PHYSICAL REVIEW B VOLUME 50, NUMBER 23 15 DECEMBER 1994-I

Electronic structure and relative stability of icosahedral Al–transition-metal clusters

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(Received 9 May 1994)

The electronic structure and relative stability of icosahedral $Al_{12}M$ (M=transition metal) clusters have been studied using the density functional theory within the local spin density approximation. Our calculations predict large binding energies for clusters with M atom in the middle of a d series in agreement with the occurrence of $Al_{12}W$ phase in these alloys and provide an insight into the understanding of the stability of Al-M quasicrystals.

Aluminum–transition-metal (M) alloys are known to have a rich variety of structures. Many of these are complex and have large unit cells.[1] This complexity was enriched further with the discovery of quasicrystals in Al-Mn,[2] and subsequently in a large number of other alloys as quasicrystals have rotational order but no translational symmetry. However, one common aspect of icosahedral quasicrystals and the corresponding complex crystalline structures is the occurrence of similar *local* icosahedral units. Such local order is also observed in related amorphous and liquid phases.[3] These experimental facts suggest that icosahedral units are particularly stable irrespective of whether there is a long range order or not. Recently it has been possible to produce stable quasicrystals, such as AlFeCu, AlRuCu, and AlPdMn, by doping and to stabilize quasicrystals with, e.g., Si or Cu.[4] However, the role of the dopant has not been clear, though band structure calculations[5] in the case of AlMnSi indicated that doping facilitated the Fermi level, E_F, to lie in a pseudogap which might stabilize the structure.

Another relevant and, in fact, remarkable structure which has *local* icosahedral order is the $Al_{12}W$ crystalline phase, in which icosahedral $Al_{12}W$ units with a W atom at the center are the building blocks of the bcc structure.[1] The same structure is also formed by Mn, Cr, Mo, Tc, and Re. This is a further indication that icosahedral units have strong stability in these systems. We call these units as *superatoms* of these structures.[6,7] While the importance of icosahedral clusters has been recognized by several workers, there has been no systematic study of their relative stability. Also an understanding of the interactions responsible for quasicrystal formation still remains an open problem. Zangwill and Redfield[8] have studied the embedding energies of M atoms in a jellium using the effective medium theory. Their calculations suggest that the charge density required for maximum embedding energy is lower for Al as compared to M atoms. Therefore in Al-M alloys, one possibility to provide optimum binding energy to both Al and M atoms is to have icosahedral arrangement of Al atoms around a central M atom, because in an icosahedron the nearest neighbor distance from vertex to vertex is about 5% larger than the distance from the center to a vertex. This qualitative picture is appealing, but these calculations did not incorporate the effects of icosahedral packing on the electronic structure. McHenry *et al.*[7] calculated the energy spectrum of 13- and 33-atom icosahedral clusters with Mn at the center by the SW-X_α method and found a very large density of states at E_F. This led them to conclude that Mn at the center of an icosahedron was not stable. The large density of states at E_F also suggested that these clusters may have a tendency to develop magnetic moments. Carlsson[9] has studied the relative structural stability of Al-M alloys. He found, in agreement with experiments, the $Al_{12}W$ structure energetically more stable than the Cu_3Au structure in the middle of a d series. However, why these alloys prefer such a complicated structure is not clear. While theoretical understanding of these complex alloys at par with elemental crystalline materials is apparently difficult, here we consider these materials from a local point of view and present results of a systematic study of the relative stability of $Al_{12}M$ icosahedral clusters with the M atom at the center of the icosahedron which are common in these complex structures. Our results show strong stability of icosahedral clusters in the middle of a d series in agreement with the occurence of the $Al_{12}W$ phase and provide an insight on the formation of Al-M quasicrystals by some M elements.

Our calculations are based on the density functional theory with a Barth-Hedin local spin density approximation.[10] A linear combination of atomic orbitals is used to expand the wave functions in the cluster. The Kohn-Sham equations are then solved by the discrete variational method.[11] The binding energy $E_b = E_{\text{tot}} - E_{\text{ref}}$ is calculated for all the clusters. E_{tot} is the total energy of the cluster and E_{ref} is the sum of the total energies of individual atoms. The structure of the clusters is optimized by calculating the binding energies for several vertex to center distances keeping the icosahedral symmetry. Calculations are also done[12] for a few clusters in the cuboctahedral geometry and we find the icosahe-

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dral structure to be lower in energy. Here we present results only for the icosahedral clusters.

In Fig. 1, we show the calculated binding energies for all the clusters at the equilibrium center to vertex distance R_0. It can be seen that the binding energy is the largest in the middle of a d series. In particular, we find large binding energies for Cr, Mn, Mo, Tc, and W all of which form the $Al_{12}W$ phase. Further, a large binding energy for Ru indicates that it may have a similar tendency. There is also a significant gain in the binding energy for V, Fe, Co, Ni, Nb, Rh, and Re as compared to Al_{13}. Re also forms an $Al_{12}W$ phase whereas Fe, Co, and Ni are known to form icosahedral quasicrystals with Al. For $Al_{12}Cu$ and $Al_{12}Pd$, our calculations predict nearly the same binding energy as in the case of Al_{13}, but significantly smaller R_0 (Table I) because of strong sp-d hybridization (see below). In the case of Zn the d states are occupied and the sp-d hybridization is weak which leads to a smaller binding energy. For Ti,[13] Zr, and Nb, there is a gain in energy as compared to Al_{13}, but R_0 is larger. The large size of these M atoms seems to be the reason why long range icosahedral order may not be favorable in alloys of these elements with aluminum. To study the size effect, we have included in Table I the relaxation energy E_{relax} of $Al_{12}M$ clusters in bringing them from Al_{12} to $Al_{12}M$ equilibrium distance. We find E_{relax} to be small ($\sim$ 0.5 eV) but large enough as compared to ordering energies. Further, there are important sp-d hybridization effects which can change the general trends of the effective size of a M atom as we find for clusters with Cu and Pd.

The energy spectra for some of the studied clusters are shown in Fig. 2. The important feature is the behavior of the d levels which are fivefold degenerate in the icosahedral symmetry and therefore hybridize only with the H_g levels of the empty center icosahedral Al_{12} cluster. In the $3d$ series from Ti to Mn, the spin-up hybridized d level shifts progressively downwards and the exchange splitting increases (being maximum for Mn). This leads to a large magnetic moment μ_M for Cr and Mn (Table I). From Mn to Ni, the spin-up d level shifts towards E_F and the exchange splitting decreases which gives rise to smaller magnetic moments for Ni. This is in good agreement with the experimental fact that Cr and Mn impurities in bulk Al have large local magnetic

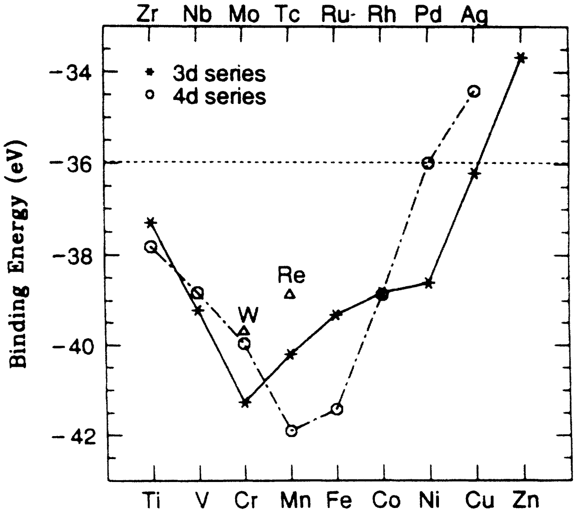

FIG. 1. Binding energies at equilibrium center to vertex distance for all calculated icosahedral $Al_{12}M$ clusters. The broken line shows the binding energy of Al_{13}.

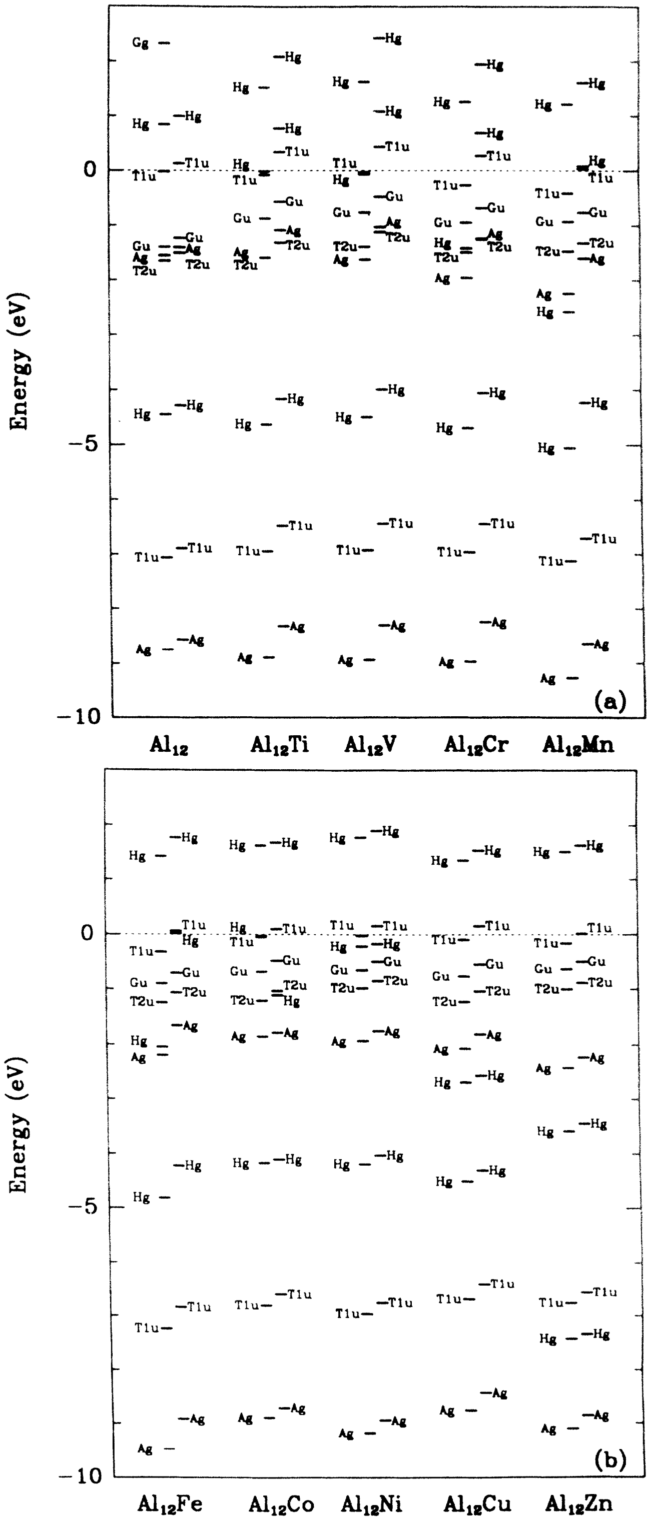

FIG. 2. Energy spectra of some studied icosahedral $Al_{12}M$ clusters. The Fermi energy is shifted to zero.

TABLE I. Calculated properties of icosahedral $Al_{12}M$ clusters. For details see text.

Cluster	E_b (eV)	R_0 (a.u.)	E_{relax} (eV)	Q	μ_M
Al_{12}	31.065	5.13			
Al_{13}	35.970	5.32	0.307		
$Al_{12}Ti$	37.299	5.41	0.657	0.504	2.61
$Al_{12}V$	39.217	5.39	0.611	0.492	3.89
$Al_{12}Cr$	41.264	5.26	0.142	0.007	5.32
$Al_{12}Mn$	40.206	5.29	0.252	0.048	5.32
$Al_{12}Fe$	39.328	5.25	0.141	0.192	4.05
$Al_{12}Co$	38.813	5.23	0.094	0.084	2.69
$Al_{12}Ni$	38.609	5.21	0.057	0.289	0.46
$Al_{12}Cu$	36.204	5.17	0.013	-0.189	0.64
$Al_{12}Zn$	33.671	5.23	0.097	-0.145	0.51
$Al_{12}Zr$	37.816	5.45	1.101	0.652	2.30
$Al_{12}Nb$	38.812	5.37	0.645	0.506	0.54
$Al_{12}Mo$	39.969	5.37	0.697	0.264	3.90
$Al_{12}Tc$	41.909	5.34	0.450	0.630	0.83
$Al_{12}Ru$	41.420	5.25	0.147	0.306	0.00
$Al_{12}Rh$	38.861	5.24	0.136	0.222	0.10
$Al_{12}Pd$	35.979	5.19	0.013	-0.131	0.31
$Al_{12}Ag$	34.411	5.28	0.130	0.005	0.60
$Al_{12}W$	39.689	5.38	0.620	0.517	3.13
$Al_{12}Re$	38.871	5.36	0.613	0.576	0.74

moments[14] and that there exist large local magnetic moments in Al-Mn quasicrystals.[15] Our results are also in agreement with those of McHenry *et al.*[16] who obtained a large local magnetic moment on Mn in icosahedral Al clusters. As it is well known, in the case of the 4*d* and 5*d* elements, the magnetic moments and the exchange splittings are smaller, but the general features of the energy spectra are similar[12] to that of the 3*d* series. We find that spin polarization has a large contribution to the binding energy of the clusters with elements in the middle of a *d* series, e.g., for Mn and Cr, it decreases E_b by about 2 eV, but it changes E_b only a little for clusters with negligible exchange splittings. The overall charge transfer Q (Table I) between Al and M atoms from a Mulliken population analysis is found to be small.

An interesting feature of the spectra is the occurrence of a gap just above E_F for Mn, Fe, Co, Ni, Cu, and Zn, all of which form icosahedral quasicrystalline phases with Al and for the elements which form the $Al_{12}W$ phase. While the effect of this gap on the stability of bulk phases cannot be predicted from the present calculations, it, however, suggests that with appropriate substitutional doping, the highest occupied level can be completely occupied and that these clusters can then be further stabilized as in the case of $Al_{12}C$ and $Al_{12}Si$ (Ref. 17) clusters. Bonding between these superatoms can then be described in terms of the interactions between the levels of the superatoms.

The variation of the *d* level as discussed above leads to an interesting trend in the *sp*-*d* hybridization in a *d* series. As the M atoms in Al-rich complex phases are far apart, interaction between them should be predominantly indirect. We can, therefore, expect the *sp*-*d* hybridization to play an important role in this interaction. Zou and Carlsson[18] have performed a model calculation where they did find a strong indirect interaction between two Mn atoms 4.7 Å apart. In Table II, we show the percentage of *d* character in the occupied *sp*-*d* hybridized H_g levels. It can be noted that for Ti and V, the hybridization of the *d* level is with the unoccupied H_g level of Al_{12}. For Cr, the *d* level starts hybridizing with the occupied H_g level of Al_{12}. This hybridization reaches a maximum for Mn. From Mn to Ni, the hybridization of the *d* level with the H_g level decreases. However, in the case of Cu the *d* level falls down and again there is a strong hybridization with the occupied H_g level of Al_{12}, whereas in the case of Zn the *sp*-*d* hybridization is negligible as the *d* level lies deep below E_F. Therefore

TABLE II. Percentage of the *d* component of the occupied *sp*-*d* hybridized levels in $Al_{12}M$ clusters. ϵ_i is the eigenvalue referenced to Fermi level.

M	Spin up		Spin down		M	Spin up		Spin down	
	ϵ_i	%	ϵ_i	%		ϵ_i	%	ϵ_i	%
Ti	0.00	50			Zr	-5.20	12	-4.70	0.08
						-0.20	33		
V	-0.07	57			Nb	-4.81	11	-4.81	11
						-0.00	38	-0.00	38
Cr	-4.80	19			Mo	-5.00	24	-4.37	11
	-1.42	64				-1.05	51	0.00	46
Mn	-5.01	39			Tc	-4.85	13	-4.75	11
	-2.50	53				-0.28	51	-0.00	46
Fe	-4.83	25	-4.22	6	Ru	-4.69	14	-4.69	14
	-2.01	64	0.0	68		-0.20	53	-0.20	53
Co	-4.44	16	0.0	73	Rh	-4.85	19	-4.79	19
	-1.40	72				-0.99	58	-0.97	58
Ni	-0.30	75	-0.22	75	Pd	-4.82	37	-4.72	39
						-2.24	53	-2.16	51
Cu	-4.43	38	-4.30	42	Ag	-6.38	85	-6.23	85
	-2.70	57	-2.5	54		-3.27	19	-3.09	18
Zn	-7.40	97	-7.32	97	W	-5.18	21	-4.61	12
						-1.0	48	0.0	42

our results suggest that the indirect interaction between M atoms in Al-based icosahedral bulk phases should be significant for Cr, Mn, Fe, Co, and Cu in the 3d series.

There is also a significant *sp-d* hybridization for Mo, Tc, Ru, Rh, Pd, W, and Re. However, it is most pronounced in the case of Pd where the *sp-d* hybridization results in a contraction of the Al-Pd bond length which is nearly the same as in $Al_{12}Cu$ (Table I). Also as the binding energy is close to that of $Al_{12}Cu$, our calculations suggest that to a large extent, Pd and Cu can be treated to be equivalent, though there could be some differences due to the different number of valence electrons. We believe that this has important implications for the stability of quasicrystals, as replacing Al by Cu or Pd would provide a better packing. Also since the d states are nearly completely occupied and lie much below E_F, their substitution can be used to shift the E_F to a pseudogap due to different number of valence electrons without affecting the states near E_F much. Actually in experiments Cu and Pd have been added to produce stable quasicrystals such as AlLiCu, AlFeCu, AlRuCu, and AlMnPd.[4] In contrast, the Al-Ag bond length is longer, and the binding energy is smaller as compared to Al-Cu. This could be related to the fact that there is no quasicrystal with Ag reported in the literature. Ru and Rh are other interesting cases, as the binding energy is large as well as the Al-Ru and Al-Rh bond lengths are shorter than that of Al_{13}. It can be noted here that similar to our results Sadoc and co-workers[19] obtained short Al-Cu and Al-Ru bonds from extended x-ray absorption fine structure (EXAFS) measurements on AlCuRu and AlCuFe quasicrystals and there is a report of quasicrystal formation in Al-Rh alloys.[20]

From these results we note that Mn, Fe, Co, Rh, and Pd, which form binary quasicrystals, have large binding energies and strong *sp-d* hybridization. Further R_0 is smaller than that in Al_{13} which should improve binding between the 12 vertex Al atoms. Our calculations also suggest that Cr, Ru, and Cu may have tendency to form binary quasicrystals. On the other hand, though Ni and Zn have been used to form quasicrystals, no binary quasicrystal of Al-Ni and Al-Zn exists. This is very likely due to a weak *sp-d* hybridization in these systems. This agrees with the experimental fact[1] that in the $(Al,Zn)_{49}Mg_{32}$ phase Zn is distributed randomly.

In summary, we have studied the relative stability of icosahedral $Al_{12}M$ clusters and obtained some trends which provide an insight into the role of the electronic structure. Clusters with the M atom in the middle of a d series have the largest binding energy which agrees with the observation of the $Al_{12}W$ phase in these systems. The binding energy is also large for Mn, Fe, Co, and Ru which form stable quasicrystals. We find a gap above E_F for some clusters. These superatoms could be made even more stable by appropriate substitution of Al atoms. Our calculations show an interesting trend of the *sp-d* hybridization in a d series, which not only provides the interaction between M atoms in the icosahedral phases, but also leads to a contraction of the Al-M bond resulting in better icosahedral packing such as in the case of Mn, Fe, Co, Ru, Pd, and Cu. For Ni and Zn, the *sp-d* hybridization is weak. These elements can therefore be expected to be distributed randomly. On the other hand Cu and Pd behave quite similarly and may be used interchangeably to produce new or stable quasicrystals. While for a proper understanding of the stability of different bulk phases, further calculations on larger systems would be required, a comparison of the trends obtained here with the experimental information has given interesting information on the role of the local electronic structure in the formation of quasicrystals and we hope that this would be helpful in furthering our understanding of these complex materials.

X.G.G. is thankful to Professor Q.Q. Zheng and YeZhen He for useful discussions, and to Professor Abdus Salam, the International Atomic Energy Agency, and the UNESCO for hospitality at the ICTP, Trieste. X.G.G. acknowledges partial support by the Climbing Research Program - China National Fundamental Project.

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