Isolated magnetic moments in icosahedral Al-Pd-Mn alloys

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We present *ab initio* calculations of the formation of magnetic moments in a large approximant to icosahedral Al-Pd-Mn quasicrystals. It is shown that large magnetic moments can form on a small number of Mn sites characterized by a loose coordination by Al atoms and some close Pd neighbors. *d*-*d* hybridization is shown to play an important role. [S0163-1829(98)04046-6]

Quasicrystalline alloys display a bewildering variety of different magnetic properties: Diamagnetism,[1,2] paramagnetism,[3] ferromagnetism,[4] and spin-glass behavior[5,6] have been reported. A very unusual feature of ferromagnetic quasicrystals is the coincidence of a small magnetization and a high Curie temperature. This has led to the assumption that only a small fraction of the atoms carries a rather large magnetic moment.[7] The existence of two classes of transition-metal sites (magnetic and nonmagnetic) in ferromagnetic and in paramagnetic crystals has been confirmed by Mössbauer spectroscopy.[8,9] In addition, it has been shown that certain quasicrystalline alloys display a dramatic increase of the magnetic susceptibility on melting.[2,10]

Very recently we have presented a detailed local-spin-density (LSD) functional study of the formation of magnetic moments in disordered face-centered-cubic alloys, intermetallic compounds, decagonal and icosahedral quasicrystals, and liquid alloys in the Al-Pd-Mn system.[11] Hereafter, this paper will be referred to as I. The general picture arising from this study is the following: (a) In the crystalline intermetallic compound strong Al-*p*–Mn-*d* hybridization leads to the formation of a Hume-Rothery pseudogap at the Fermi level suppressing the formation of magnetic moments. (b) The other extreme exists in the substitutionally disordered solid solution: Due to the disorder, Al-*p*–Mn-*d* hybridization is nearly completely suppressed, and an impurity-like local Mn-DOS peaked at the Fermi level favors a spin-glass-like ground state. In the liquid alloy fluctuations in the local environments lead to a situation where certain sites carry large moments, while the others are only marginally magnetic. Decreasing local order (i.e., increasing temperature) favors magnetism, in agreement with experimental observations.[2,10] (c) The situation is qualitatively similar in quasicrystals. In low-order approximants to decagonal (*d*) Al-Mn we predicted substantial magnetic moments on a small number of Mn sites characterized by a higher number of Mn neighbors and increased Mn-Al distances and coordination numbers (i.e., reduced Al-*p*–Mn-*d* hybridzation). In 1/1 and 2/1 approximants icosahedral *i*-Al-Mn-Pd alloys, on the other hand, all Mn sites were found to be nonmagnetic or marginally magnetic (the LSD calculation converging to moments $\leqslant 0.1\mu_B$). The complete absence of magnetic moments in *i*-AlPdMn would contradict the spin-glass behavior of diluted large Mn moments reported at certain compositions.[6]

Here we return to the question of the possible existence of localized magnetic moments in *i*-Al-Pd-Mn by extending our earlier investigations to higher-order approximants. In our previous work LSD calculations have been performed for the 1/1 and 2/1 approximants of a structural model constructed by projections from six-dimensional space.[12] The model is based on triacontahedral acceptance domains proposed by Cockayne *et al.*[13]

The 1/1 and 2/1 approximants contain 128 and 544 atoms in the periodically repeated cell, respectively. The 3/2 approximant considered here contains 2292 atoms (1612 Al, 472 Pd, and 208 Mn). The spin-polarized electronic structure calculations have been performed using the real-space tight-binding linear-muffin-tin orbital (TB-LMTO) technique described in detail in I and in our work on the paramagnetic electronic structure of *i*-AlPdMn.[12] The screened structure constants have been calculated for all sites that are topologically inequivalent within a distance equal to 2.7 the Wigner-Seitz radius. In the 3/2 approximant there are 199 inequivalent sites (138 Al, 41 Pd, 20 Mn). Charge and spin densities and LMTO-potential parameters are calculated self-consistently on each inequivalent Pd and Mn site, while the Al densities and potentials are self-consistent only on average.

Figure 1 shows the local paramagnetic electronic densities of states (DOS) on the 20 inequivalent Mn sites as well as the average Al-, Pd-, and Mn DOS's. In I we had found that the formation of magnetic moments is governed by a local Stoner criterion $n_i(E_F)\cdot I>1$, where $n_i(E_F)$ is the local DOS (per spin) and I is the Stoner intraatomic exchange integral. In all Al-(Pd)-Mn alloys we had found $I\sim 0.92\pm 0.01$ eV (cf. I for a more detailed discussion). Hence the local Stoner criterion is that the local paramagnetic DOS $n_i^{\mathrm{para}}(E_F)$ is larger than 2.17 states per eV. According to this criterion we would expect the formation of a substantial magnetic moment on sites Mn2 and Mn13, while site Mn3 is predicted to

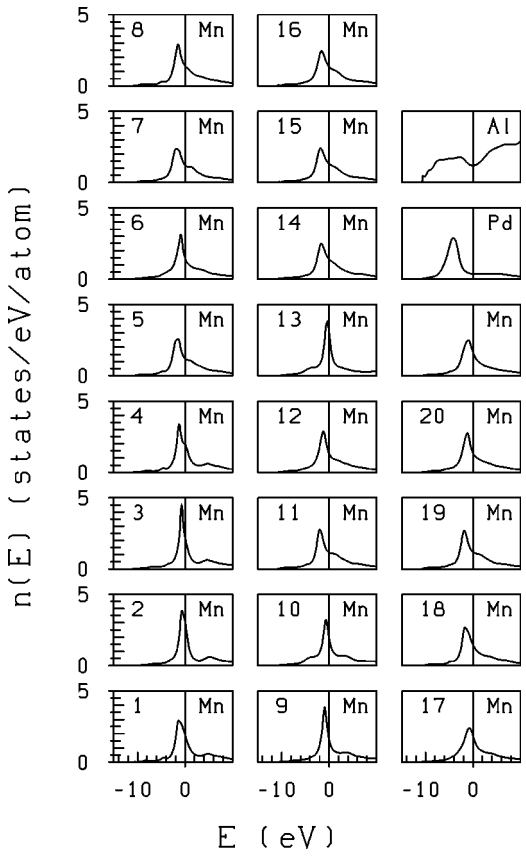

FIG. 1. Local paramagnetic electronic density of states on the 20 topologically inequivalent Mn sites in the 3/2 approximant to icosahedral Al-Pd-Mn and average density of states on the Al, Pd, and Mn sites.

be marginally magnetic and sites Mn10 and Mn17 just fall short of satisfying the local criterion. A spin-polarized calculation initialized with moments of $0.5\mu_B$ on sites Mn2 and Mn13 converges to a large magnetic moment on site Mn13 [$\mu(\mathrm{Mn13})=2.365\mu_B$], while the spin density on site Mn2 disappears rather quickly as self-consistency is approached. The question is now for the mechanism leading to the formation of a large magnetic moment on an isolated site (only 12 out of 208 Mn atoms carry a moment).

For the decagonal alloys we had noted two factors favoring moment formation: (a) A loose packing of Al around Mn reduces Al-p–Mn-d hybridization, leads to an impuritylike local DOS peaked close to E_F and favors the formation of a magnetic moment. (b) All magnetic sites have a Mn-Mn coordination above average, confirming the important role of direct Mn-Mn interactions. Table I lists the partial local and average coordination numbers, the local DOS at E_F as well as the binding energy at which the local DOS has its maximum. The first important observation is that in *i*-AlPdMn Mn atoms have no direct Mn neighbors within a distance of 4.03 Å (which is the cutoff for all pair distances) — hence a direct Mn-Mn interaction cannot contribute to the formation of a magnetic moment. Sites with a high paramagnetic local DOS are characterized either by (a) a very low Mn-Al coordination of seven Al atoms at a distance of 2.544 Å and a complete absence of transition-metal (TM) neighbors (sites Mn1 to Mn4) or by (b) a somewhat larger number of Al neighbors distributed over distances of 2.544 and 2.938 Å and in addition two or three Pd neighbors at the shorter distance (sites Mn10 and Mn13). Here we mention only very briefly that the low Mn-Al coordination numbers are confirmed by extended x-ray-absorption fine structure experiments,[14] for a more detailed discussion we refer to our work on the structural modeling and the paramagnetic electronic structure.

TABLE I. Average partial coordination numbers $\overline{N_{XY}}$ (a) and local partial coordination numbers N_{Mni-X}, paramagnetic DOS at E_F $n_i^{\mathrm{para}}(E_F)$ (in states/eV/atom), and peak position E_{peak} (in eV relative to the Fermi level) of the DOS for the inequivalent Mn sites (b).

(a)

X	$N_{X-\mathrm{Al}}$	$N_{X-\mathrm{Pd}}$	$N_{X-\mathrm{Mn}}$
Al	10.81	3.22	1.31
Pd	11.32	2.24	0.21
Mn	10.15	0.48	0.00

(b)

Site	Multiplicity	$N_{\mathrm{Mn}i\text{-Al}}$ [a]	$N_{\mathrm{Mn}i\text{-Pd}}$	$N_{\mathrm{Mn}i\text{-Mn}}$	$n_i^{\mathrm{para}}(E_F)$	E_{peak}
Mn1	(4)	7	0	0	1.95	−0.78
Mn2	(4)	7	0	0	2.98	−0.42
Mn3	(12)	7	0	0	2.23	−0.44
Mn4	(12)	7	0	0	1.90	−0.81
Mn5	(12)	7+4	0	0	1.17	−0.89
Mn6	(12)	6+4	1+0	0	1.38	−0.53
Mn7	(12)	7+5	0	0	1.10	−1.06
Mn8	(12)	7+2	0	0	1.29	−0.91
Mn9	(12)	7+2	0	0	1.61	−0.59
Mn10	(12)	5+5	2+0	0	2.02	−0.39
Mn11	(12)	7+5	0+1	0	1.09	−1.23
Mn12	(12)	7+4	0+1	0	1.19	−0.70
Mn13	(12)	3+6	3+0	0	3.01	−0.19
Mn14	(12)	7+4	0	0	1.33	−0.92
Mn15	(12)	7+5	0	0	1.24	−1.10
Mn16	(12)	7+5	0	0	1.22	−0.93
Mn17	(4)	6+3	1+0	0	1.96	−0.46
Mn18	(4)	7+3	0	0	1.39	−1.05
Mn19	(12)	7+5	0	0	1.19	−1.09
Mn20	(12)	7+4	0	0	1.21	−0.73

[a]We list separately Al and Pd neighbors at distances of $d_1 = 2.544$ Å and $d_2 = 2.938$ Å.

In the LSD calculations, an initial magnetic moment on the sites of type (a) vanishes even if the local Stoner criterion is satisfied, whereas on the (b)-type site Mn13 a large magnetic moment develops (site Mn10 just falls short of satisfying the local criterion). The important point is that on sites Mn1 to Mn4 the local DOS is slightly skewed to the left, with its peak 0.5 to 1.0 eV below E_F. As indicated by the side peak in the DOS at $E\sim 4$–5 eV, the asymmetry of the DOS is related to some remnant Al-Mn hybridization. On site Mn13, on the other hand, the local DOS is quite symmetric, with a peak very close to the Fermi level and a shoulder at binding energies of ~ -3.5 eV close to the peak of the local Pd-DOS. The shift of the Mn-DOS towards E_F is the consequence of the Mn-Pd interaction: The two transiton-metal d bands repel each other, shifting the nearly full Pd-d band to higher and the only half-filled Mn-d band to lower binding energies, as confirmed by soft x-ray spec-

troscopy (cf. I for a detailed discussion). Similar, but even more pronounced *d*-band shifts have also been found in higher-order approximants to *d*-AlPdMn (Ref. 15) and *d*-Al-Cu-Co (Ref. 16) alloys and confirmed by photoelectron and soft-x-ray spectroscopy. The shift of the nearly full *d*-band towards higher binding energies lowers the band energy and is an important factor in stabilizing the quasicrystalline state.[16]

In summary: We have demonstrated that large localized magnetic moments can be formed on a small percentage of Mn sites in *i*-Al-Pd-Mn alloys, explaining the experimental observations based on magnetic neutron scattering, susceptibility, and specific-heat measurements.[2,6,7] As previously reported for *d*-Al-Pd-Mn alloys, a loose Mn-Al coordination and hence a reduced Al-p–Mn-d hybridization is an important factor facilitating moment formation. The role of interactions between transition metals is important, but different in the icosahedral and in the decagonal alloys: Whereas in the decagonal phase with a higher Mn content direct Mn-Mn interaction plays an important role in promoting moment formation, in the icosahedral phase with a lower Mn content and a chemical short-range order characterized by a preferred TM-Al coordination, reduced TM-TM contacts (and no Mn-Mn neighbors at all) direct magnetic interactions are suppressed. Direct Mn-Pd contacts—which exist in a substantial number only on a very few number of Mn sites—on the other hand, lead to a locally enhanced Mn-d–Pd-d hybridization and a repulsion of the two *d* bands promoting moment formation.

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[1] P. Lanco, T. Klein, C. Berger, F. Cyrot-Lackmann, G. Fourcondot, and A. Sulpice, Europhys. Lett. **18**, 227 (1992).
[2] F. Hippert, M. Audier, H. Klein, R. Bellissent, and D. Boursier, Phys. Rev. Lett. **76**, 54 (1996).
[3] M. Eibschütz, M. E. Lines, H. S. Chen, J. V. Waszczak, G. Papaefthymiou, and R. B. Frankel, Phys. Rev. Lett. **59**, 2443 (1987).
[4] J. J. Hauser, H. S. Chen, and J. V. Waszczak, Phys. Rev. B **33**, 3577 (1986).
[5] C. Berger and J. J. Préjean, Phys. Rev. Lett. **64**, 1769 (1990).
[6] M. A. Chernikov, A. Bernasconi, C. Beeli, A. Schilling, and H. R. Ott, Phys. Rev. B **48**, 3058 (1993).
[7] J. C. Lasjaunias, A. Sulpice, N. Keller, J. J. Préjean and M. de Boissieu, Phys. Rev. B **52**, 886 (1995).
[8] Z. M. Stadnik, G. Stroink, H. Ma, and G. Williams, Phys. Rev. B **39**, 9797 (1989).
[9] Z. M. Stadnik and G. Stroink, Phys. Rev. B **43**, 894 (1991).
[10] V. Simonet, F. Hippert, H. Klein, M. Audier, D. Boursier, and R. Bellissent, *Proceedings of the 6th International Conference on Quasicrystals*, edited by S. Takeuchi and T. Fujiwara (World Scientific, Singapore, 1998), p. 7.4.
[11] J. Hafner and M. Krajčí , Phys. Rev. B **57**, 2849 (1998).
[12] M. Krajčí , M. Windisch, J. Hafner, G. Kresse, and M. Mihalkovič, Phys. Rev. B **51**, 17 355 (1995).
[13] E. Cockayne, R. Phillips, X. B. Khan, S. C. Moss, J. L. Robertson, T. Ishimasa, and M. Mori, J. Non-Cryst. Solids **153-154**, 140 (1993).
[14] A. Sadoc and J. M. Dubois, J. Non-Cryst. Solids **153-154**, 83 (1993); Philos. Mag. B **66**, 541 (1992).
[15] M. Krajčí, J. Hafner, and M. Mihalkovič, Phys. Rev. B **55**, 843 (1997).
[16] M. Krajčí, J. Hafner, and M. Mihalkovič, Phys. Rev. B **56**, 3072 (1997).