

Bound Impurity Orbitals and Giant Impurity Diamagnetism in Metals*

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The bound electron states associated with higher-valence impurities in alkali-metal solvents are calculated by using Hartree-Fock-Slater methods and a dielectric approximation to the electron-gas response. The core diamagnetism and the conduction-electron magnetism together provide a quantitative account of the observed giant diamagnetism.

In recent years, a considerable amount of work has been devoted to the investigation of magnetic impurities in metals. Previous calculations of the magnetism of nontransitional impurities in metals¹ have failed to reproduce even the observed sign of the susceptibility, mainly because the impurity structure was not known. Very recently, the giant diamagnetism² and the anomalously small spin-flip scattering cross section³ of higher-valence impurities in alkali-metal solvents have been ascribed by Rigert and Flynn² to a novel impurity structure. These impurities were assumed to have complete outer valence p shells of six electrons bound in localized orbitals below the band bottom; for example, I enters solution as I^- with a $5s^25p^6^1S_0$ configuration. The closed-shell ions are neutralized by a repulsion of band states which creates a hole in the electron gas near the ions, thereby greatly reducing spin-flip scattering through spin-orbit coupling in the impurity core.

In this Letter, we present a calculation of the structures and magnetic susceptibilities of certain impurities in metals. Our calculations confirm that higher-valence impurities adopt the hypothesized structure² and predict impurity susceptibilities in quantitative agreement with the observed giant diamagnetism.

To calculate the impurity structure, we proceed in the following manner: Let us denote by $V_I(r)$ the potential due to the impurity ion, including all bound orbitals, and by V_S the potential of the solvent ion; also, we denote by $V_\rho(r)$ the potential due to the electron gas in the Wigner-Seitz cell. When the impurity atom is introduced to replace the solvent ion, the perturbation potential is

$$V_{\text{pert}}(r) = V_I(r) - V_S(r). \quad (1)$$

The conduction-electron-gas response to this perturbation, in the linear response approximation, is to create a potential $V_g(r)$ with Fourier

components

$$V_g(k) = V_{\text{pert}}(k)[1/\epsilon(k) - 1], \quad (2)$$

in which $\epsilon(k)$ is the dielectric function of the host metal. The impurity electrons therefore experience an external potential

$$V_{\text{ext}}(r) = V_g(r) + V_\rho(r). \quad (3)$$

In the present calculation, we have employed the random-phase approximation for the dielectric function and have approximated the potential $V_\rho(r)$ by that of a charge e spread uniformly through the Wigner-Seitz sphere. The potential $V_{\text{ext}}(r)$ resembles the Madelung well in ionic crystals and acts to localize the impurity levels. Using the Slater approximation⁴ to the exchange potential, we have computed the electron states of various impurities in alkali-metal host materials. The $V_{\text{ext}}(r)$ calculated from Eqs. (1)–(3) was introduced as an external potential into a modified version of the Herman-Skillman program,⁵ and the core and conduction-electron distribution were iterated to self-consistency. In practice, since the linear-response approximation is poor for strong potentials, we have invariably used for the solvent potential $V_S(r)$ that of an alkali ion having the same core structure as the impurity (e.g., Rb as the host for Se, etc.). Differences among various alkali-metal solvents then enter entirely from the different electron densities and hence from k_F in $\epsilon(k)$. This procedure is obviously correct when *differences* among the alkali-metal pseudopotentials are negligible. More generally, the approximate treatment is satisfactory because the ions are negatively charged. For this reason electrons rarely experience the potential in the impurity core. Figure 1 shows the binding energy with respect to the band bottom for the $5s$ and $5p$ levels of the $5s^25p^6^1S_0$ configuration of Xe, I, Te, Sb, and Sn impurities in K. It is apparent that the orbitals are strongly bound by several electron volts in the first four cases. An erroneous-

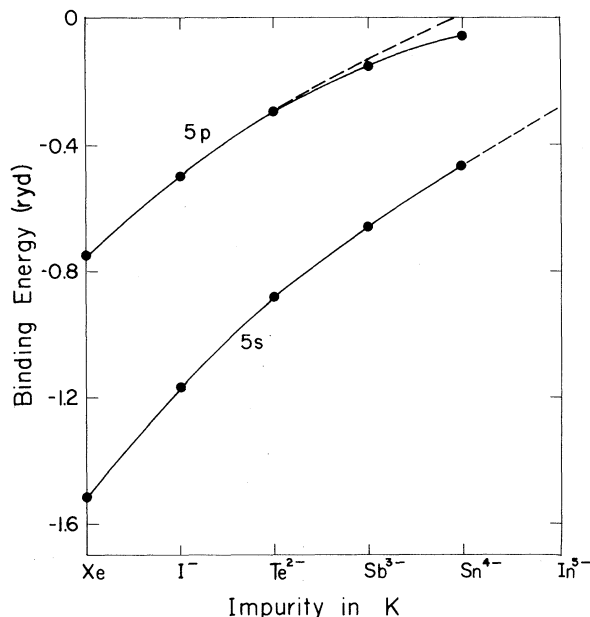


FIG. 1. The solid circles are the calculated binding energies (in rydbergs) for the bound 5s and 5p states of various impurities in K. In each case the energy is calculated for the configuration $5s^2 5p^6 4s_0$.

ly large V_{pert} introduced by a major difference between the solvent and solute core structures can perturb the energy levels by ~ 0.1 Ry.

The impurity susceptibility is calculated in two parts associated with the bound impurity orbitals and with the conduction electrons, respectively. The first part is easily evaluated using the expression⁶

$$\chi_c = -0.791987 \times 10^{-6} \langle \sum_i r_i^2 \rangle \text{ cm}^3/\text{mole}, \quad (4)$$

for r_i in atomic units, in which the sum is over all bound impurity orbitals. The second contribution, of comparable importance, arises from the perturbed conduction band in a way that has been discussed by Kohn and Luming.¹ The evaluation of this term requires the conduction-electron scattering phase shifts as functions of the energy throughout the band. Unfortunately, these quantities can be derived from first principles only through calculations which present formidable computational difficulties. However, in the case of small impurity screening charges, it should be sufficient to replace the actual phase shifts by their asymptotic form for small E . For an x^{n-} ion, the model phase shifts

$$\eta_0(E) = -\frac{1}{2}\pi(E/E_F)^{1/2}, \quad \eta_1(E) = -\frac{1}{6}n\pi(E/E_F)^{3/2} \quad (n \geq 0) \quad (5)$$

TABLE I. Columns 1-3 give various contributions to the theoretical partial molar impurity susceptibilities χ_i^{th} listed in column 4 (see text for details). The final column gives observed values χ_i^{exp} of the susceptibility. All values are given in units of $10^{-6} \text{ cm}^3/\text{mole}$.

	χ_c	χ_p	χ_d	χ_i^{th}	χ_i^{exp}
Impurities in Na					
Te	-69	-65	26	-108	-108 ± 14
Sb	-92	-93	28	-157	-148 ± 15
Bi	-103	-93	28	-168	-136 ± 14
Impurities in K					
Se	-51	-93	37	-107	-123 ± 15
Te	-69	-93	37	-125	-112 ± 30
Sb	-95	-133	40	-188	-154 ± 13
Bi	-105	-133	40	-198	-202 ± 20

satisfy this criterion and also the Friedel sum rule; they also preserve the correct totals of s- and p-like orbitals in the neighborhood of the impurity.

With these phase shifts the impurity spin magnetism (i.e. the change in spin susceptibility when a solvent atom is replaced by an impurity) takes the form

$$\chi_p = \frac{2\mu_B^2}{\pi} \sum_l (2l+1) \left(\frac{d\eta_l}{dE} \right)_{E_F} = -(n + \frac{1}{3})\chi_e, \quad (6)$$

in which $\chi_e = 3\mu_B^2/2E_F$ is the solvent spin paramagnetism. It appears that exchange enhancement in the pure alkali metals is very insensitive to the electron density.⁷ Furthermore, the reduced spin-flip scattering³ cross section of higher-valence impurities demonstrates that even electrons near k_F rarely enter the impurity cores; therefore the solute core potential can have no strong influence on enhancement. It appears reasonable, then, that the observed enhanced χ_e should be used in Eq. (6). While derived for impurity atoms, Eq. (6) also gives a good estimate for large voids of $n+1$ missing solvent ions for which $\chi_p = -(n+1)\chi_e$. We therefore believe that it provides a reliable estimate of the impurity spin paramagnetism.

There remains a small correction χ_o for orbital magnetism. Kohn and Luming¹ show that $\chi_o = (n+1)\chi_L/3$, with χ_L the solvent Landau diamagnetism, for weak general perturbations. It is easily shown that this value holds also for strong highly localized perturbations (e.g., a small strongly repulsive barrier), and this correction ($\approx 10\%$) to the large spin contribution will be used here. In Table I, we collect the susceptibility contributions for the various impurities in Na

and K for which experimental data are available.⁸ Column 1 gives the calculated core diamagnetism, column 2 the spin magnetism using values of χ_e from Ref. 7, and in column 3 are tabulated values χ_d of the diamagnetic correction χ_o plus the solvent band susceptibility required to change the theoretical results into the required partial molar impurity susceptibilities χ_i . The latter correction is needed because phase-shift arguments give the susceptibility change when a solvent ion is *replaced* by an impurity, whereas the experimental quantities give the change when unit quantity of impurity is *added* to the solvent. The sum of columns 1-3, χ_i^{th} , is given in column 4. These theoretical values are in very good agreement with the observed susceptibilities χ_i^{exp} given in column 5; they constitute the first successful calculations of nontransitional impurity magnetism in metals, and confirm the proposed model of impurity structure. Calculations for the alternative structure,¹ in which the impurity valence states resonate with the host (Cu) conduction band, yield susceptibilities which are an order of magnitude smaller and have the wrong sign.

The present methods break down for very shallow levels. Indeed, the sharp distinction between localized and propagating states in metals disappears as dynamical correlations blur the bound orbitals into the band bottom with decreasing impurity binding.⁹ The agreement between theory and experiment for Sb in Na and K and for Bi in K seems to tie down these effects as important only for binding energies $\lesssim 0.1$ Ry; deeper levels are probably given rather accurately by our static dielectric approximation.

The transition from bound to band states cannot be predicted by means of a time-averaged potential $V_I(r)$. Nevertheless, the sequence of $5p$ levels shown in Fig. 1 does point accurately (broken line) to the observed¹⁰ transition of Sn

orbitals at about the conduction-band density of K. Experimental details of the Sn and Bi transitions will be reported in due course.

Finally we note that excited impurity configurations may also be bound. In rare-gas and ionic crystals, $np^6 - np^5(n+1)s^1$ transitions of closed-shell ions possess a characteristic doublet structure¹¹ due to spin-orbit splitting of the core-hole levels. Attempts to observe these excitations and to predict their energies are at present in progress in our laboratories.

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