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Electronic structure of a single manganese impurity in aluminum

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The electronic structure of a single manganese impurity in aluminum is studied using the discrete-variational local-spin-density-functional method with cluster models. The effects of size, geometry, and environment of clusters are considered. The results show that the dilute *Al*-Mn alloy is *not* a spin-fluctuation system and that the ground state of a single Mn in Al at $T=0$ K is magnetic. The result of about a $3.2\mu_B$ local moment on the Mn impurity, which is partially compensated by an antiferromagnetic coupling to the Al conduction band, verifies the analysis of Cooper and Miljak. The value of the exchange splitting of the Mn 3*s* level is 2.92 eV, in excellent agreement with the experimental one (2.9 eV). In contrast with all previous computational results, but in agreement with results from recent x-ray-absorption spectra of Al-Mn alloys, we find a transfer of about one electron from the Mn impurity to the Al host.

I. INTRODUCTION

For a long time there has been interest in the behavior of dilute transition-metal impurities alloyed in nonmagnetic metals.[1–3] Two different models have been proposed to describe the magnetic properties of dilute alloys, namely, the Friedel-Anderson virtual-bound-state model[4,5] and the Schrieffer-Hirst impurity-ion crystal-field model.[6,7] In order to explain the collapse of Curie-Weiss behavior or the nonmagnetic states of these systems at low temperatures, two concepts are widely used: (i) the Kondo compensation cloud[8] and (ii) the localized spin fluctuation.[1] From the point of view of the former, the nonmagnetic state is the result of the compensation of the well-defined high-temperature impurity spin by the surrounding electron gas and a buildup of a nonperturbative long-range spin polarization around the impurity. On the other hand, the localized-spin-fluctuation concept regards the impurity as nonmagnetic at $T=0$ K with $S=0$, and therefore no extra spin correlations are expected in the surrounding electron gas.

The dilute alloy Al-Mn has been described as a spin-fluctuation system with a high Kondo temperature.[1] Experimentally, Steiner *et al.*[9] observed, from the x-ray photoemission spectroscopy (XPS) experiment, a splitting of 2.9 eV of the Mn 3*s* level in dilute *Al*-Mn alloys at room temperature, and suggested that in *Al*-Mn the Mn ion is magnetic, at least in the time scale of the XPS measurement. Cooper and Miljak[10] measured the static magnetic susceptibility of dilute *Al*-Mn alloys in the temperature range 2–300 K. After a complicated analysis with an experimental fit, they estimated that the high temperature moment of an isolated Mn atom in Al should be $3.2\pm0.2\mu_B$.

There have been several first-principles theoretical calculations of the electronic structure of *Al*-Mn at $T=0$ K. Nonetheless, the question whether the ground state of a single Mn in Al at $T=0$ K is or is not magnetic has not yet a definite answer and a complete quantitative description is required. Nieminen and Puska,[11] using a jellium model, obtained a local moment of $2.46\mu_B$ on the Mn atom with the *d* resonance being split by 2.38 eV. Using the Korringa-Kohn-Rostoker Green's-function method, Deutz, Dederichs, and Zeller[12] calculated the electronic structure of *Al*-Mn and found that the Mn impurity is magnetic, with a local moment of $2.5\mu_B$. Based on the calculation of a free MnAl_{18} cluster in the frame of local-spin-density (LSD) theory, Bagayoko *et al.*[13] reported that the local moment of Mn is $1.74\mu_B$ and the exchange splitting of the Mn 3*s* level is 1.88 eV. A recent multiple-scattering $X\alpha$ free MnAl_{18} cluster calculation by McHenry *et al.*[14] gave the result that Mn in Al is nonmagnetic. In this calculation, a cluster moment of $1\mu_B$ is obtained, but it is explained simply as the requirement of the size and geometry of the cluster.

In this paper, we report the result of discrete-variational (DV)-LSD calculations for the electronic structure of a single manganese impurity in aluminum. We also use cluster models, but the effects of size, geometry, and environment of cluster are considered. These considerations are reflected in our four cluster models, which may be described as follows: (a) A free MnAl_{18} cluster. It represents a Mn impurity coordinated by first- and second-nearest-neighbor Al atoms with fcc geometry. (b) Also a free MnAl_{18} cluster. In this model, we allow levels near the Fermi energy to have partial (nonintegral) occupation numbers, as if the cluster were at a finite but small temperature.[15] The Fermi distribution for the thermal population of these levels is

$$\omega_i = \frac{1}{1+e^{(\varepsilon_i-\varepsilon_F)/\xi}} , \tag{1}$$

where ε_i is the energy eigenvalue, ε_F is Fermi energy, and ξ is a *temperature factor* which specifies the sharpness of the Fermi function. (c) An embedded MnAl_{18} cluster. In this model, the cluster is embedded in a microcrystal consisting of several hundreds atoms simulating the rest of the solid. The charge density $\rho(\mathbf{r})$ which determines both Coulomb and exchange-correlation potentials includes the contribution from the embedding lattice.[16] (d) A free MnAl_{42} cluster. This model contains the third-nearest-neighbor Al atoms on the basis of model (a).

II. METHOD

The DV-LSD method is a kind of molecular-orbital calculation method and its theoretical foundation is LSD theory. Since it has been described in detail elsewhere,[17,18] here we only recall its essential features and discuss the choice of computational parameters.

The method may be summarized as follows.

(a) In the effective Schrödinger equation for the one-particle orbitals, the usual nonlocal Hartree-Fock exchange potential is replaced by an exchange-correlation potential depending only on the local electron spin density $\rho_\sigma(\mathbf{r})$. In this paper, the exchange-correlation potential is taken to be of the von Barth–Hedin form,[19] with the parameters taken from Moruzzi, Janak, and Williams.[20]

(b) The matrix elements of the Hamiltonian and overlap matrices are obtained by a weighted summation over a set of discrete sample points (Diophantine points)[17] $\mathbf{r}_k$, i.e.,

$$\begin{aligned} H_{i\sigma,j\sigma'} &= \langle \chi_{i\sigma}|H|\chi_{j\sigma'}\rangle \\ &= \sum_k \omega(\mathbf{r}_k)\chi^*_{i\sigma}(\mathbf{r}_k)H(\mathbf{r}_k)\chi_{j\sigma'}(\mathbf{r}_k) , \\ S_{i\sigma,j\sigma'} &= \langle \chi_{i\sigma}|\chi_{j\sigma'}\rangle \\ &= \sum_k \omega(\mathbf{r}_k)\chi^*_{i\sigma}(\mathbf{r}_k)\chi_{j\sigma'}(\mathbf{r}_k) , \end{aligned} \tag{2}$$

where $\omega(\mathbf{r}_k)$'s are appropriate integration weights. We choose 300 Diophantine points per atom for all atoms in our calculations.

(c) The calculation of Coulomb integrals is simplified by introducing the average self-consistent charge density ρ_{SCC} (SCC approximation):[21]

$$\rho=\rho_{\mathrm{SCC}}=\sum_{\nu,n,l,\sigma} f^{\nu}_{nl\sigma}R_{nl\sigma}(\mathbf{r}_\nu)|^2 , \tag{3}$$

where $f^{\nu}_{nl\sigma}$ is the Mulliken population for the nl atomic shell with spin σ of atom ν, $R_{nl\sigma}(\mathbf{r}_\nu)$ is the corresponding radial function evaluated at distance $(\mathbf{r}_\nu)$ from the nuclear position.

(d) The one-electron states $\chi_{i\sigma}$ and energy eigenvalues $\varepsilon_{i\sigma}$ are obtained through the following charge self-consistent process:

$$\begin{tikzcd} \rho_{\mathrm{atom}} \arrow[r] & \rho_{\mathrm{SCC}} \arrow[r] & V_c+V_{\mathrm{xc}} \; . \arrow[dl] \\ & \{\varepsilon_{i\sigma},\chi_{i\sigma}\} \arrow[u] & \end{tikzcd} \tag{4}$$

(e) The numerical atomic wave functions obtained from a self-consistent atomic LSD calculation are chosen as the variational basis set.

In our calculations the variational basis set are the 1*s*-3*p* wave functions of a free Al atom and the 1*s*-4*p* of a Mn atom within a potential well of 2 a.u. extending out up to a radius of 6 a.u.; the lower-energy orbitals (i.e., 1*s*-2*p* both of Al and Mn) are treated as frozen cores. In model (b), ξ is chosen to be equal to 0.0001 a.u.

III. RESULTS AND DISCUSSION

Table I lists our main results. As the first note, there are not great differences among our results for the four cluster models. This shows that the free cluster model with an appropriate size is still a good model for the local electronic structure of the dilute *Al*-Mn alloy. Even for the host Al, being a nearly-free electron metal, Salahub and Messmer[22] have shown that a free Al_{43} cluster yields a manifold of energy states having a total band width and energy distributions which are consistent both with band-structure calculations and with measured XPS data for crystalline aluminum.

All our calculations give a magnetic ground state for the Mn impurity in Al which agrees with conclusions of previous calculations except that of McHenry *et al.*[14] A cluster moment of $1\mu_B$ is obtained for all cases. This implies that the cluster moment is not an artifact of an unpaired electron on the manganese site.

Defining a local moment on atom ν as

$$\mu^{\nu}=\sum_{n,l,\sigma} 2\sigma f^{\nu}_{nl\sigma}\mu_B , \tag{5}$$

in all models considered we obtain a local moment on the Mn impurity which is substantially larger than that found in all calculations mentioned above, and in much better agreement with the value of the analysis of Cooper and Miljak.[10]

Recalling that Delley, Ellis, and Freeman[23] used the same method to calculate the electronic structure of dilute *Pd*-Fe alloys and obtained a local moment in excellent agreement with the experimental one, it is not surprising that we obtain such a good value here. The calculation of Nieminen and Puska[11] was performed by using a jellium model, where the real atomic structure of Al was ignored. In the calculation of Deutz, Dederichs, and Zeller,[12] only the impurity potential was calculated fully self-consistently, while the host potential was assumed to be that of bulk aluminum without impurities. McHenry *et al.*[14] used the muffin-tin and $X\alpha$ exchange-potential approximations, and the correlation potential was not included explicitly in their calculation.

As for the discrepancy between the result of our model (a) and that of Bagayoko *et al.*,[13] at first we attributed it to the fact that the basis sets and the local exchange-correlation potentials used in the two works are different, but these differences cannot completely account for the

TABLE I. Local and total moments and exchange splittings of the Mn impurity in Al.

		Present calculations				Previous calculations				Experimental
		Model (a)	Model (b)	Model (c)	Model (d)	Ref. 11	Ref. 12	Ref. 13	Ref. 14	results
Magnetic	Local	3.43	3.43	3.41	3.26	2.48	2.53	1.74	0.00	3.20±0.2
moments (μ_B)	Total	1.00	1.00	1.00	1.00		2.24	1.00	1.00	
Exchange	Mn 3*s*	2.98	2.98	2.97	2.92			1.88		2.9
splittings (eV)	Mn 3*d*	0.55–1.22	0.55–1.22	0.55–1.22	0.42–1.10	2.38	0.93	0.50–0.70		

discrepancy. In the calculation of Bagayoko *et al.*,[13] a Gaussian-type basis set containing *d*-orbital components of Al atom was used, and the local exchange-correlation potential was taken to be of the Rajagopal-Singhal-Kimball (RSK) form.[24]

Extending our basis set to include the 3*d* of Al and the 4*d* of Mn in the calculation of model (a), we obtained a local moment of $3.27\mu_B$, which is only slightly smaller than the value of $3.43\mu_B$ obtained with the previous basis set. Using the RSK local exchange-correlation potential in the calculation of model (a), we found a local moment of $3.23\mu_B$ for Mn. We also performed a calculation for model (a) using both the extended basis set and RSK local exchange-correlation potential and obtained a local moment of $3.01\mu_B$ for Mn.

Thus, even if we cannot regard as precise the numerical value of the local moment due to its slight dependence on the basis set and on the form of the exchange-correlation potential and due to the uncertainties of the Mulliken population analysis, we may claim that in all cases our result is in the range of the value of Cooper and Miljak.[10]

Table I also lists the exchange splittings of the Mn impurity in Al. For the Mn 3*s* core level we obtain an exchange splitting of 2.92 eV, in excellent agreement with the measured XPS data[9] (2.9 eV). This result, in turn, verifies the correctness of our local moment value. The 3*d* levels of Mn atom also have a significant exchange splitting, in a range from 0.42 to 1.10 eV. Our larger value is smaller than that of Nieminen and Puska,[11] larger than that of Bagayoko *et al.*,[13] and close to that of Deutz, Dederichs, and Zeller.[12]

Figures 1 and 2 present one-electron energy levels and densities of states (DOS) for model (d). The DOS is obtained by a Gaussian extension of the energy levels (extension width is 0.015 a.u.) and a summation over them. In Fig. 1, the Fermi level coincides with a partially occupied e_g spin-down level, which is the same as that of

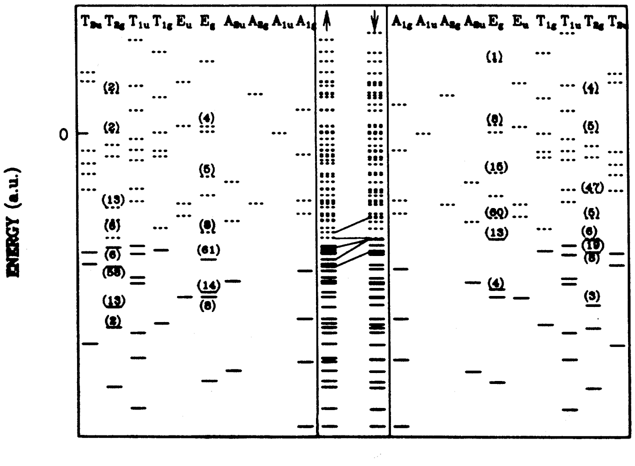

FIG. 1. One-electron energy levels for $MnAl_{42}$ cluster. Filled orbitals are represented by solid lines, unfilled levels by dashed lines. Numbers in parentheses give the percent Mn 3*d* character, values less than 1% are not marked.

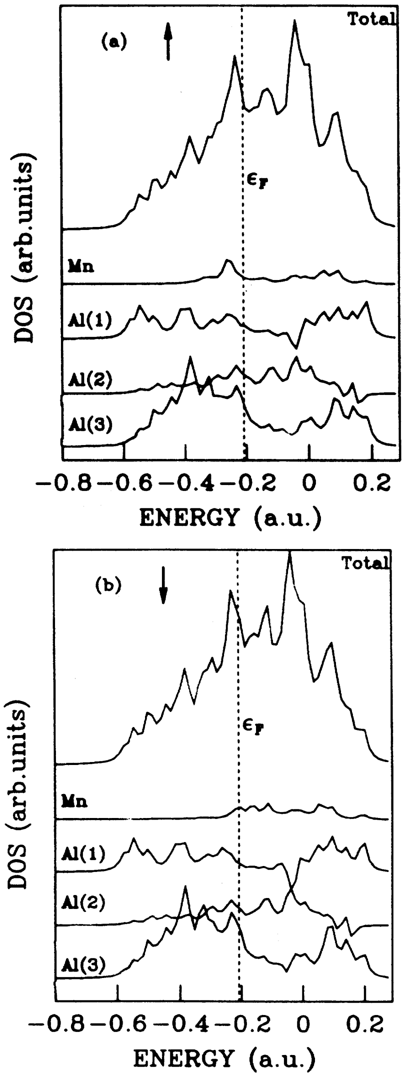

FIG. 2. DOS for $MnAl_{42}$ cluster: (a) spin up and (b) spin down.

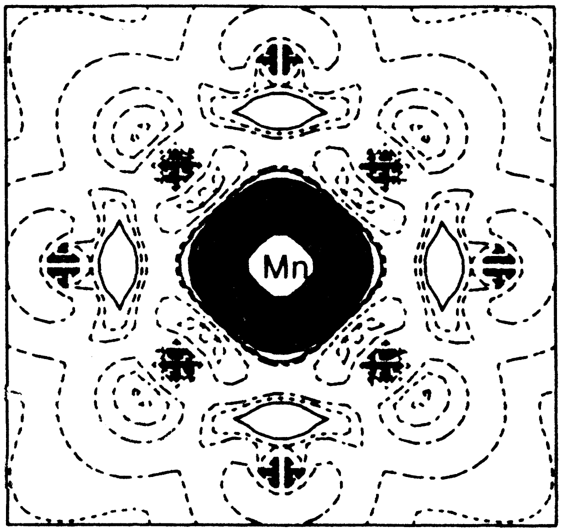

FIG. 3. Spin-density distribution of $MnAl_{42}$ cluster in the *xy* plane. Positive and negative values of the spin density are indicated by solid and dashed lines, respectively, and the increment of contour step is $0.0005e/a^3$.

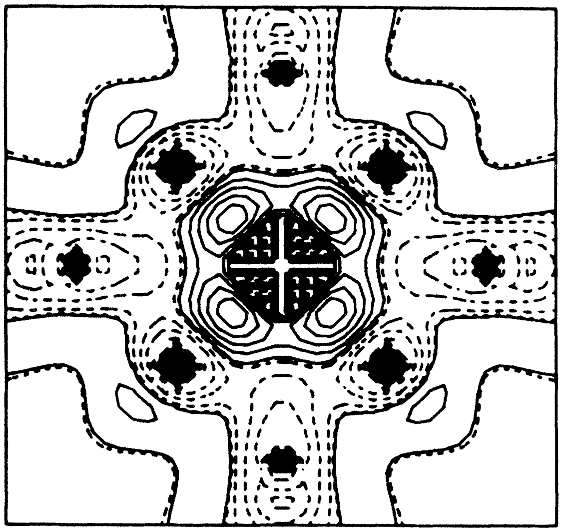

FIG. 4. Difference density [$\Delta\rho = \rho$ (self-consistent field)$-\rho$ (overlapping atoms)] plots for $MnAl_{42}$ cluster in the *xy* plane. Positive and negative values of the $\Delta\rho$ are indicated by solid and dashed lines, respectively, and the increment of contour step is $0.0004e/a^3$.

Bagayoko *et al.*,[13] but is in disagreement with that of McHenry *et al.*[14] where the Fermi level falls in a t_{1g} level. In Fig. 2, the partial densities of Mn resemble the virtual bound states of the Anderson model; however, they cannot be fitted by a single Lorentzian. According to the representation of the O_h point group, the *d* orbitals of a central Mn hybridize with the *s* and *p* orbitals of the neighboring Al atoms, forming t_{2g}-type and e_g-type molecular orbitals. From these figures, we can see that this kind of hybridization is observed predominantly in the upper bands. Moreover, among these t_{2g} and e_g levels, the low-lying levels are Al *s*–Mn *d* bonding in character, whereas the levels near ε_F have Al *p*–Mn *d* bonding character.

The spin-density distribution of model (d) is shown in Fig. 3, where the positive polarization of the central Mn and the negative polarizations of surrounding Al atoms are apparent. This distribution is similar to the picture of the Kondo compensation cloud,[7] and contradicts the description of spin-fluctuation theory[1] suggesting that at $T = 0$ K the local moment of the impurity is compensated by an infinite-lifetime localized moment at the impurity site. All the above results obviously suggest that the dilute *Al*-Mn alloy should not be a spin-fluctuation system. Hence, all the theoretical considerations based on the spin-fluctuation theory for this system should be reexamined.

Mulliken populations for the atomic orbitals of model (d) listed in Table II suggest that the Mn impurity loses

TABLE II. Mulliken population analysis for the atomic orbitals of $MnAl_{42}$ cluster.

		$MnAl_{42}$	
	Orbital	Charge (a.u.)	Net spin ($\frac{1}{2}$ a.u.)
Mn	3*s*	1.995	−0.003
	3*p*	5.991	−0.001
	3*d*	5.378	3.100
	4*s*	0.196	0.071
	4*p*	0.418	0.088
	Total	13.978	3.255
Al(1)	3*s*	1.356	−0.010
	3*p*	1.951	−0.073
	Total	3.307	−0.083
Al(2)	3*s*	1.449	−0.039
	3*p*	1.634	0.003
	Total	3.083	−0.042
Al(3)	3*s*	1.665	0.003
	3*p*	1.204	−0.046
	Total	2.869	−0.043

about one electron; the analogous populations calculated in the other models we considered give a slightly larger total population on Mn, corresponding to a transfer of about 0.7 electrons from the Mn impurity to the Al host. In all models, this result differs completely from all previous computational results.[3,12,13] Although the diagonal weighted Mulliken population[18] we used does not have a strict accuracy, we believe that it is qualitatively correct. In fact, our result is in agreement with Pauling's electronegativity rules. The electronegativity value of Mn is 1.55, lower than that of Al which is 1.61.[25] Recently, Deshpande and Mande[26] studied the Mn K-absorption discontinuity in Mn and in Al-Mn alloys. They found that the K-absorption discontinuity of Mn in alloys shifts towards higher energies with respect to that in the metal. This indicates that Mn in Al acts as a cation, in agreement with our Mulliken populations.

To show how Mn loses its electron in model (d), we have prepared charge-density difference plots where a reference density from overlapping atomic Mn and Al densities is subtracted (Fig. 4). From the figure, we can see that Mn loses its electron mainly in the core region, and in the interstitial region of Mn and Al atoms the charge density is enhanced compared with that obtained by overlapping atomic charge densities.

In conclusion, we have presented the electronic structure of a single manganese impurity in aluminum, showing that the dilute *Al*-Mn alloy is *not* a spin-fluctuation system and that the ground state of a single Mn in Al at $T=0$ K is magnetic. A local moment of about $3.2\mu_B$ for Mn in Al, partially compensated by an antiferromagnetic coupling to the Al conduction band, is obtained. It verifies the analysis of Cooper and Miljak based on experimental measurements for the first time.

The value of the exchange splitting of the Mn 3s level is 2.92 eV, in excellent agreement with the experimental one (2.9 eV). A transfer of about one electron from the Mn impurity to the Al host is found, which is in contrast with all previous computational results, but agrees with results of the recent x-ray absorption spectra of Al-Mn alloys.

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