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Brief Reports

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Electronic and magnetic properties of manganese impurities in aluminum

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We studied the electronic structure of manganese impurities in a fcc aluminum matrix by means of calculations for a free $MnAl_{18}$ cluster. Our *ab initio* self-consistent computations employed the Rajagopal-Singhal-Kimball RSK local-spin-density potential and a symmetrized Gaussian-orbital basis. The local and cluster magnetic moments are, respectively, $1.74\mu_B$ and $1.0\mu_B$. Substantial screening of the Mn moment by opposite polarization of the surrounding Al atoms was found.

I. INTRODUCTION

The question of the magnetic properties of Mn impurities in aluminum has turned out to be quite complex. In general, $3d$ transition-metal impurities in aluminum have nonmagnetic ground states, and are described in terms of the Anderson model of a resonant $3d$ level situated in a broad band.[1] Al-Mn has been described as a spin-fluctuation system with a high Kondo temperature[2] about 600 K,[3] the supposition being that at high temperatures, a reasonably permanent local moment would be found. At room temperature, x-ray photoemission spectroscopy (XPS) measurements revealed an exchange-split Mn $3s$ state[4] so that at least on a short-time scale, a local moment should be present.

Additional interest in the state of Mn in Al has resulted from the discovery of an icosahedral phase in Al_6Mn alloys. Mn has a well-defined local moment in the quasicrystalline phase which increases with Mn content up to a maximum of about $(1.5\pm0.5)\mu_B$.[5] The moment disappears if the sample is annealed into the crystalline orthorhombic phase. A magnetic moment has also been found in amorphous films and in crystalline (fcc) ribbons[6] according to measurements of the magnetic susceptibility. In particular, a crystalline film of composition $Al_{95}M_5$ was found to have a moment of $1.55\mu_B$. Moreover, amorphous films showed somewhat smaller moments than crystalline samples of the same composition and a crystalline film with only half the Mn content mentioned above showed no moment.

Evidently a definitive understanding of the magnetic properties of Mn in Al does not yet exist. The indications are that moment formation depends critically on the geometry of the Mn sites, the number, and the arrangement of aluminum neighbors. Possibly also the formation of manganese clusters is important.

We report here briefly a calculation of the properties of a manganese atom in a cluster of aluminum atoms. This calculation is part of an investigation of several transition-metal impurities in aluminum. We believe that there is sufficient current interest in the Al-Mn system to justify separate publication of this result.

We will first mention some related previous calculations. Several have employed model potentials in scattering calculations related to Anderson's approach.[7-10] McHenry *et al.*[11] have reported $X\alpha$ scattered wave calculations for icosahedral clusters, $MnAl_{12}$ and $MnAl_{32}$. They found an unusually high density of states at the Fermi energy. A high density of states at the Fermi energy would be expected to favor local moment formation, in agreement with the observation of a local moment in the icosahedral structure, by McHenry *et al.* do not discuss this possibility.

Local moment formation has been investigated by Nieminen and Puska,[12] using a jellium model. These authors found a moment of $2.46\mu_B$ on the manganese atom, with the d resonance being split by 2.38 eV. Deutz, Dederichs, and Zeller reported KKR-Green's function calculations for many impurities in aluminum.[13] Chromium, manganese, and iron were found to possess local moments. The local moment of manganese was $2.53\mu_B$, and the total moment (which includes induced polarization on neighboring atoms) was 2.24. In these calculations only the impurity potential is calculated fully self-consistently; the host potential is assumed to be that of bulk aluminum without impurities.

The present calculation is based on a free cluster model. The specific system studied is $MnAl_{12}Al_6$. The Mn atom is at the center of an arrangement of aluminum atoms with fcc geometry; these atoms form the first- and second-neighbor shells. The atomic positions correspond to a crystalline lattice constant of 7.635 a.u. The manganese concentration is close to that of some of the samples studied in the experiment of Hauser *et al.*[6] The calculation is based on the local-spin-density approximation. We obtain a local moment substantially smaller than that of the calculations cited above, and in much better agreement with (one of) the crystalline samples studied in Ref. 6 than any previous calculation. In the remainder of this Brief Report, we briefly describe our method, present our results, and compare them with experiment and with other calculations.

II. METHOD

The present calculations are similar to our previous studies of transition-metal impurities in copper.[14,15] We use the RSK local-spin-density potential.[16] The calculations are variational in nature, and employ a basis set consisting of symmetrized combinations of independent (uncontracted) Gaussian orbitals.[17,18] All electrons are included in the self-consistent computations. No frozen core or muffin-tin approximations are made. The cluster is treated as a free particle. A supplementary charge fitting was made in the calculations of matrix elements of the Coulomb potential.[19] Matrix elements of the exchange correlation potential are calculated numerically using a three-dimensional grid.[17]

The apparent sensitivity of the local manganese moment to the environment suggests that it is important to use a large basis set in order to approach basis set completeness. We have therefore enlarged the basis sets employed in our previous calculations. Here we use 14*s*, 11*p*, and 12*d* Gaussian orbitals for Mn and 12*s*, 9*p*, and 5*d* orbitals for each aluminum atom. The sets were formed by supplementing published atomic bases[20] by even-tempered diffuse orbitals. These basis sets are shown in Table I.

TABLE I. Exponents for the Gaussian orbitals used in our calculations.

s	*p*	*d*
	Manganese	
243 694.0	1500.39	37.8977
35 995.0	358.800	10.5201
8 223.56	116.699	3.537 64
2 353.12	44.6132	1.212 17
780.965	18.5985	0.387 912
288.519	8.137 78	0.259
115.701	3.337 34	0.172
49.117 5	1.378 95	0.115
16.088 5	0.538 639	0.077
6.704 30	0.127 65	0.051
1.805 17	0.040 78	0.034
0.703 011		0.023
0.106 385		
0.039 616		
	Aluminum	
55 000.00	260.00	25.00
8 200.0	60.90	9.0
1 860.0	19.30	2.1
530.0	7.00	0.5
175.0	2.67	0.21
64.0	1.03	
25.300	0.308	
10.600	0.150	
3.210	0.069	
1.150		
0.178		
0.059 45		

III. RESULTS AND DISCUSSION

The energies of the levels above the core are shown in Fig. 1. The levels between −1 and −0.5 Ry are predominantely aluminum levels, hybridized where symmetry permits, with manganese *s*, *p*, and *d*. The exchange splitting of these levels is small. Levels of e_g and t_{2g} symmetry lying between −0.5 Ry and the Fermi energy at −0.34 Ry contain manganese *d* functions, but are strongly hybridized with aluminum *s* and *p* functions. These levels have a significant exchange splitting, in a range of 0.5 to 0.7 eV. The Fermi level falls on an e_g state.

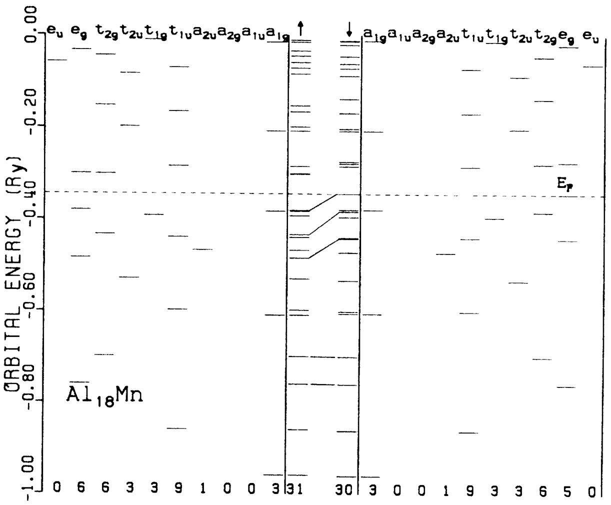

FIG. 1. Energy-level diagram for the $Al_{18}Mn$ cluster for up and down spins. Some levels are connected by a line to illustrate the spin splitting. The numbers at the bottom of the diagram are the total occupancies of states whose symmetry is specified at the top.

Our calculated density of states for the cluster is shown in Fig. 2(c). The principal influence of the manganese atom is the introduction of peaks which are emphasized by cross hatching in the diagram. Figures 2(a) and 2(b) show the Mn density of states separately as determined with the aid of a Mulliken population analysis. The spin slitting of the upper Mn states is apparent in this figure. In some qualitative aspects, our results resemble the predictions of the simple conventional Anderson model, but there is a major difference in detail. There is not a single *d* level. Instead, the *d* states are split between t_{2g} and e_g representations. Since func-

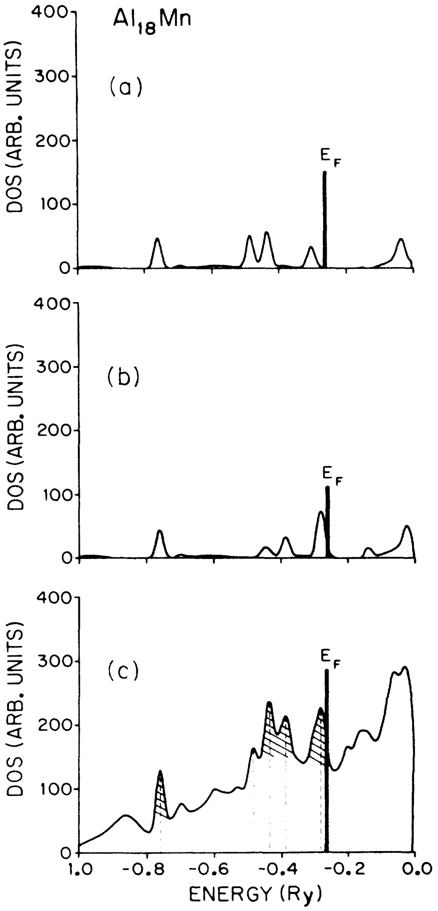

FIG. 2. Cluster density of states for $Al_{18}Mn$. (a) Mn partial density of states for majority spin; (b) Mn partial density of state for minority spin; (c) total density of states for the cluster. The cross hatching shows the portions of the density of states below the Fermi energy containing the manganese *d* electrons.

tions belonging to these representations can be constructed from aluminum *s* and *p* functions which hybridize strongly with the manganese *d*, the manganese *d* functions are mixed into several occupied states spread over an interval of about 6 eV. The lower states of these symmetries have small exchange splittings.

Table II contains the results of a Mulliken population analysis for the cluster. This shows roughly a transfer of one electron from the first neighbor shell of aluminum atoms into the manganese 3*d* shell. The manganese atom is approximately in the configuration d^7s^1, in contrast with the isolated free atom configuration d^5s^2.

Because the cluster we study contains an odd number of electrons, the cluster must have a moment of at least 1 μ_B. This will be true for any cluster built up of complete shells of aluminum atoms in fcc geometry surrounding a central manganese as long as fractional occupancy is not considered because all such shells contain an even number of atoms. It is therefore difficult to extrapolate from a finite cluster to an infinite system to argue whether a single manganese atom in a bulk sample of aluminum would be expected to show a moment.

TABLE II. Mulliken population analysis from integrated cluster density of states (CDOS) for $MnAl_{18}$.

Central	
Mn *sp* ↑	0.572
Mn *sp* ↓	0.594
Mn *d* ↑	4.403
Mn *d* ↓	2.641
Mn tot	8.211
First shell	
Al_{12} *sp* ↑	1.363
Al_{12} *sp* ↓	1.405
Al_{12} *d* ↑	0.053
Al_{12} *d* ↓	0.059
Al^{12} tot	2.880
Second shell	
Al_6 *sp* ↑	1.467
Al_6 *sp* ↓	1.492
Al_6 *d* ↑	0.044
Al_6 *d* ↓	0.045
Al_6 tot	3.048

However some information can be obtained by considering the spatial distribution of the moment we calculate.

The Mulliken population analysis shows a moment of 1.74μ_B on the manganese atom. Because of uncertainties of the Mulliken analysis, the specific numerical value cannot be regarded as precise. There is a compensating negative polarization of the surrounding aluminum atoms. The spin density is shown graphically in Fig. 3. The positive polarization of the central manganese and negative polarizations of the surrounding aluminums are apparent in the figure. There is also a region of positive spin polarization close to the aluminum nucleus, while, as is characteristic of 3*d* transition metals, the spin density at the manganese nucleus is opposite to that of the 3*d* electrons. The net spin density at the nuclear site is given quantitatively in Table III. The net negative polarization of the aluminum atoms reduces the cluster moment to the minimum possible for this system.

We have calculated the exchange splitting of the Mn

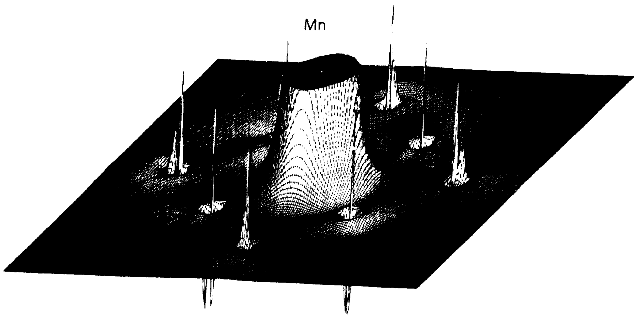

FIG. 3. Spin-density distribution of $Al_{18}Mn$ in the (100) plane. The range of plotted values is from −0.01 to +0.01; the heights of the major structures around the nuclei are truncated; the fine structures in interatomic regions are fully exhibited.

TABLE III. Spin density at the nuclei (in $e/\mathrm{a.u.}^3$).

	MnAl_{18}
Mn	-0.108
Al_{12}	$+0.030$
Al_6	$+0.028$

3*s* level; our result is 1.88 eV which is smaller than the experimental result of Steiner, 2.9 eV.[4] It is to be noted that our value for the local moment is reasonably close to that found in some Al-Mn alloys in the composition range studied here. However, there does not seem to be any simple extrapolation available to the zero concentration limit. Cooper and Miljak[21] estimated after a complicated analysis involving a fit to the temperature dependence of the magnetic susceptibility that the high-temperature moment of an isolated Mn atom in Al would be about $3.2\mu_B$. This result is to be interpreted as the moment that would be exhibited by an isolated manganese atom in a bulk aluminum sample if it were possible to make measurements significantly above the Kondo temperature. Since the actual measurements are made at modest temperatures on samples which contain finite concentrations, the moment inferred from the data may not be certain.

IV. CONCLUSIONS

We calculated on the basis of local-spin-density functional theory that a manganese atom in a MnAl_{18} cluster with fcc geometry has a local moment of $1.74\mu_B$. This value is reasonably close to that observed in some Al-Mn alloys with about 5 at. % Mn concentration. However, the moment of an isolated Mn atom in bulk aluminum is apparently obscured by Kondo screening. Our calculations are consistent with this in that they show significant compensating screening of the local moment, so that the total moment is $1\mu_B$, which is required by the size and geometry of the cluster.

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