Giant Moments in Palladium

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(Received 10 October 1985)

Electronic structure calculations based on density-functional theory and the Korringa-Kohn-Rostoker Green's-function method yield a consistent picture of the behavior of local moments of $3d$ impurities in Pd. The calculated local impurity moments are in good agreement with experiments. The giant moments arise from rather extended polarization clouds consisting of very small induced host moments.

PACS numbers: 75.20.Hr, 71.55.Dp

$3d$ impurities in palladium represent very interesting local-moment systems. The susceptibility of pure palladium is strongly exchange enhanced, with a Stoner enhancement factor of about 10, so that palladium can be considered as nearly ferromagnetic. Consequently, magnetic $3d$ impurities induce large host polarizations. The total moments per impurity can be as large as $10\mu_B$ and are known as giant moments. Since the local impurity moment cannot exceed $5\mu_B$, the polarization cloud gives a very important contribution to the giant moment. From early neutron-scattering measurements[1] the clouds are generally believed to be rather extended, containing up to 200 host atoms.

Despite the large amount of experimental work on giant moments in Pd (see, e.g., Nieuwenhuys[2]), the experimental information is not particularly clear. For instance, values for the giant moments for Fe between $4.5\mu_B$ and $12.9\mu_B$ are reported.[2] Also from recent neutron-scattering work[3] the spatial extent of the polarization cloud is not clear at all. Ododo[4] even suggests that the cloud is essentially confined to the first neighboring shell. Concerning the local moments it is not known if Cr or V impurities are magnetic. Isolated Ni impurities are usually believed to be nonmagnetic in Pd and only Ni atoms in clusters of three or more atoms are believed to have local moments.[5,6] This view has recently been challenged by Loram and Mirza[7] who concluded that isolated Ni impurities have a local moment of about $1\mu_B$.

A quantitative theoretical understanding of the giant moments in Pd is therefore rather desirable. The work by Moriya[8] based on tight-binding calculations can at most give trends but no quantitative information. *Ab initio* cluster calculations were recently performed for Fe in Pd by Rodriguez and Keller[9] and by Delley, Ellis, and Freeman.[10] Such calculations are limited in accuracy because of the finite size of the clusters. The calculated Fe impurity moment of Ref. 10 is $3.54\mu_B$ or $3.24\mu_B$ if 43 or 55 atoms (3 or 4 shells) are taken into account. Whereas this difference is tolerable for Fe in Pd, it makes the method questionable in critical cases like Ni in Pd. The method seriously fails for the host polarization: The moment of a nearest-neighbor Pd atom is reduced by almost a factor of 2 if 55 instead of 43 atoms are taken into account. This shows the need for better calculations.

In this Letter we report on self-consistent calculations for $3d$ impurities in an infinite crystal of Pd atoms. We apply the Korringa-Kohn-Rostoker Green's-function method.[11,12] The perturbation of the potentials on the impurity atom and on three shells of surrounding Pd atoms is taken into account. For the atoms outside of this region we use the potential of an ideal Pd host. All potentials are treated in the muffin-tin approximation. The Dyson equation which describes the multiple scattering in the perturbed region and the embedding of this region into the host is solved exactly. The potentials of the impurity and the three shells of perturbed host atoms are determined self-consistently. For more details about the computational scheme we refer to Refs. 11 and 12.

The results for the local moments of the impurities are given in Fig. 1, together with the available experimental data. For Co, Fe, and Mn our results agree within the error bars with the neutron-scattering data by Low and Holden[1] and Cable and David.[13] For Cr

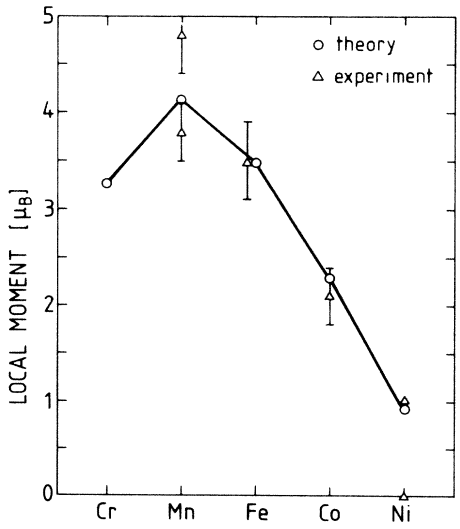

FIG. 1. Comparison between calculated local impurity moments (circles) and experimental results (triangles with error bars).

we obtain a moment larger than $3\mu_B$. No experimental data exist here. Ti and V impurities have also been investigated and turn out to be nonmagnetic. The result for Fe ($3.47\mu_B$) is in reasonable agreement with cluster calculations by Delley, Ellis, and Freeman.[10] Rodriguez and Keller[9] obtain a value of $3.2\mu_B$ for Fe. We consider our somewhat larger value as better because of the superior Green's-function technique.

For Ni we obtain a local moment of $0.92\mu_B$, appreciably larger than the moment of elemental Ni. This is in contrast to the generally accepted view that isolated Ni atoms have no local moments. From an analysis of their susceptibility and magnetization measurements Chouteau[5] and others[6] conclude that in the paramagnetic region of the *Pd*Ni alloy only nearest-neighbor clusters of three or more Ni atoms are magnetic and lead to giant moments. On the other hand, our value of $0.92\mu_B$ is in very good agreement with the Ni moment of $(0.9 \pm 0.18)\mu_B$ measured by Aldred, Rainford, and Stringfellow[14] in the ferromagnetic phase, i.e., for Ni concentrations larger than 2.5%. Furthermore, our estimated giant moment for Ni (see below) agrees very well with the total moment $(4.6 \pm 1.8)\mu_B$ per Ni atom as determined by these authors. Thus our calculations do not support the accepted view that the Ni moment breaks down in the dilute limit. Instead they suggest a stable Ni moment essentially independent of concentration. This is confirmed by our calculations for pairs of Ni impurities on nearest-neighbor sites which yield an almost unchanged local moment ($0.93\mu_B$ for each atom of a ferromagnetic Ni pair instead of $0.92\mu_B$ for a single Ni impurity). Also the Korringa-Kohn-Rostoker coherent-potential approximation calculations by Akai[15] for the concentrated ferromagnetic phase show that the moment changes only slightly with concentration. According to Akai, the unusually large Ni moment is due to the large lattice constant of Pd. Compared to pure Ni the *s*-*d* hybridization is much reduced, so that the *d* charge on the Ni impurity increases by about 0.3 whereas the *sp* charge decreases by the same amount. As a result the impurity moment is about $0.3\mu_B$ larger than the moment in pure Ni ($0.6\mu_B$). Recently the experimental situation has been challenged by Loram and Mirza.[7] From a reanalysis of the experimental data they conclude that Ni impurities are spin-fluctuating or Kondo systems with a spin-fluctuation temperature of 55 K and a local moment of about $1\mu_B$, very much independent of the concentration. Our calculations give an additional strong argument in favor of their interpretation.

The induced moments M_1, M_2, and M_3 of Pd atoms in the first three shells around the impurity are listed in Table I, together with the impurity moment M_0 and the total moment M_{cl} of the considered cluster of 43 atoms. The experimental values for the impurity moments and the giant moments are also included. The induced Pd moments are very small. The largest Pd moment is $0.11\mu_B$ obtained for the nearest neighbor of a Co impurity. The total cluster moments are far off the reported giant moments of about $10\mu_B$. We have checked that these results do not sensitively depend on changes of the exchange-correlation potential and on the number of shells of perturbed Pd potentials taken into account in the calculation. Using the exchange-correlation potential of Vosko, Wilk, and Nusair[16] instead of the one of Moruzzi, Janak, and Williams[17] we find almost no changes for the impurity moments and only small changes for the induced Pd moments. To examine the convergence with respect to the number of shells we have performed detailed calculations in which we change the number of perturbed potentials. A single-site calculation, where only the impurity potential is assumed to be perturbed and all Pd potentials are kept fixed to their values as in the ideal Pd host, already gives a good description of the impurity moments. The results differ by less than a few percent from the values given in the table. Similarly, the polarization of the nearest Pd shell is already obtained

TABLE I. The moments M_0 on the impurity site, $M_{1,2,3}$ on the first-, second-, and third-nearest-neighbor Pd sites, and the cluster moment M_{cl} of all 43 atoms. M_0^{exp} and M_t^{exp} denote the experimental values for the local and giant moments.

Impurity	M_0	M_1	M_2	M_3	M_{cl}	M_0^{exp}	M_t^{exp}
Cr	3.14	−0.024	−0.012	−0.004	2.69	. . .	. . .
Mn	4.13	0.048	0.011	0.015	5.12	3.8 ± 0.3[a]	6.5–8[c]
						4.8 ± 0.4[b]	
Fe	3.47	0.102	0.028	0.028	5.53	3.5 ± 0.4[d]	10–12[c]
							10[e]
Co	2.28	0.114	0.032	0.031	4.60	2.1 ± 0.3[d]	9–10[c]
Ni	0.92	0.063	0.022	0.015	2.18	0[f], 1[g]	4.6 ± 1.8[h]

[a]Reference 11.
[b]Reference 20.
[c]Reference 2.
[d]Reference 1.
[e]Reference 21.
[f]Reference 5.
[g]Reference 7.
[h]Reference 14.

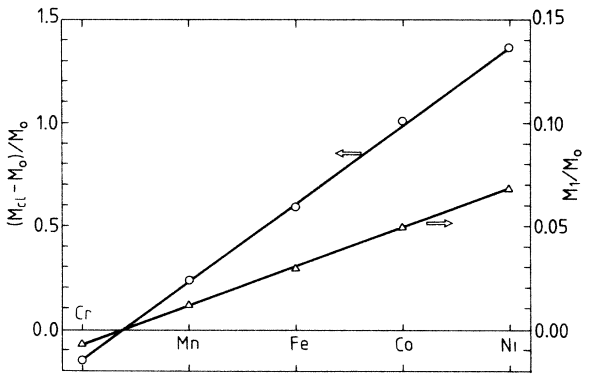

FIG. 2. Linear ΔZ dependence of the ratio M_1/M_0 (right scale) and the total induced cluster moment $(M_{cl}-M_0)/M_0$ (left scale).

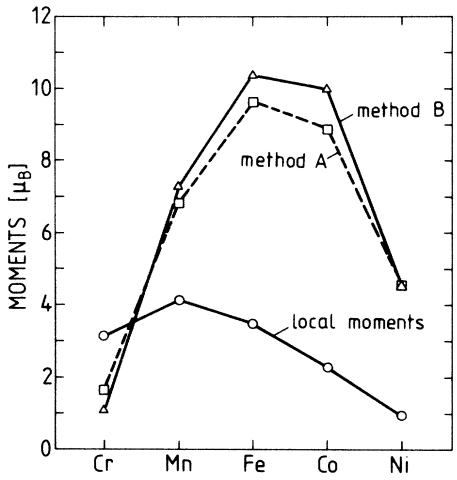

FIG. 3. The giant moments of the $3d$ impurities in Pd as estimated by two different methods (see text). For comparison the impurity moments are also shown.

within a few percent if only the potentials of these twelve atoms and the impurity are assumed to be perturbed. From this we conclude that the results given in the table are reliable and will not change appreciably, if further neighboring shells are included or if other local exchange-correlation potentials are used.

By comparing the calculated cluster moments M_{cl} with the reported giant-moment values of about $10\mu_B$, we conclude that less than 30% of the total induced moment is confined to the 42 Pd atoms in the first three shells. This is also supported by the relatively slow decrease of the moments in the first three shells and is in qualitative agreement with the early neutron-scattering results by Low and Holden,[1] which, however, have been questioned recently.[3,4] The polarization cloud must be very extended and is clearly not confined to the first shell as suggested by Ododo.[4] This conclusion is in line with recent *ab initio* calculations for the susceptibility of pure Pd by Stenzel and Winter[18] which also indicate a long-range interaction.

Our calculations reveal a remarkable ΔZ dependence of host polarization, where ΔZ denotes the difference in valence electrons ($\Delta Z=0,-1,-2,\ldots$ for Ni, Co, Fe, ...). If we plot M_n/M_0 as a function of ΔZ, we find nearly the same linear ΔZ dependence for all shells:

$$\frac{M_n}{M_0} \cong \left.\frac{M_n}{M_0}\right|_{\Delta Z=0} (1+0.28\Delta Z), \quad n=1,2,3.$$

This behavior is shown in Fig. 2 for the nearest-neighbor Pd moments and for the sum over all 42 Pd atoms. Physically this means that the spatial form of the polarization cloud is nearly equal for all impurities; only its amplitude is different. The relative polarization, i.e., the host polarization divided by the impurity moment, is largest for Ni, small for Mn, and even negative for Cr.

Because of the limited size of our cluster, we cannot directly calculate the giant moments. The required cluster size would be enormous and a perturbative treatment using calculated susceptibilities[18] seems to be more attractive. Nevertheless, we can give some reasonable estimates based on the following two methods. In the first method we assume that the above formula is valid for all shells and therefore also for the total induced moment M_{ind} of the polarization cloud. This assumption is reasonable since the asymptotic form of the polarization cloud is determined by the Pd host susceptibility. By fitting the unknown parameter $[M_{ind}/M_0]_{\Delta Z=0}\approx 4$ by the experimental value of $4.6\mu_B$ (Ref. 13) for the giant moment of Ni we obtain the giant moments as displayed in Fig. 3 and denoted by curve "method A." The unknown parameter might as well be fitted to the giant-moment values of Co, Fe, or Mn without essentially changing the curve. For the second method we consider the impurity as a purely magnetic disturbance. As discussed by Moriya,[8] the enhanced total induced moment M_{ind} is directly proportional to the unenhanced total induced moment $\bar{M}_{ind}$:

$$M_{ind}=S\bar{M}_{ind},$$

where S is the Stoner enhancement factor of Pd. Here enhanced or unenhanced refers to a self-consistent or non-self-consistent treatment of the Pd host polarization. We expect this formula based on a perturbative treatment to be reasonably accurate because the induced moments are rather small. The unenhanced moments are calculated with use of the self-consistent impurity potential but the unperturbed host potentials for the Pd atoms of the first three shells. We determine $\bar{M}_{ind}$ by summing the resulting unenhanced host

moments in the first three shells, thus neglecting contributions from more distant shells. This is not unreasonable because the unenhanced cloud should be appreciably better localized than the enhanced one. For the Stoner enhancement we take the value $S = 7.8$ as calculated by Jarlborg and Freeman[19] which is in good agreement with the experiments. The resulting values for the giant moments in Fig. 3 are denoted by the curve "method B." Both curves in Fig. 3 clearly show the same trend. The cloud moment is largest for Co and Fe, considerably smaller for Mn, and negative for Cr. Thus the "giant" moment of Cr is really a dwarf moment, being much smaller than the local Cr moment of $3.14\mu_B$. This trend for the giant moments has already been obtained in the tight-binding calculation by Moriya.[18] Our results are in reasonable agreement with the experimental data (see Table I).

In summary, our calculations yield a consistent picture of the behavior of local moments in Pd. The calculated local moments for Mn, Fe, and Co [(4.13, 3.47, and 2.28)μ_B] are in good agreement with experiment. For Ni we obtain a local moment of $0.92\mu_B$, in contrast to previous experimental conclusions, but in agreement with the reanalysis of Loram and Mirza.[7] For Cr we predict a local moment of $3.14\mu_B$. The induced host moments are quite small and the polarization cloud is very extended, in contrast to recent conclusions.[4] The estimated giant moments are in agreement with the experimental trends and a "dwarf" moment is predicted for Cr.

We thank Dr. Akai for interesting discussions and Dr. Loram for sending a preprint of his work prior to publication.

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