IC/93/352

INTERNATIONAL CENTRE FOR
THEORETICAL PHYSICS

ELECTRONIC STRUCTURE AND RELATIVE STABILITY OF ICOSAHEDRAL SUPERATOMS IN Al–TRANSITION–METAL ALLOYS

X.G. Gong

and

Vijay Kumar

INTERNATIONAL
ATOMIC ENERGY
AGENCY

UNITED NATIONS
EDUCATIONAL,
SCIENTIFIC
AND CULTURAL
ORGANIZATION

MIRAMARE-TRIESTE

IC/93/352

International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

ELECTRONIC STRUCTURE AND RELATIVE STABILITY OF ICOSAHEDRAL SUPERATOMS IN Al–TRANSITION-METAL ALLOYS

X.G. Gong [1] and Vijay Kumar [2]
International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

The elecronic structure and relative stability of icosahedral $Al_{12}TM$ superatoms in Al–transition–metal (TM) alloys have been studied using the density functional theory within the local spin density approximation. Our calculations predict large binding energies for superatoms with TM 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–TM quasicrystals.

MIRAMARE – TRIESTE

October 1993

Aluminium-transition-metal(TM) 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 the 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 binary quasicrystal 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 facilitates the Fermi level 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 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 *superatoms* of these structures. 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 [6] have studied the embedding energies of TM 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 TM atoms. Therefore in Al-TM alloys, one possibility to provide optimum binding energy to both Al and TM atoms is to have icosahedral arrangement of Al atoms around a central TM atom, because in an icosahedron the nearest neighbour distance from vertex to vertex is about 5 percent

---

[1] Permanent address: Institute of Solid State Physics, Academia Sinica, 230031-Hefei, People's Republic of China

[2] Permanent address: Materials Science Division, Indira Gandhi Center for Atomic Research, Kalpakkam – 603 102, India.

larger than the distance from center to 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 very large density of states at the Fermi level. This led them to conclude that Mn at the center of an icosahedron was not stable. Carlsson[8] has studied the relative structural stability of Al-TM 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. In this letter, we present results of a systematic study of the relative stability of icosahedral $Al_{12}TM$ clusters with the TM atom at the center of the icosahedron. Our results not only show strong stability of icosahedral clusters in the middle of a d-series in agreement with experiments, but also provide for the first time an explanation of the role played by different elements in the formation of Al-TM quasicrystals.

Our calculations are based on the density functional theory with Barth-Hedin local spin density approximation[9]. 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[10]. The binding energy $E_b = E_{tot} - E_{ref}$ 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[11] for a few clusters in the cuboctahedral geometry and we find the icosahedral 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 large in the middle of a d-series. In particular, our results of very large binding energies for Cr, Mn, Mo, Tc and W are in agreement with the experimental observation of the $Al_{12}W$ phase for these elements and in addition a large binding energy for Ru indicates that it should have a similar tendency. The binding energies are also large for V, Fe, Co, Ni, Nb, Rh and Re. Re also forms the $Al_{12}W$ 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 because of strong sp-d hybridization (see below). In the case of Ag and Zn, the d-states are occupied and the sp-d hybridization is weak, which leads to a smaller E_b. For Ti, V, Zr, Nb, Mo, Tc, W, and Re though E_b is larger than that of Al_{13}, however, R_0 for these clusters also becomes larger than in the case of Al_{13}. This seems to us to be the reason why *long*-range icosahedral order may not be favorable in these alloys. To study the size effect, we have included in Table I the relaxation energy E_{relax} of $Al_{12}TM$ clusters in bringing them from Al_{12} to $Al_{12}TM$ equilibrium distance. We find E_{relax} to be small (~0.5eV). However, there are important sp-d hybridization effects which can change the general trends of the effective size of a TM atom such as in Cu and Pd.

The energy spectra for some of the studied clusters is shown in Fig.2. The important feature is the behavior of the d-levels which are 5-fold 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 moments μ_M for Cr and Mn (Table I). From Mn to Ni, the spin-up d-levels shift towards E_F and the exchange-splitting decreases which gives rise to smaller magnetic moments for Ni, Cu and Zn. This is in good agreement with the experimental fact[12] that Cr, Mn and Fe impurities in bulk Al have large local magnetic moments. However, our results are contrary to those of McHenry et al.[13] who found Mn in Al cluster to be nonmagnetic. In fact, we have also made a test calculation on $Al_{12}Mn$ cluster in the fcc structure[11], and obtained a large local magnetic moment on Mn in agreement with

Yang's results[14]. As is well known, in the case of the 4d and 5d elements, the magnetic moments and exchange splittings are smaller, but the general features of the energy spectra are similar[11] to that of the 3d-series. We find that the 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 2eV, but it changes E_b little for clusters with a negligible exchange-splitting. From Mulliken population analysis, the overall charge transfer Q (Table I) between Al and TM atom, is found to be small.

A prominent 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 and for the elements which form the $Al_{12}W$ phase. The occurrence of this gap suggests that with appropriate doping, these clusters can be further stabilized, as in the case of $Al_{12}C$ and $Al_{12}Si$[15]. Bonding between these superatoms can be described in terms of the interactions between the levels of superatoms. From this point of view, the H_g levels near E_F appear to be the most important. Due to interaction between superatoms, these would form bonding and antibonding states leading to a depletion of electronic density of states near the Fermi level, as noted in some of the calculations on bulk alloys[8].

The variation of the d-levels as discussed above leads to an interesting trend in the sp-d hybridization in a d-series. As the TM 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[16] have performed a model calculation where they did find strong indirect interaction between two Mn atoms 4.7$\mathring{A}$ 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-levels is with the unoccupied H_g level of Al_{12}. For Cr, the d-levels start 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-levels with the Al_{12} H_g levels decreases. However, in the case of Cu the d-levels fall much below E_F 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 and the d-levels lie deep below the Fermi level. Therefore our results suggest that the indirect interaction between TM atoms in icosahedral bulk phases should be significant for Cr, Mn, Fe, Co and Cu.

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 as 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, since 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, it can be used to shift the E_F to a pseudogap due to the different number of valence electrons without effecting 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 reported in the literature with Ag. Ru and Rh are other interesting cases because the binding energy is larger and the Al-Ru and Al-Rh bond lengths are shorter than that of Al_{13}.

From these results we note that Mn, Fe, Co 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, Rh and Cu may have a 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 facts[1] that in the $(Al,Zn)_{49}Mg_{32}$

phase, Zn is known to be randomly distributed and there are AlCoNi quasicrystals[4].

In summary, we have studied the relative stability and electronic structure of icosahedral $Al_{12}TM$ clusters and obtained large binding energies in the middle of a d-series in agreement 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. Our calculations show an interesting trend of the sp-d hybridization in a d-series, which not only provides the interaction between TM atoms in the icosahedral phases, but also leads to a contraction of the Al-TM bond resulting in better packing such as in the case of Mn, Fe, Co, Ru, Pd and Cu. While for Ni and Zn, the hybridization is weak and so these elements can be expected to be distributed randomly. We find a gap above E_F for some clusters and so these superatoms could be made more stable by appropriate substitiution of Al atoms. Thus our calculations provide an insight into the role of the electronic structure in the stability of icosahedral clusters as well as into the role of various elements in the formation of quasicrystals.

Acknowledgments

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

REFERENCES

1. W.B. Pearson, *The crystal chemistry and physics of metals and alloys (New York Wiley), 1982*
2. D.S. Shechtman, L. Blech, D. Gratias, and J.W. Cahn, Phys. Rev. Lett. **53**, 1951(1984).
3. D. Holland-Moritz, D.M. Herlach, and K. Urban, Phys. Rev. Lett. **71**, 1196(1993).
4. See articles in the Proceeding of the Fouth International Conference in Quasicrystals, St. Louis, USA 1992, Published in J. Non-crystal Solid, **153** & **154**, (1993).
5. T. Fujiwara, Phys. Rev. B, **40**, 942(1989); T. Fujiwara nd T. Yokokawa, Phys. Rev. Lett. **66**, 333(1991).
6. A. Zangwill and A.C. Redfield, J. Phys. F **18**, 1(1988).
7. M.E. McHenry, M.E. Eberhart, R.C. O'Handley, and K.H. Johnson, Phys. Rev. Lett. **56**, 81(1986).
8. A.E. Carlsson, Phys. Rev. B **43**, 12176(1991).
9. U. von Barth and L. Hedin, J. Phys. C, **5**, 1629(1972).
10. D.E. Ellis and G.S Painter, Phys. Rev. B **2**, 2887(1970).
11. X.G. Gong and Vijay Kumar, unpublished.
12. J.J. Hauser, H.S. Chen, and J.Y. Wasczak, Phys. Rev. B **33**,3577(1986); J.R. Cooper and M. Miljak, J. Phys. F **6**, 2151(1976).
13. M.E. McHenry, D.D. Vvedensky, M.E. Eberhart, and R.C.O'Handley, Phys. Rev. B **37**, 10887(1988).
14. J.L. Yang, H.B. Lan, K.L. Wang, L.F. Dona Dalle Rose and F. Toigo, Phy. Rev. B **44**, 10508(1991).
15. X.G. Gong and V. Kumar, Phys. Rev. Lett. **70**, 2078(1993).
16. J. Zou and A.E. Carlsson Phys. Rev. Lett. **70**, 3748(1993).

Table I. Calculated properties of icosahedral $Al_{12}TM$ 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

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

TM	Spin Up		Spin Down		TM	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

Figure Captions

Fig.1 . Binding energies at equilibrium vertex-to-center distance for all calculated icosahedral Al_{12}TM clusters. Broken line shows the binding energy of Al_{13}.

Fig.2 . Energy spectra (spin-up and spin-down levels) of some of the studied icosahedral Al_{12}TM clusters. The Fermi energy is shifted to zero.

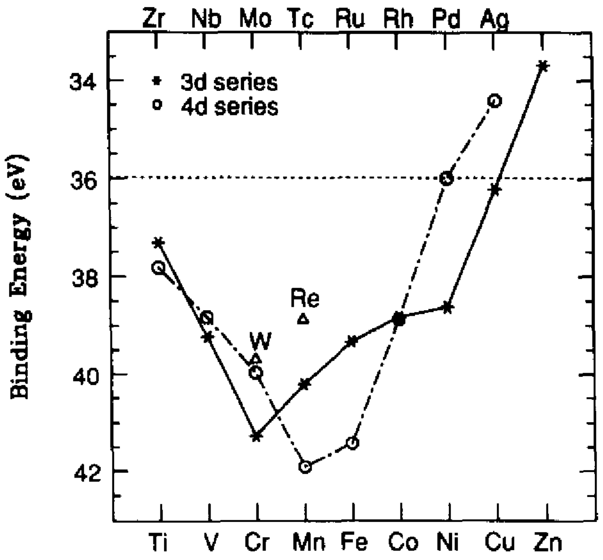

Fig.1

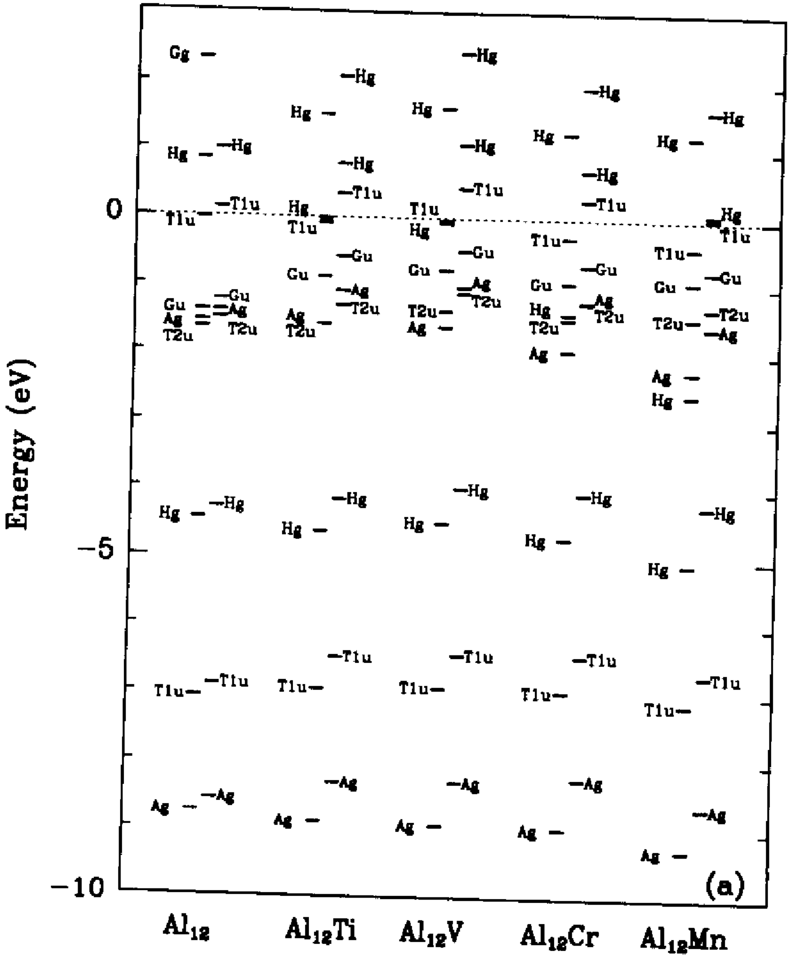
Energy (eV)
0
−5
−10
(a)
Al_{12}
$Al_{12}Ti$
$Al_{12}V$
$Al_{12}Cr$
$Al_{12}Mn$

Fig.2a

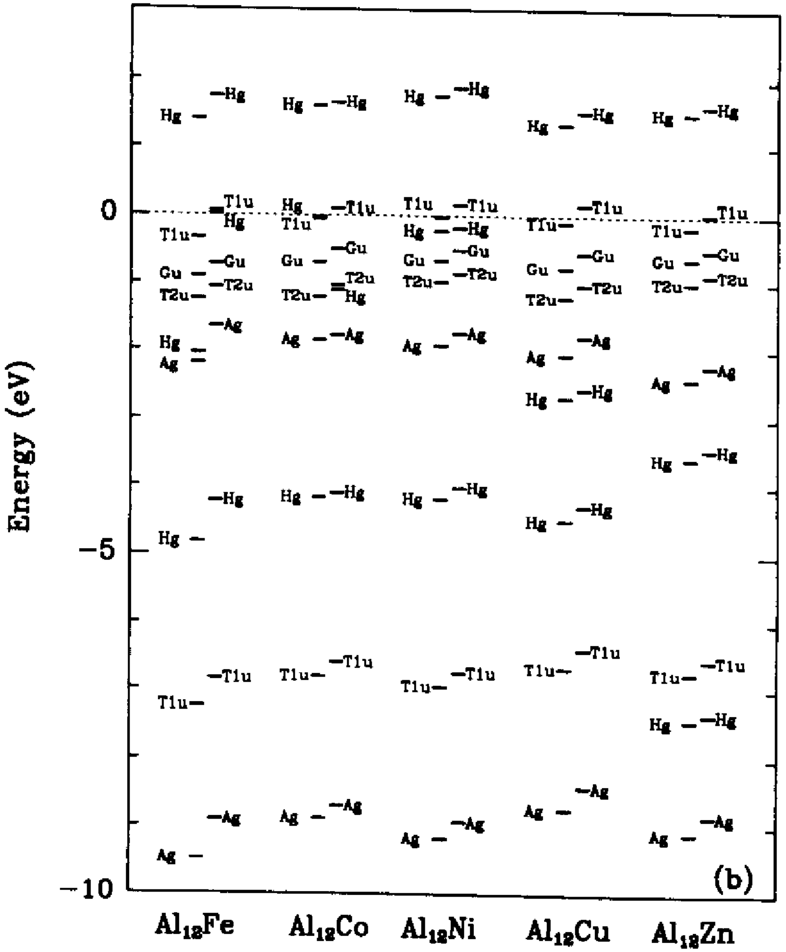
Energy (eV)
0
−5
−10
(b)
$Al_{12}Fe$
$Al_{12}Co$
$Al_{12}Ni$
$Al_{12}Cu$
$Al_{12}Zn$

Fig.2b