity $s$ moment is negative and so is $H_{\text{hf}}$. As we change $Z$ to the next impurities, the antibonding hybrids come to lower energies and are progressively populated. First to cross the Fermi level $E_F$ is the spin-up antibonding hybrid, thus the $s$ moment and $H_{\text{hf}}$ increases and changes sign, peaking at Iodine. Then the spin-down antibonding hybrid is gradually populated, the $s$ moment decreases again, and so does $H_{\text{hf}}$.

Next we turn to cases of reduced coordination. Several coordinations can be realized with the impurity at (001), (111), and (110) surfaces as shown in Table. The results for $H_{\text{hf}}(Z)$ for these coordination numbers $N$ are shown in Fig. We see that, as the coordination is gradually reduced, the single-peaked structure of $H_{\text{hf}}(Z)$ evolves to a double-peaked one. Already for $N = 8$ a “shoulder” appears at Sb, and for $N = 5, 4$ and 3 there are clearly two maxima of $H_{\text{hf}}$ with a local minimum of almost vanishing $H_{\text{hf}}$ in-between, at Te. A second observation is that, at the beginning of the series, $H_{\text{hf}}$ changes sign to positive much earlier at the surface that in the bulk — for $N = 4$ and 3 the change occurs already between Ag and Cd, while in the bulk it occurs at Sn.

To interpret the results we note that the reduced coordination has three effects. Firstly, the reduction in the transferred magnetic moment, secondly the reduction in the strength of the $s$-$d$ hybridization, and thirdly the reduction of symmetry. As for the first effect, a smaller impurity moment does not necessarily lead to a reduced $s$ moment and weaker $H_{\text{hf}}$. Indeed, when the second effect is also considered, a weaker $s$-$d$ hybridization leading to a smaller bonding-antibonding splitting of the $s$-$d$ hybrids. The antibonding hybrids (in particular for spin-up) appear lower in energy for smaller $N$, and are populated earlier in the $sp$ series and also $H_{\text{hf}}$ increases earlier. This is consistent with the rise of $H_{\text{hf}}$ for Ag and Cd.

\[ \text{FIG. 1: Magnetic hyperfine field of 5p impurities in Ni bulk and on various Ni surfaces as a function of the impurity atomic number Z. The coordination number N depends on the surface and position (see Table I).} \]

As $N$ increases from 3 to 12, the double-peaked structure of $H_{\text{hf}}(Z)$ transforms progressively to a single-peaked one. This is related to the gradual decoupling of the $s$ from the $p$ states as explained in the text. For $N = 12$ the triangles show the experimental values.
impurities with reducing the coordination.

But there is still the important third effect, i.e., the reduction of symmetry, which results in an interaction of the s with the p states that coexist around $E_F$ for sp atoms. In the bulk the impurity has a cubic environment, and the s and p orbitals transform according to different irreducible representations, i.e., an eigenfunction cannot contain both kinds of orbitals simultaneously. As the coordination number is reduced at the surface, cubic symmetry no longer holds and the s and p orbitals are no more decoupled. In the cases studied here, if we choose the z axis to be normal to the surface, it is actually the $p_z$ orbital that is coupled with the s (but in a more asymmetric case as at a step all p orbitals would couple). Then s-p hybrids must exist, here in the form $|s > \pm |p_z >$. The s LDOS becomes more complicated, and in particular each of the s-d hybrids discussed above is expected to split in two (one for each s-p hybrid). Although the s-p hybridization should happen even for $p_z$ orbitals that are coupled), Then s LDOS must exist, here in the form $|s > \pm |p_z >$.

The new picture is as follows. With reduced coordination, two antibonding s-d hybrids exist per spin, one for each s-p hybrid. In the beginning of the sp series (Ag) only bonding hybrids are occupied and $H_{\text{hf}}$ is negative, similar to the bulk case. In the next elements the first antibonding hybrid (which is more s-like since the p states are still high) crosses $E_F$, first for spin up, leading to an increase of $H_{\text{hf}}$, and then for spin down, leading to a decrease. Thus the first peak of $H_{\text{hf}}$ is formed (for $N = 7, 5, 4,$ and $3$, at Sb, Sn, In, and Cd, respectively). As $N$ is reduced the first peak moves toward the beginning of the series because the s-d hybridization is weaker and the first s-d antibonding states are lower in energy. Afterward the second antibonding hybrid (now more p-like, since the p states are lower) crosses $E_F$ and becomes populated, again first for spin up (increasing $H_{\text{hf}}$) and then for spin down (decreasing $H_{\text{hf}}$); the second peak in $H_{\text{hf}}$ is thus formed. In this way the reduction in symmetry for smaller coordination results in a double-peak structure in $H_{\text{hf}}$. The cases for $N = 8$ and 9 are intermediate, in which the s-p hybridization is weak and the first peak merges with the second one creating the shoulder at Sb.

In Fig. 2 the s LDOS is shown for Cd, Xe, and Te impurities in bulk Ni (N=12) and on top of the (001) Ni surface as adatoms (N=4). In the adatom case the $p_z$ LDOS is presented in dotted lines. First we discuss the progressive filling of the states for impurities in bulk. For Cd, the bonding s-d hybrids are occupied for both spins, and the spin-up antibonding hybrid is just starting to pass through $E_F$; $H_{\text{hf}}$ starts to increase. For Te, the antibonding hybrids are more occupied, and for Xe the spin-down antibonding peak becomes occupied. Thus we have the single-peaked structure of $H_{\text{hf}}(Z)$. Now we turn to the adatom case. The s LDOS (full line) looks different. For Cd, the first antibonding hybrid is at $E_F$, and is more pronounced than in the bulk due to the reduced coordination and hybridization. The $p_z$ states (dotted line) are energetically a little higher, but we can already recognize some correlation between s and p at the peaks at $-1$ eV. $H_{\text{hf}}$ is approaching its first maximum. Next, for Te, the first antibonding s hybrid is populated for both spins, while the second is above $E_F$; a “neck” of almost zero s LDOS is at $E_F$, and the s moment and $H_{\text{hf}}$ are almost zero. The p states are lower, and an s-$p_z$ correlation is seen as the peaks coincide between $-5$ eV and $E_F$. Finally, for Xe, the first antibonding hybrid is low (at $-8$ eV accompanied by a peak in $p_z$), while the second is passing by $E_F$, first for spin up giving the second rise to $H_{\text{hf}}$.

Now the observed coordination dependence of $H_{\text{hf}}$ of Cd probe atoms can be understood. In Fig. 3 $H_{\text{hf}}(N)$ is shown, together with the experimental results $\mathbf{8}$ and the calculated results for Te probes. For Cd $H_{\text{hf}}$ increases and changes sign for lower N as the spin-up antibonding s-d hybrids come lower in energy, because of the weaker s-d hybridization. The calculated trends agree with the measured data. For $N = 5$ and 6 the positive values are reported in $\mathbf{8}$, but with the remark that the sign has not been measured but rather deduced from comparison to calculations for 4sp impurities; thus here we show the same values but also with different sign, according to our calculations. The Cd s moment is also shown, to demonstrate its proportionality to $H_{\text{hf}}$. The trends are opposite for Te, where the on-site s-p hybridization for lower N splits the s-d hybrids in two, one populated
and one unpopulated, for each spin. This means that the parabolic decrease of $H_{hf}(N)$ measured for Cd is not necessarily present for other impurities. Rather, each impurity has its own characteristic trend, seen also in the data of Fig. 4 depending on the position of the hybrids.

We now discuss the limitations of the calculations. The local density approximation has been known to underestimate the core electron contribution to $H_{hf}$ in transition elements in the middle of the 3d (Mn and Fe) and 4d series (Ru and Rh) [5,12], but otherwise it gives reasonable agreement with experiment for impurities in bulk. Other terms than the Fermi contact interaction neglected in the present work are the dipole and orbital moment terms. They can contribute to $H_{hf}$ in the absence of cubic symmetry, and can be of the order of a few percent compared to the contact term for $sp$ impurities at Fe/Ag interfaces [5]; for Ni they should be smaller due to the smaller magnetic moment. Finally, atom relaxations, which are not included here, are known to affect $H_{hf}$ for impurities in bulk Fe by a few percent, by changing the strength of the $s$-$d$ hybridization and shifting the antibonding states in the LDOS [12]; they should have a similar effect in Ni.

In conclusion, using first-principles calculations we have interpreted the measured [8] coordination dependence of $H_{hf}$ in Cd impurities in Ni. Our results show a strong, nonlinear dependence on the coordination number $N$, in agreement with the experiment. We have also predicted that the dependence of $H_{hf}(N)$ of the other $5p$ impurities in Ni is not decreasing as in Cd; rather, each impurity exhibits its own “fingerprint” behavior. The reduced coordination gradually lowers the antibonding $s$-$d$ hybrids in energy, and more importantly reduces the symmetry causing an on-site $s$-$p$ hybridization. Thus the trends of $H_{hf}$ for reduced coordination are different than the ones in the bulk. The effects should be similar for $sp$ impurities of the other lines of the periodic table, and also for other ferromagnetic hosts. We hope that our results will be stimulating for future experiments.

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