Interaction energies of ^{111}In perturbed-angular-correlation probes with $3d$ and $4sp$ impurities in Ag, Pd, and Rh

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We present systematic *ab initio* calculations for the nearest-neighbor interaction energies of ^{111}In perturbed-angular-correlation probe atoms with $3d$ and $4sp$ impurity atoms (Sc-As, with $Z=21$–33) in Ag, Pd, and Rh. The calculations are based on local-spin-density theory and apply the Korringa-Kohn-Rostoker Green's-function method for spherical potentials. The full nonspherical charge density is evaluated to calculate the double-counting contributions to the total energy. The present calculations reproduce very well the chemical trend of the available experimental interaction energies; attractive interaction of In with $3d$ impurities in Ag and repulsive interaction with $4sp$ impurities in Ag. For Mn-In pairs in Ag, the detailed comparison between the calculated results with and without spin-polarization energy shows the importance of magnetism for the $3d$ impurity-probe interaction enegies and is also useful to elucidate the physical mechanism for the magnetic energy anomalies in cohesive, surface, and solution energies of $3d$ systems.

The knowledge of interatomic interactions in metals is indispensable for the understanding of many basic physical process, such as diffusion, short-range order, segregation, ordering, etc. Królas succeeded in measuring the interaction energies of impurities with the radioactive probes (^{99}Rh, ^{100}Pd, ^{111}In) in metals by use of the perturbed-angular-correlation (PAC) experiments.[1] These experiments are important since they allow a direct and accurate determination of interaction energies which normally is not possible in binary alloys. Following these PAC experiments, we have been able to perform realistic *ab initio* calculations for the interaction energies of $4d$ and $5sp$ impurities with an In probe atom in Ag and Pd and have successfully reproduced most of the available experimental data.[2] The calculations are based on the density-functional theory in the local-spin-density approximations (LSDA) and apply the Korringa-Kohn-Rostoker Green's-function method for impurity calculations. Details about the calculational method are given elsewhere.[3] The good agreement between the theoretical and experimental results seems to ensure the validity of LSDA for the impurity interaction energies.[4]

In the present work we apply the same method to the interaction energies of $3d$ and $4sp$ impurities with an In probe atom in Ag, Pd, and Rh, some of which have been recently measured by Sternik and Królas.[5–7] They have found a very weak (almost zero) attraction of In-Mn in Ag, which is very different from the calculated result for In-Tc in Ag,[2] yielding a strong attraction (~ -0.2 eV). The difference between the interactions of In-Mn (In $3d$ impurity) and In-Tc (In $4d$ impurity) shows the importance of magnetism in the In-Mn interaction since a Mn impurity has a local magnetic moment, while Tc has not; otherwise both are isoelectronic impurities with a similar electronic structure. The present calculations reveal that the weak attraction of Mn-In in Ag can be explained by considering the decrease of spin-polarization energies due to the decrease of magnetic moment causd by the In-Mn pair formation. We can also show

that the physical origin of this very small attraction of In-Mn in Ag is similar to the magnetic energy anomalies found in cohesive, surface, and solution enegies of $3d$ systems.[8]

Figure 1(a) shows the measured ($+$) and calculated results ($\bullet$) for interaction energies of $3d$ and $4sp$ impurities with an In probe atom in Ag. For a comparison, the measured and calculated results for interaction energies of $4d$ and $5sp$ impurities with an In probe atom in Ag are shown in Fig. 1(b). It is noted that the attraction around $3d$ impurities and the repulsion around $4sp$ impurities are reproduced by the present calculations, although the agreement between the PAC experiments and the present calculations is not so gratifying as the agreement obtained for the interaction energies of In-($4d$, $5sp$) in Ag. This seems to be due to the neglect of the lattice relaxation effects which become important for the impurity systems considered in the present work since the Wigner-Seitz radii of $3d$ and $4sp$ impurities are fairly smaller than those of the Ag host and the In probe; it is noted that the Wigner-Seitz radii of $4d$ and $5sp$ impurities are not so different from those of Ag host and In probe, since all the elements are located on the same row of the periodic table.

In order to elucidate the micromechanism of these interactions, we also show in Fig. 1(a) the calculated results for $3d$ and $4sp$ impurities with a vacancy in Ag, which have been already discussed in Refs. 3 and 9; the linear behavior of the attraction around $4sp$ impurities is explained by the screened charge model,[10] while the parabolic behavior of attraction around $3d$ impurities (Δ, the calculated results without spin-polarization effect), is understood by the narrowing of $3d$ virtual bound state due to the interaction with the vacancy and the progressive band filling of this state within the $3d$ series. It is noted that the essential difference between the In-($3d$, $4sp$) interaction energies and the vacancy-($3d$, $4sp$) interaction energies is the sign of the interaction. For $4sp$ impurities the difference is understood by considering the effective valence difference between an In probe and a vacancy in Ag; the effective valence seems to be positive
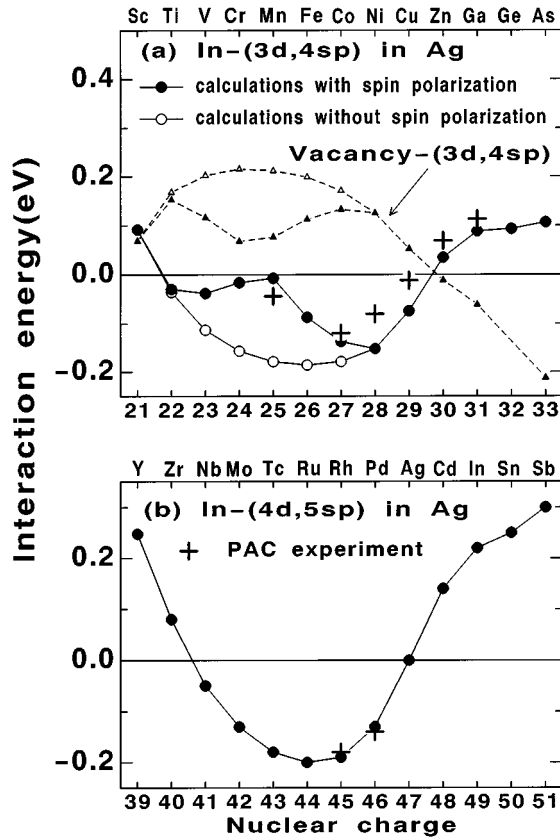
FIG. 1. Calculared interaction energies (●) of (a) $3d$ and $4sp$ impurities with a ^{111}In PAC probe and (b) $4d$ and $5sp$ impurities with a ^{111}In PAC probe, in Ag as well as the experimental results (+). For $3d$ impurities, the calculated results (○) without spin-polarization effect are also shown. For a comparison, the theoretical results (▲) for the interaction energies of $3d$ and $4sp$ impurities with a vacancy in Ag are also included; for $3d$ impurities the calculated results (△) without spin-polarization effect are also shown.

for an In probe and negative for a vacancy. Therefore the repulsion of In-Zn and In-Ga may be understood by use of the screened charge model.[9,10] For In-Ge and In-As, however, the covalent interaction between $4sp$ impurities and In becomes important; it is attractive and cancels a main part of the electrostatic repulsion. Consequently, the interaction energies for In-Ge and In-As may change more smoothly, as seen in Fig. 1(a).

Here we will discuss the role of magnetism for an attraction of $3d$ impurities with an In probe atom in Ag. In order to investigate the magnetic energy, we have also performed calculatons without spin polarization. The calculated results (○), being also shown in Fig. 1(a), are very similar to those of In $4d$ in Ag, shown in Fig. 1(b); consequently the covalent interaction of $3d$ is similar to that of In $4d$ impurities. Therefore the weak attraction of In-Mn, compared with In-Tc, should be understood by considering the change of spin-polarization energy due to the pairing of In and Mn. Figures 2 show the local magnetic moments (a) and spin-polarization energies (b) of single $3d$ impurities in Ag, Pd, and Rh; the magnetism is strongest around Mn and the magnetic moments (MM's) and spin-polarization energies (SPE's) are as large as 4.4 μ and -2.0 eV in Ag. It is also noted that the MM's and SPE's are small in Rh. As will be shown later, the
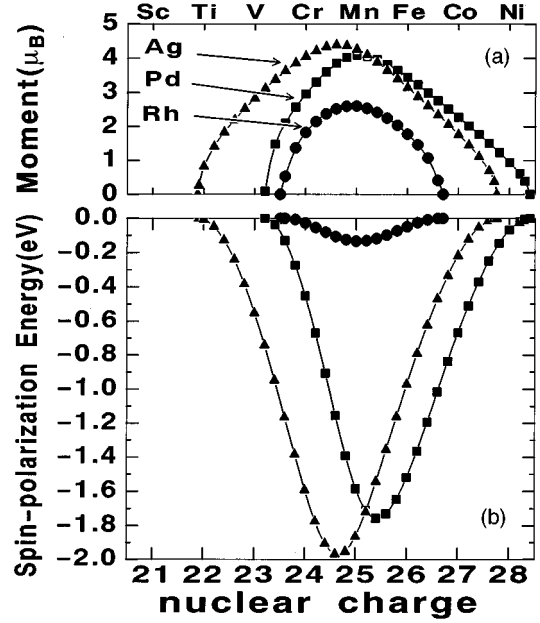

FIG. 2. Local magnetic moments (a) and spin-polarization energies (b) for single $3d$ impurities in Ag, Pd, and Rh. The calculations have also been performed for noninteger nuclear charges.

magnetic interaction of $3d$ impurities with an In probe atom will be also small in Rh. Now we will discuss that the change of SPE due to the changing atomic environment becomes important for the interaction of Mn impurity with an In probe or a vacancy in Ag. Figure 3 and Table I show the MM's for the three different atomic configurations of $3d$ impurities in Ag, i.e., single impurities, single impurties adjacent to a vacancy, and single impurities adjacent to an In probe. By the formation of In-$3d$ pairs in Ag, the hybridization of the $3d$ states with the states of the surrounding atoms increases and the $3d$ virtual states are broadened; hence the MM's of Mn decrease. This decrease of MM's of $3d$ impurities is just opposite to the increase of MM's of $3d$ impurities due to the neighboring of a vacancy, being also listed in Table I. Since the decrease of MM's results in a decrease of SPE's, as will be evident in the next paragraph, the magnetic interaction acts repulsively for the interaction and partly cancels the attractive covalent interaction. As a result we obtain a very small interaction energy for Mn-In in Ag.

In order to clarify the role of the spin-dependent part of the exchange correlation functional of the density-functional theory, we introduce a coupling parameter λ

$$\Delta E_{xc}^{\lambda}\{n(\mathbf{r}),m(\mathbf{r})\}=\lambda e_{xc}\{n(\mathbf{r}),m(\mathbf{r})\}, \qquad (1)$$

$$e_{xc}\{n(\mathbf{r}),m(\mathbf{r})\}=\int d\mathbf{r}\, n(\mathbf{r})[\varepsilon_{xc}(n(\mathbf{r}),m(\mathbf{r}))-\varepsilon_{xc}(n(\mathbf{r}),0)]. \qquad (2)$$

For $\lambda=0$ only the paramagnetic functional $\varepsilon_{xc}(n(\mathbf{r}),0)$ is included in the calculations, whereas $\lambda=1$ refers to the correct functional $\varepsilon_{xc}(n(\mathbf{r}),m(\mathbf{r}))$ including the spin dependence. According to the Hellmann-Feynman theorem, the derivative of the total enegy $E(\lambda)$ with respect to λ is given by
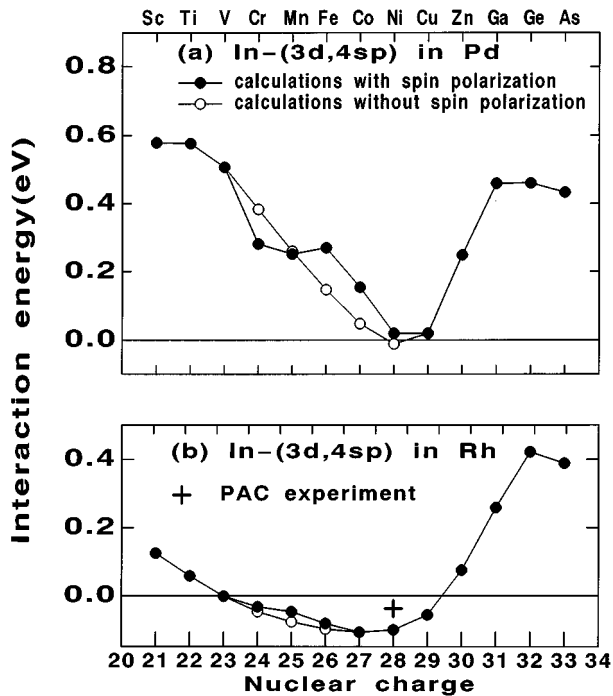
FIG. 3. Local magnetic moments for three different atomic configurations of $3d$ impurities in Ag, Pd, and Rh; single impurities, single impurities adjacent to a vacancy, and single impurities adjacent to an In probe. Please see Table I for the numerical values.

$$\frac{dE(\lambda)}{d\lambda} = e_{xc}\{n_\lambda(\mathbf{r}), m_\lambda(\mathbf{r})\}. \tag{3}$$

By integrating over λ one can obtain the SPE directly from the spin-dependent exchange-correlation energy along, being basically determined by the λ dependence of the magnetization m_λ,

FIG. 4. Variation of (a) the local moment M_λ and (b) the exchange-correlation energy $e_{xc}(\lambda)$ of Eq. (2) as a function of λ for a Mn impurity ($\bigcirc$), a Mn impurity adjacent to a vacancy ($\triangle$), and a Mn impurity adjacent to a ^{111}In PAC probe ($\square$) in Ag.

$$E_{sp} = E(1) - E(0) = \int_0^1 d\lambda \; e_{xc}\{n_\lambda(\mathbf{r}), m_\lambda(\mathbf{r})\}. \tag{4}$$

It is obvious that Eq. (4) verifies the strong correlation between SPE's and MM's, as has been discussed in Ref. 8. In Figs. 4(a) and 4(b), we show the λ dependence of M_λ and $e_{xc}\{n_\lambda(\mathbf{r}), m_\lambda(\mathbf{r})\}$ for a Mn impurity adjacent to an In probe or a vacancy as well as for an isolated Mn impurity in Ag. It is obvious that the MM's and $e_{xc}\{n_\lambda(\mathbf{r}), m_\lambda(\mathbf{r})\}$, hence

TABLE I. Local magnetic moments for three different atomic configurations of $3d$ impurities in Ag, Pd, and Rh, i.e., single impurities, single impurities adjacent to a vacancy, and single impurities adjacent to an In probe.

Impurity	Ti	V	Cr	Mn	Fe	Co	Ni
			Ag host				
Single impurities	0.842	2.852	4.063	4.243	3.121	1.724	
Single impurities with a vacancy	1.089	2.929	4.124	4.308	3.174	1.789	
Single impurities with an In probe	0.610	2.810	4.025	4.178	3.066	1.666	
			Pd host				
Single impurities			2.964	4.086	3.444	2.276	0.938
Single impurities with a vacancy			3.126	4.147	3.470	2.285	0.952
Single impurities with an In probe			3.068	4.051	3.358	2.165	0.788
			Rh host				
Single impurities			1.826	2.603	1.779		
Single impurities with a vacancy			2.127	2.808	1.987		
Single impurities with an In probe			1.608	2.443	1.600		

FIG. 5. Calculated interaction energies ($\bullet$) of $3d$ and $4sp$ impurities with a ^{111}In PAC probe in Pd (a) and Rh (b) as well as the experimental results ($+$). For $3d$ impurities, the calculated results ($\bigcirc$) without spin-polarization effect are also shown.

SPE's [Eq. (4)], decrease by the neighboring of an In probe atom, while they increase by the neighboring of a vacancy; the change of SPE due to the pairing is as large as 0.17 eV (repulsion) for In-Mn and -0.14 eV (attraction) for vacancy-Mn. It is also noted in Fig. 4(b) that the difference of the $e_{xc}\{n_\lambda(\mathbf{r}), m_\lambda(\mathbf{r})\}$ for small values of $\lambda(0.3 \sim 0.5)$ are important for the change of SPE's, while for larger values of λ the $e_{xc}\{n_\lambda(\mathbf{r}), m_\lambda(\mathbf{r})\}$ is saturated and does not change very much for the different environments. Thus the magnitude of SPE is directly connected with the value of the MM. We can conclude that the larger the SPE is, the smaller the hybridization with neighbors.

Lastly we discuss the calculated results of the interaction energies of In-$(3d, 4sp)$ in Pd and Rh. Figures 5 show the calculated interaction energies as well as an available experimental value for In-Ni in Rh. It is noted that the attractive interaction of In-Ni in Rh is reproduced well, although the quantitative agreement is not so gratifying. We found that the calculated results without spin polarization for the Pd host and the Rh host are qualitatively similar with the important difference that in Rh a broad region of attraction exists for In with $3d$ elements between V and Cu; we may expect that the mechanism of nonmagnetic interactions of In-$(3d, 4sp)$ in Rh is similar to those of In-$(3d, 4sp)$ in Pd. We also found that the results of In-$(3d, 4sp)$ in Pd are very similar to those of In-$(4d, 5sp)$ in Pd, shown in Fig. 3(b) in Ref. 2.

Thus the mechanism of In-$(4d, 5sp)$ interactions in Pd discussed in Ref. 2, where the role of $4d$ states of the host Pd is also important, is also useful for nonmagnetic interactions of In-$(3d, 4sp)$ in Pd and Rh: The interaction energies of In-$(3d, 4sp)$ in Pd and Rh may be qualitatively explained by a simple bond model and a repulsion between ion cores. Now we concentrate on the magnetic interaction of In-$3d$ in Pd and Rh. Almost all the calculated results of magnetic interaction (repulsion) can be explained by the mechanism given in the discussion for In-$3d$ in Ag; the smallness of the magnetic interaction (repulsion) of In-$3d$ in Rh directly follows from the very small SPE's of $3d$ impurities in Rh, seen in Fig. 2. However, we found one anomaly, namely the attractive magnetic interaction for the In-Cr pair in Pd, being in contrast to the repulsive magnetic contribution found in all other cases which is caused by the reduction of $3d$ moment due to the interaction with an In probe. This anomalous behavior of the In-Cr interaction may be explained by considering the characteristics of $3d$ virtual states of Cr; the sharp peak of $3d$ majority local up-spin density of states is situated just at the Fermi level, as seen in Fig. 1 in Ref. 11. This sharp peak of $3d$ up-spin states is down shifted by the hybridization of Cr $3d$ with the In $5p$ states being energetically located above the $3d$ level. As a result the Cr moment in Pd increases due to the interaction with an In probe, representing a singular case in Fig. 3 and Table I. Thus, for In-Cr in Pd we obtain an attracive magnetic interaction due to the increase of MM caused by the shift of the d level. For Mn-In, as seen in Fig. 1 in Ref. 11, the upper part of $3d$ up-spin states is situated at the Fermi level, while the peak of $3d$ down-spin states is situated fairly above the Fermi level. Thus we may expect only a small increase of MM due to the down $band$-$shift$ of $3d$ up-spin states, caused by hybridization of Mn $3d$ with In $5p$, which is almost cancelled by the small decrease of MM due to the $band$ $broadening$ of $3d$ states; hence the magnetic interaction practically vanishes, as seen in Fig. 5(a).

We already discussed in Ref. 8 that the magnetic energy anomalies for the $3d$ solution energies, for their binding energies to vacancies, and the binding energies of $3d$ impurity pairs in metals, as well as the surface energies of elemental $3d$ metals are due to the same mechanism (*reduction of coordination number or decrease of hybridization with neighbors*). The present paper also shows that the change of SPE's due to the change of MM's caused by the change of hybridization with neighbors is important for the understanding of the interaction energies of $3d$ impurities with an In probe atom in Ag and Pd. For In-Cr and In-Mn in Pd, the *band-shift* effect together with the *band broadening* of $3d$ virtual states becomes important because of the characteristic features of $3d$ virtual states of Cr and Mn in Pd.

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